

## Laboratory Session 4: Determination of the Surface Tension of Hydroethanolic Mixtures by the Du Nouy Method

**Objectives.** The practical aims to:

- Determine the surface tension ( $\gamma$ ) of binary ethanol-water mixtures.
- Establish an equation for the variation of  $\gamma$  with the concentration of ethanol in aqueous solutions.
- Approximately determine the surface excess of ethanol and the average area of a surface molecule.

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### 1. Introduction

The average energy of the molecules located on the surface of a liquid is different from the energy of the molecules located within the liquid phase. *For surface molecules, the result of attractive forces is not zero and is directed perpendicularly from the surface towards the bulk liquid phase.* Experimentally it has been proven that to increase the surface of a liquid it is necessary to carry out work proportional to the increase in surface area:

$$dW = \gamma dA \quad (1)$$

The coefficient  $\gamma$  is the surface tension of the liquid, and is always positive and independent of the area  $A$ . According to equation 1, the surface tension can be measured as the work done per unit area ( $\text{J m}^{-2}$ ), which is equivalent to measuring the force per unit length ( $\text{N m}^{-1}$ ):

$$\gamma = \frac{F}{l} \quad (2)$$

In the Du Nouy method, a torsion dynamometer is used to measure the force necessary to separate a metal ring from the surface of a liquid. The force is exerted against the surface tension of the liquid and acts along the circumference of the ring. In equation 2, the length is equal to twice the circumference of the ring, since the liquid is in contact with both the inside and outside of it:  $l = 2 \times 2\pi r$ . This method requires an empirical correction factor,  $f$ , to take into account the shape of the raised liquid and the thickness of the ring. With all these considerations we can write:

$$\gamma = f \frac{F}{4\pi r} \quad (3)$$

The diameter of the metal ring used is:  $2r = 19.65$  mm.

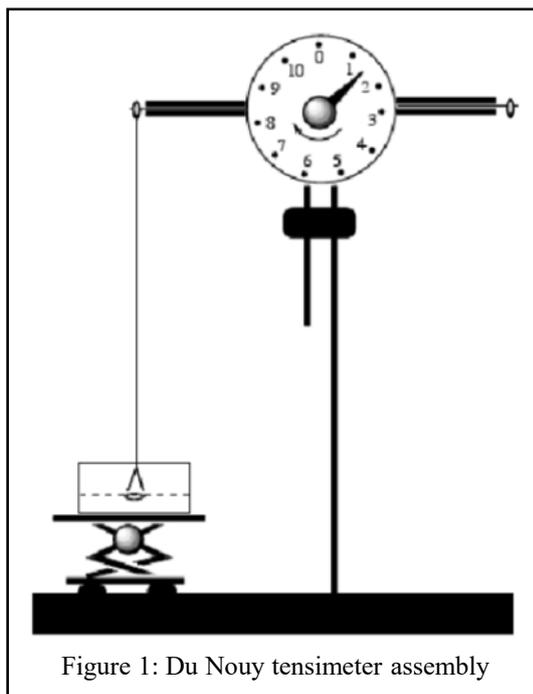


Figure 1: Du Nouy tensimeter assembly

## 2. Experimental Procedure

1. The device used in the *Du Nouy* method is shown in Figure 1. The measuring ring must be completely clean. Therefore, always taking the ring with the fork, first it should be cleaned with alcohol to remove any grease, and then washed with distilled water and left to drain. This operation must be carried out very carefully, since the welding between the ring and the fork is very fragile and can break easily.

The ring is hung from the left arm of the torsion dynamometer using a silk thread attached to the fork of the ring. The dynamometer is calibrated (adjusted to zero) by placing the scale indicator at the “0” position and the weight of the ring is compensated with the **adjustment button** (located at the back of the measurement scale) so that the arm of the balance is in the **white area** between the marks. In this position, the arm is **leveled**.

To carry out the measurement, proceed as follows: The liquid under investigation is poured into the clean glass bucket. The bucket is placed on the mobile platform, which rises until the ring is submerged in the liquid, and the arm is leveled by turning the scale indicator to the right. Then, we turn the scale indicator very slowly to the right and at the same time we lower the platform so that the arm remains continuously level (in the white area between the marks). The moment the ring is released from the liquid surface, the reading of the scale corresponding to the separation force in mN is recorded.

2. Using the technique described in the previous section, we will carry out a series of experiments to determine the surface tension of different ethanol-water mixtures at room temperature. Different volumes of absolute ethanol are successively added to water in order to achieve the mixtures indicated in the table (SERIES 1). In a second series of experiments, the operation is

repeated but starting with ethanol and adding water (SERIES 2). It is convenient to repeat each measurement three times.

3. Measure the temperature of the mixtures.

**Table 1.** Volumes of ethanol and water in the series of mixtures to be made.

<i>Series 1: 100 mL of H<sub>2</sub>O adding x mL of ethanol</i>	
Measure	x mL EtOH
1	-
2	+1
3	+1
4	+1
5	+1
6	+1
7	+1
8	+1
9	+1
10	+1
11	+1
12	+5
13	+5
14	+20
15	+20
16	+20
17	+20

<i>Series 2: 100 mL of ethanol adding x mL of H<sub>2</sub>O</i>	
Measure	x mL H <sub>2</sub> O
1	-
2	+25
3	+25
4	+25
5	+25

### 3. Results

#### 3.1 Determination of the surface tension ( $\gamma$ ) of binary ethanol-water mixtures

Calculate the value of the correction factor  $f$  from the surface tension of water using the results in series 1, and of absolute ethanol using the results in series 2 at the temperature of the solution. Calculate the surface tension of the mixtures of the two series of experiments using equation (3).

Represent  $\gamma$  against the mass fraction of ethanol.

Calculate the molar concentration ( $c_2$ ) of ethanol in each of the mixtures and plot a graph of  $\gamma$  vs  $c_2$ . For the most **dilute** solutions, find the function  $\gamma = \gamma(c_2)$  that best fits the results obtained.

#### 3.2 Determination of the empirical equation empirica of Szyszkowsky for binary ethanol-water mixtures

The empirical equation of **Szyszkowsky** gives the surface tension of dilute aqueous solutions of organic compounds such as:

$$\gamma = \gamma_0 - \alpha \ln(1 + \beta c_2) \quad (4)$$

or equivalently

$$\gamma = \gamma_0 - RT\Gamma_\infty \ln(1 + Kc_2) \quad (5)$$

where  $\gamma_0$  is the surface tension of pure water,  $c_2$  the concentration of the solute;  $T$  the temperature,  $K$  the equilibrium constant between ethanol in solution and ethanol adsorbed on the surface, and  $\Gamma_\infty$  is the maximum excess surface concentration of EtOH at the interface (maximum concentration of molecules per unit area).  $\alpha$  and  $\beta$  are constants characteristic of the organic compound.

Check if the  $\gamma$  values obtained fit equation 4 and, if this is the case, determine the best values for  $\alpha$  and  $\beta$ . From there, using equation 5, determine  $\Gamma_\infty$  and  $K$  for ethanol.

#### 3.3 Determination of the excess surface concentration of ethanol, $\Gamma$ , and the average area occupied by a molecule on the surface, $\sigma$

In the hypothetical case that hydroethanolic mixtures behave as ideal solutions, calculate the excess surface concentration of ethanol ( $\Gamma$ ) and the average area occupied by an ethanol molecule on the surface ( $\sigma$ ) in some of the mixtures.

$$\Gamma = \Gamma_\infty \left( \frac{Kc}{1 + Kc} \right) \quad (6)$$

$$\sigma = \frac{1}{\Gamma N_A} \quad (7)$$

Remember that Gibbs (relative) adsorption isotherm is:

$$\Gamma = \frac{n_2^\sigma}{A} = - \left( \frac{\partial \gamma}{\partial \mu_2} \right)_T \quad (8)$$

and that for the ideal solutions the chemical potential of the solute,  $\mu_2$ , is given by:

$$\mu_2 = \mu_2^o + RT \ln c_2 \quad (9)$$

In equation 8,  $n_2^o$  is the number of moles of solute adsorbed on a surface of area A. Therefore,  $\Gamma$  is defined as the excess surface concentration. (Sometimes,  $\Gamma$  is written as  $\Gamma_{21}$ ).

### 3.4 wo-dimensional equation of state of ethanol adsorbed at the interface

The behavior of some substances adsorbed at the interface responds to an equation of state analogous to that of an ideal gas in two dimensions ( $p=cRT$ ):

$$\Pi = \Gamma RT \quad (10)$$

where  $\Gamma$  is the surface concentration and  $\Pi = \gamma_o - \gamma$  is the surface pressure (force per unit length). Represent  $\Pi$  against  $\Gamma_{ideal}$  y a  $\Gamma_{real}$  (equation 6) and check if in the case of ethanol this equation of state is achieved and, in any case, indicate in which region it should be better satisfied.

$$\Gamma_{ideal} = \frac{\Pi}{RT} = \frac{\gamma_o - \gamma}{RT} \quad (11)$$

## 4. Questions

### 4.1. Preliminary Questions

1. Find the literature value for the surface tension of water and absolute ethanol between 20 and 30 °C.
2. Find the literature density value of water and absolute ethanol solutions between 20 and 30 °C.

Suggestion: You can connect to ChemNetBase via a VPN connection if you do it outside the UV.

### 4.2. Post-laboratory Questions

1. In the Langmuir model it is considered that the balance of adsorption of a species on a surface of any nature (gases on solids or surfactants in fluid interfaces) results from the balance of two competitive kinetic processes: adsorption and desorption. Assuming that both processes follow first-order kinetics, the Langmuir adsorption isotherm is obtained:

$$K = \frac{\theta}{c_2(1-\theta)} \quad (12)$$

where  $K$  is the adsorption-desorption equilibrium constant,  $c_2$  is the concentration of the solute in the solution and  $\Theta$  is the fraction of adsorbed molecules on the surface, which is defined as the ratio between the number of adsorbed molecules on the surface ( $N$ ) and the maximum number of molecules that can be adsorbed ( $N_\infty$ ):

$$\theta = \frac{N}{N_{\infty}} = \frac{N/A}{N_{\infty}/A} = \frac{\Gamma}{\Gamma_{\infty}} \quad (13)$$

a) Check that the substitution of equation 13 in the Langmuir adsorption isotherm (12) leads to equation 6.

b) Check that the combination of Gibbs and Langmuir adsorption isotherms leads to another equation, the Langmuir state equation (5), which is equivalent to the empirical equation of Szyszkowsky and, therefore, the constants of Equation 4 can be related with those of 5,  $\beta = K$  and  $\alpha = \Gamma_{\infty} RT$ .

## Material

### Material per pair:

- One 500-mL glass crystallizer.
- One 100-mL beaker.
- One torsion dynamometer assembly with mobile platform.
- One ring for measuring surface tension.

### Shared Material:

- One 1-mL graduated pipette.
- One 5-mL graduated pipette.
- One thermometer.
- Four 50-mL burettes with deposit.

### Products:

- Distilled water.
- Absolute ethanol.

## References

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