SURFACE TENSION

(stalagmometric method)

1. PURPOSE OF THE WORK

Determination of surface tension coefficient for acetic acid solutions of different concentrations.

2. THEORETICAL NOTIONS

Interaction forces called cohesive forces are exerted between the molecules of a liquid. The molecules in the inner layers of the liquid are subjected to equal forces, evenly distributed, the result of which is null. The molecules in the surface layer undergo different attractions from the molecules of the outer environment (air) and as a result, the distribution of these forces is no longer the same in all directions. Thus, the surface molecules are subjected to a resultant force perpendicular to the free surface of the liquid and directed toward the interior of the liquid. These forces are quite large, giving rise to a pressure called internal pressure that acts on the molecules in the surface layer. The internal pressure exerted by the superficial layer on the liquid is very high (of the order of tens of thousands of atmospheres), thus explaining why the liquids are difficult to compress.

The attraction between the liquid molecules of the peripheral layer has the effect of bringing them as close as possible, so that the liquids tend to take forms with minimal surface area. This explains the spherical shape of the droplets, the spherical shape ensuring the smallest surface / volume ratio. The force that tends to shrink as much as possible the area of this peripheral surface is called the surface tension force.

The ratio between the surface tension force and the length *l* of the surface film on which this force acts is ***the surface tension coefficient*** or ***the surface tension*** (γ). The surface tension can also be defined as the mechanical work required to increase the free surface of a liquid by 1 cm^2 in an isothermal and reversible manner. Surface tension has dimensions of force / length or energy / surface. The values for γ can be expressed in N / m or J / m^2 in S.I. or dyne / cm or erg / cm^2 in the C.G.S system:

$$1\frac{dyne}{cm}=1\frac{erg}{cm^2}=\frac{10^{-7}J}{10^{-4}m^2}=10^{-3}\frac{J}{m^2}=10^{-3}\frac{N}{m}=1\frac{mN}{m}$$

The surface tension coefficient depends on the temperature. For this reason, when expressing a certain value of the surface tension to a contact surface, the temperature must be explicitly specified. The surface tension decreases with increasing temperature, becoming zero at the critical temperature.

The presence of substances dissolved in a liquid can alter the surface tension. Dissolved substances can cause surface tension to rise or fall.

Based on the Gibbs equation, conclusions about the amount of substance adsorbed in the surface film can be drawn from the variation of the surface tension with the concentration:

$$\Gamma = -\frac{1}{RT} \cdot \frac{d\gamma}{d\ln a_2} \quad \text{or} \quad \Gamma = -\frac{a_2}{RT} \cdot \frac{d\gamma}{da_2} \qquad (1)$$

where Γ is the surface concentration (excess moles adsorbed on the surface film unit) and a_2 the activity of the dissolved component (for dilute solutions a_2 can be replaced with the concentration).

The graphical representation of the surface tension γ depending on the concentration of the dissolved substance (C_2) leads to 3 types of curves (Fig. 1). Curves 1 and 2 illustrate a decrease in surface tension with the concentration of the dissolved substance. According to the Gibbs equation, when the concentration of the dissolved substance increases, the decrease of the surface tension of the solution ($d\gamma < 0$) results in a positive adsorption ($\Gamma > 0$), respectively an increase in the number of solute molecules in the surface layer. Such substances are called ***surfactants*** or ***surface active agents***. In the case of substance 1, however, a continuous, monotonous decrease of the surface tension with the concentration is observed, while for the species 2 there is a change of slope, with the constant maintenance of the surface tension after a certain concentration. Substances that behave after curve 1 are called *general surfactants* and include organic compounds such as alcohols or organic acids.

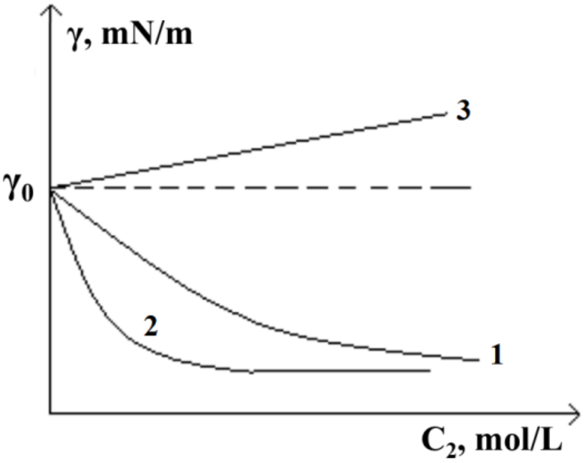

Fig. 1. Variation of surface tension with solution concentration: 1- general surfactants; 2- surfactants; 3- surface-inactive substances (γ0 = surface tension of the solvent)

Type 2 substances are called surfactants and have the property of forming *association colloids*. The concentration corresponding to the change of the slope of the curve is called *critical micellar concentration (CCM)*.

Curve 3 illustrates an increase in the surface tension of the solution as the concentration of the solute increases. Substances of this type are called *surface-inactive substances* and are generally inorganic electrolytes. These properties are due to the strong interactions between inorganic ions and water, which makes the transfer of ions from the solution to the air / water interface require additional energy consumption necessary for their partial dehydration. According to the Gibbs equation, with the increase of the concentration of the substance 3 there is an increase of the surface tension ($d\gamma > 0$), there is a negative adsorption ($\Gamma < 0$), respectively a decrease of the number of molecules of solute adsorbed in the surface layer.

A particular case of figure 1 is illustrated below:

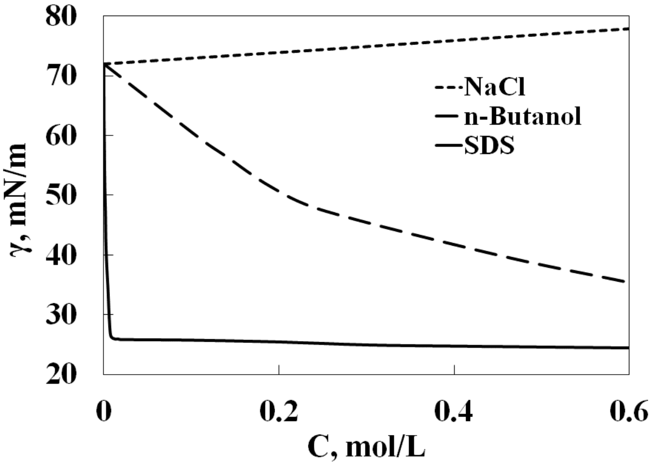

Fig. 2. The effect of the concentration of the different substances on the surface tension of the water

3. EXPERIMENTAL PART

3.1. APPARATUS AND SUBSTANCES

- stalagmometer, rubber pump, pipette, reference fluid, study liquids.

3.2. PROCEDURE

The surface tension of liquids can be measured by different methods. One of the simplest methods is the stalagmometric method. It is based on the fact that when the liquids flow through a capillary tube terminated with a polished disc (stalagmometer) drops are formed whose size depends on the surface tension and their density. Thus, the method consists in determining the number of drops of solvent and solutions of different concentrations contained in the same volume of liquid contained between two marks marked on the stalagmometer.

The liquid is introduced into the stalagmometer by suction with a rubber pump until it passes the upper mark (a). By opening of the clamp, the flow rate of the water drops is adjusted so that they can be counted. When the level of the liquid reaches the upper mark (a) the counting of droplets begins to continue until the level of the liquid reaches the lower mark (b).

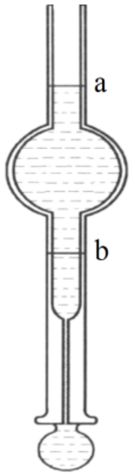

Fig. 3. Schematic illustration of the experimental installation

Each drop is detached from the end of the tube when the drop weight (*mg*) becomes equal to the surface tension force exerted on the circular contour (with radius *r*), which forms the line of contact between the edge of the tube and the base of the drop ($2\pi r\gamma$).

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

The stalagmometric method is a *relative method*. The use of a relative method allows the elimination of volume and radius measurements. Thus, the surface tension of a solution can be determined with respect to the surface tension of the solvent (water) for which, at 20 ° C, γ_0 = 72.9 mN / m (for each temperature degree it decreases by 0.3 mN / m).

For the solvent, the relation (2) can be written as:

$$m_0 g = 2\pi r\gamma_0 \tag{3}$$

Replacing the mass of a drop of solvent or solution with the ratio of mass of liquid to the number of drops: $\frac{Vd_0}{n_0}$ and respectively $\frac{Vd}{n}$, (where n_0 and n represent the number of drops of solvent and solution contained in volume *V*, and d_0 and *d* the densities of solvent and solution) and the ratio of relations (3) and (2) is obtained

$$\frac{\dfrac{d_0 V}{n_0}}{\dfrac{dV}{n}} = \frac{\gamma_0}{\gamma}\text{, which leads to } \gamma = \gamma_0 \frac{n_0}{n} \frac{d}{d_0} \qquad (4)$$

Determinations are made with acetic acid solutions in water of different concentrations.

4. EXPERIMENTAL DATA PROCESSING

4.1. For each solution you can face 3 determinations. The data will be passed in the form table:

Sample	***Concentration*, % mass**	***Density*, g/cm³ (20 °C)**	**Number of drops**				**γ, mN/m**
			n_1	n_2	n_3	**Average (*n*)**	
Water	**0**	**0,9982**					**72,9**
Acetic acid solution	**2,5**	**1,0019**					
	5,0	**1,0055**					
	7,5	**1,0091**					
	10	**1,0126**					

4.2. Draw curve $\gamma = f(c)$.

5. QUESTIONS

5.1. Using the Gibbs equation, calculate the surface acetic acid concentration for 3% and 8% (mass percent) solutions. What does the sign of it indicate?