SURFACE TENSION DETERMINATION

INTRODUCTION

Surface tension is a phenomenon observed at the interphase surface. A particle inside the phase is subjected to identical forces on all sides and the resultant force is zero. In turn, the forces acting on the particle found in the surface layer are not in equilibrium.

At liquid-gas interphases, the resultant forces acting on the particle are perpendicular to the phase surface and directed into the bulk. As a result of this action particles from the surface are pulled into the liquid.
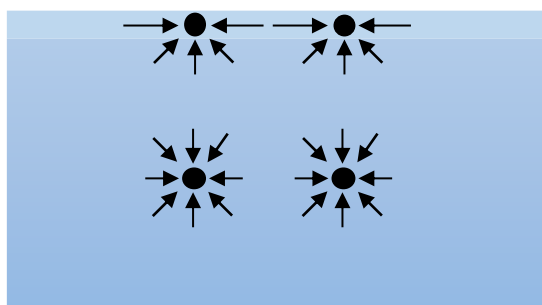

Figure 1.
Diagram the forces acting on molecules in the liquid.

Figure 2.
The force necessary to increase the surface area

For this reason, liquids tend to adopt the shape, in which the surface area is the smallest (sphere). Formation or an increase in the interface is connected with the work required to overcome opposite surface forces. This work is needed to transfer an adequate number of molecules from inside the phase to its surface. Surface tension may be defined as work L required to form a unit interface A:

$$\gamma = \frac{L}{A} \tag{1}$$

Value of γ is expressed in J·m^{-2}. The quotient of work L and area A equals the ratio of force F per unit length L. Thus, alternatively, the surface tension value can be expressed in N·m^{-1}, and the formula defining surface tension may take the equivalent form:

$$\gamma = \frac{F}{L} \tag{2}$$

The physical sense of this definition is that surface tension is numerically equivalent to force F acting tangentially to the interface per unit length L of the linear section of this surface. The surface tension of a liquid depends on the type of the adjacent phase. The surface tension at the liquid-saturated vapour interface is assumed to be the characteristic value. This value is practically equal to the surface tension of the same liquid in relation to air saturated with vapours of the same substance.

The surface tension of a liquid decreases with an increase in temperature, reaching the zero value at a temperature of approx. 6 K lower than the critical temperature of a given chemical substance.

The dependence of γ on temperature is expressed by the **Eötvös equation**:

$$\gamma \left(\frac{M}{d}\right)^{\frac{2}{3}} = K(T_{cr} - T) \tag{3}$$

where M is the molar mass of a substance, d – density, ($M/d = V_{mol}$ – molar volume), T_{cr} – temperature by approx. 6 K lower than the critical temperature of a given substance, while K is the factor of proportionality (i.e. the Eötvös number), which for a liquid not undergoing association is 2.1×10^{-7} J·K^{-1}

The surface tension of a solution generally differs from that of a pure solvent and depends on the type of the added substance and its concentration. In the surface layer, the concentration of the solute is typically different from that inside the solution. If forces acting between identical molecules of the solvent (due to **cohesion**) are greater than the interactions between the molecule of the substance and the molecule of the solvent, then the substance accumulates mainly on the solution surface, where it forms an adsorption layer. When the concentration of a substance in the surface layer is greater than its concentration within the solution, the phenomenon is referred to as **positive adsorption**. In such a case surface tension of the solution is lower than the surface tension of pure solvent and the added substance is referred to as a surface-active agent or **surfactant**. When molecules of the solvent attract less strongly than molecules of the solute attract molecules of the solvent, then the substance accumulates within the solution and its concentration on the surface is very low. This phenomenon is called **negative adsorption** and the solute is said to be surface inactive.

Surface-active substances in aqueous solutions include many organic compounds, e.g. soaps, long-chain fatty acids, alcohols, esters, salts of sulfonic acids and amine salts. Surfactants typically have an asymmetrical structure. A molecule of such a compound contains at least one **hydrophilic group** (e.g. carboxylic, amine, ester, hydroxy, sulfonic) and a **hydrophobic** carbon chain. Due to the presence of hydrophilic and hydrophobic groups, the molecule is arranged perpendicular to the interface. Hydrophilic groups are arranged towards the aqueous solution and thus the molecule is absorbed into the solution, while hydrophobic groups are oriented towards the other phase and counteract it. The capacity to reduce surface tension is referred to as **surface activity**.

The quantitative relationship between adsorption, surface activity of substances and concentration is given by the **Gibbs isotherm**:

$$\Gamma = -\frac{c}{RT}\left(\frac{\delta\gamma}{\delta c}\right)_{T,A} \tag{4}$$

where: Γ is surface excess and denotes the amount of the substance adsorbed from the solution per unit area.

It results from the Gibbs isotherm that adsorption depends on the surface activity of the substance. In the case of positive adsorption, the substance accumulates in the surface layer and the Γ value is positive and the derivative is negative, i.e. with an increase in the concentration of the substance in the solution, the surface tension of this solution decreases. If adsorption is negative, then Γ is negative and the derivative takes positive values, i.e. surface tension increases with an increase in the substance concentration in the solution. In the case of strong positive adsorption at a specific concentration of the solution, the interface is completely covered with molecules of the surface-active substance. In such a situation we observe saturated conditions in the surface layer and a further increase in the concentration of the substance in the solution no longer changes surface tension.

The Gibbs isotherm may be determined experimentally by measuring at a constant temperature the surface tension of several solutions differing in the concentrations of the surface-active substance.

The **stalagmometric method** is a method to measure the surface tension of liquids. A stalagmometer is a vertical glass tube, which in its central part has a widened section of several cubic centimetres in volume and which ends with a capillary. The capillary is typically several centimetres long, with a diameter of approx. 0.05 cm and with a flat tip. The lower part of the capillary is immersed in the tested liquid and the liquid is sucked in to fill the stalagmometer container. Next, the liquid is allowed to flow freely out of the stalagmometer. The liquid at the capillary outlet forms a gradually growing drop, which separates to fall when the drop weight (mg) is in an equilibrium state with surface tension force ($2\pi r\gamma$) acting along the capillary circumference. The equilibrium of these forces is expressed by the equation:

$$2\pi r\gamma = mg \tag{5}$$

which means that

$$\gamma = \frac{mg}{2\pi r} \tag{6}$$

Surface tension is thus proportional to the weight of the drop and the measurement method consists in the determination of the weight of individual drops. However, it is easier to determine the mean weight of drops. For this purpose, we need to calculate how many drops are formed from the liquid flowing out of the constant volume V contained between the two container levels. We may also weigh the liquid, which flowed from the stalagmometer volume and divide its weight by the number of drops.

If we denote the constants in equation (5) as:

$$k = \frac{g}{2\pi r} \tag{7}$$

then equation (6) is simplified to the following form:

$$\gamma = m \cdot k \tag{8}$$

Constant k called the capillary constant, may be determined based on the measured mass of drops of a liquid with known surface tension. Frequently water is adopted as the reference, particularly when determining the surface tension of aqueous solutions.

The capillary rise method is based on the phenomenon of liquid rising in capillary tubes. A liquid rises until the surface tension force $2\pi r\gamma$ is in equilibrium with the gravity force of the column of the liquid in the capillary $\pi r^2 hdg$:

$$2\pi r\gamma = \pi r^2 hdg \tag{9}$$

Measurement of the liquid rise in the capillary when we know the value of capillary radius r and liquid density d makes it possible to calculate surface tension from the formula:

$$\gamma = \frac{rhdg}{2} \tag{10}$$

The bubble pressure method is based on the principle of proportionality between the value of surface tension γ (at the interface of liquid$_1$-liquid$_2$) and the pressure required to push air bubbles or a drop of one liquid to the other from the capillary immersed in a liquid:

$$p = \frac{2\gamma}{r} \tag{11}$$

When taking measurements using a liquid with known surface tension (e.g. water) we may determine the pressure p_o required to separate the air bubble based on the formula:

$$p_o = \frac{2\gamma}{r} \tag{12}$$

which leads to the dependence: or

$$\frac{p}{p_o} = \frac{\gamma}{\gamma_o} \qquad \text{or} \qquad \gamma = \gamma_o \frac{p}{p_o} \tag{13}$$

EXERCISE PURPOSE

The aim of the task is to determine the dependence of surface tension at the interface of propionic acid aqueous solution and air on the concentration of the acid and to determine the Gibbs isotherm coefficients based on the obtained data.

APPARATUS

- an analytical balance.
- a stalagmometer.

LAB GLASS

- measuring flasks   - 25 ml - 4 pcs.
- a pipette   - 10 ml.
- lab glass funnel   - 1 piece
- beakers   - 10 and 25 ml.
- a wash bottle   - 1 piece
- glass weighing bottles - 2 pieces.

CHEMICALS

- Aqueous solution of propionic acid (1 mol·dm^{-3}).

EXPERIMENT PROCEDURES

1. Prepare propionic acid solutions with the following concentrations: 0.5 mol·dm^{-3}, 0.25 mol·dm^{-3}, 0.125 mol·dm^{-3} and 0.0625 mol·dm^{-3}. Add the appropriate volume of into volumetric flasks (25 ml).
2. Determine the capillary constant value as follows:

   a. Weigh an empty weighing bottle (with the cover),
   b. Fill the stalagmometer with distilled water by sucking the water in from a beaker using a plunger (until the plunger is drawn from the container),
   c. when the water level in the container drops to the upper mark, put a weighing bottle under the outlet of the capillary and collect 20 (and the next 40 and 60) drops of water flowing out,
   d. weigh the bottle with 20 (and next with 40 and 60) drops of water.
3. Perform analogous measurements of mass for 20 (and next 40) drops flowing out of the capillary for propionic acid solutions with the following concentrations: 0.0625 mol·dm^{-3}, 0.125 mol·dm^{-3}, 0.25 mol·dm^{-3}, 0.5 mol·dm^{-3} and 1 mol·dm^{-3} in the order given above.

PREPARATION OF RESULTS:

1. Based on the measurement results for water calculate the capillary constant k (per one drop) assuming that the surface tension of water is 71.98 J·m^{-2}.
2. Determine the mean mass of a drop flowing out of the capillary for individual liquids and calculate the surface tension of propionic acid solutions at different concentrations.
3. Plot the graph of the function: $\gamma = f(c)$
4. Determine the derivative $\left(\frac{\delta\gamma}{\delta c}\right)_{T,S}$ (e.g. by graphical differentiation).
5. Calculate the surface excess of propionic acid Γ using the Gibbs isotherm.
6. Obtained results are place in the table:

c	c	γ	γ	$\left(\dfrac{\delta\gamma}{\delta c}\right)_{T,S}$	Γ
mol·dm^{-3}	mol·m^{-3}	N·m^{-1}	J·m^{-2}	J·m·mol^{-1}	mol·m^{-2}
0.0625					
0.125					
0.250					
0.50					
1.0					

Template of the table and draft of the study

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Group no.: ………………… Team no.: …………………	………..……………… *Exercise no.:*	……………………………………. *Instructor:*

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1. Temat ćwiczenia
2. Cel ćwiczenia:
3. Wstęp teoretyczny:
4. Pomiary:
5. Obliczenia:
6. Wykresy:
7. Wnioski

1. Exercise title:
2. The aim of the exercise:
3. Theoretical introduction:
4. Results:
5. Calculations:
6. Graphs:
7. Conclusions: