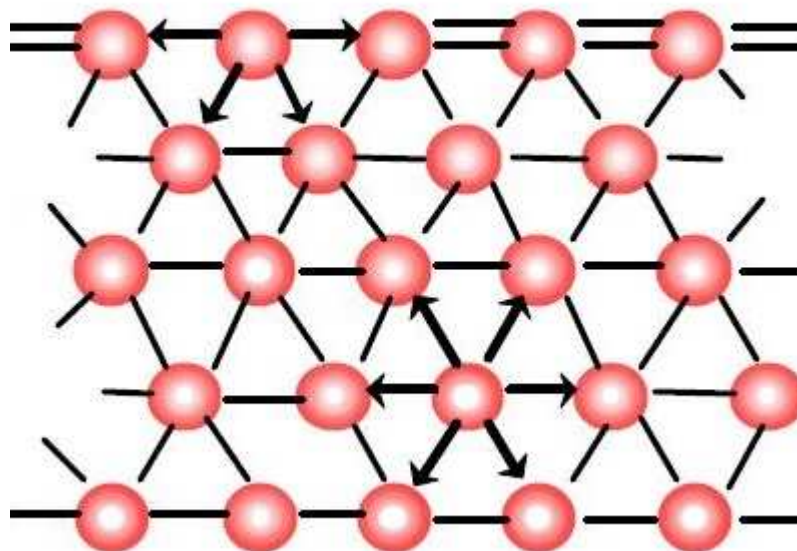


MSc in Chemical Technology

Surface and Interface Chemistry

Practical Classes Guide



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2015

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Preface

With the syllabus of surface and Interface chemistry we want that students will be able to understand the main models that describe the physicochemical behavior of surfaces and interfaces, and apply these concepts to important systems in the context of chemical technology.

On the other hand, the laboratory lessons, or practical classes, are an important component of education within the framework of the exact sciences and their application in technology. With this guide it is intended that students have contact with some simple techniques that will enable them to relate the theoretical contents acquired throughout the course with their practical application.

To improve the teaching-learning process students have a web page, maintained by the lecturer and dedicated to this curricular unit (in Portuguese):

<http://www.docentes.ipt.pt/valentim/ensino/qsi.htm>

1. Measurement of surface tension

1.1. Introduction

The molecules on the surface of a liquid are subjected to forces of attraction of the molecules inside the liquid. The resultant of these forces, whose direction is the same tangent plane to the surface, acts in such a way that the liquid surface is the lowest possible. The magnitude of this force acting perpendicularly (per unit length) to the plane on the surface is called surface tension (γ). The surface or interface where there is tension lies between the liquid and the saturated steam or the air, usually at atmospheric pressure. The tension can also exist between two immiscible liquids, being then called interfacial tension. The dimensions of the surface tension are force per unit of length, in the SI system $\text{N} \cdot \text{m}^{-1}$. One of the methods used to measure the surface tension is the drop weight method. This method, as well as all those involving separation of two surfaces, depends on the assumption that the circumference multiplied by the surface tension is the force that keeps united two parts of a liquid column. When this force is balanced by the weight of the lower portion, the droplet is released. The surface tension can be calculated by equation (Tate's law):

$$\gamma = \frac{m_i \cdot g}{2\pi r} \quad (1.1)$$

Where: m_i is the mass of one ideal drop; r is the radius of the tube (external if the liquid dips the tube) and g is the acceleration of gravity.

In practice, the drop weight obtained is always less than the ideal drop weight. The reason for this becomes clear, when the process of drop formation is observed in detail. Figure 1 illustrates what actually happens. It is observed that only the outermost portion of the drop reaches the position of instability and crashes. Around 40% of the liquid that forms the drop remains connected to the tube.

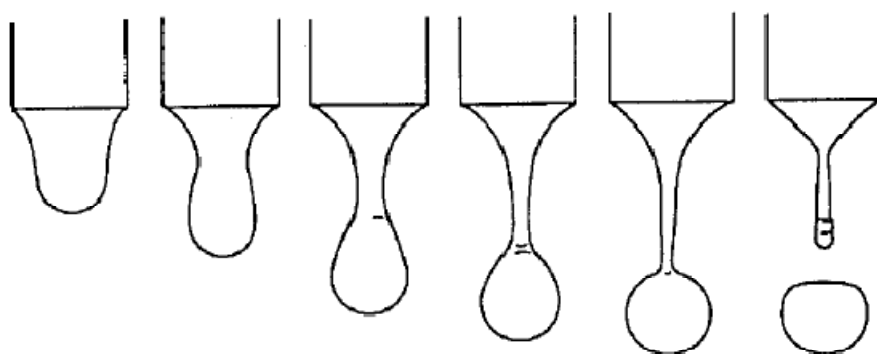


Figure 1. Some images of the falling of a drop.

To correct the error caused by the weight of the drop, we add to the equation a correction factor f , and the modified equation comes:

$$\gamma = \frac{m_j \cdot g}{2\pi r f} \quad (1.2)$$

The correction factor f is a function of the radius of the tube and the volume of the drop. These values are tabulated below:

Table 1. correction factor for the drop weight method.

$r/V^{1/3}$	f	$r/V^{1/3}$	f	$r/V^{1/3}$	f^a
0.00	(1.0000)	0.75	0.6032	1.225	0.656
0.30	0.7256	0.80	0.6000	1.25	0.652
0.35	0.7011	0.85	0.5992	1.30	0.640
0.40	0.6828	0.90	0.5998	1.35	0.623
0.45	0.6669	0.95	0.6034	1.40	0.603
0.50	0.6515	1.00	0.6098	1.45	0.583
0.55	0.6362	1.05	0.6179	1.50	0.567
0.60	0.6250	1.10	0.6280	1.55	0.551
0.65	0.6171	1.15	0.6407	1.60	0.535
0.70	0.6093	1.20	0.6535		

As can be seen in most cases we can use a value of $f \approx 0.6$.

1.2. Experimental Part

1.2.1. Material

- 100 mL volumetric flasks
- 25 mL or 50 mL burettes
- Erlenmeyer Flasks
- Analytical balance
- Solution of SDS (sodium dodecyl sulfate) 50.0 mM.

1.2.2. Determination of the diameter of glass tube

The tube diameter can be measured using a caliper or obtained from the mass of a standard liquid drop, whose value of surface tension is known. The masses of a drop of pure water at 20° C, for tubes of different diameters, are in table 2. For temperatures above or below 20° C, but not too different, we can use the following relationship to calculate the mass of the drop of water at 20° C:

$$m_{20^\circ\text{C}} = m_{t^\circ\text{C}} \times \frac{\gamma_{20^\circ\text{C}}}{\gamma_{t^\circ\text{C}}} \quad (1.3)$$

where γ is the surface tension of water at their respective temperatures.

Table 2: mass of a drop of water that falls from different tube diameters

massa da gota (g)	Raio do tubo (cm)	massa da gota (g)	Raio do tubo (cm)
0.033450	0.09946	0.90467	0.31891
0.042347	0.13062	0.091620	0.32362
0.046901	0.14769	0.096392	0.34188
0.054678	0.17750	0.096918	0.34385
0.059700	0.19666	0.09868	0.35022
0.068026	0.23052	0.10623	0.37961
0.069869	0.23790	0.10966	0.39262
0.072682	0.23135	0.11161	0.39968
0.007753	0.26802	0.11957	0.42765
0.079680	0.27605	0.12522	0.44755
0.084270	0.29423	0.12575	0.44980
0.084880	0.29694	0.14142	0.50087

With the values of the table it is possible to verify that there is a linear relationship between the radius and the mass of the drops (Figure 2):

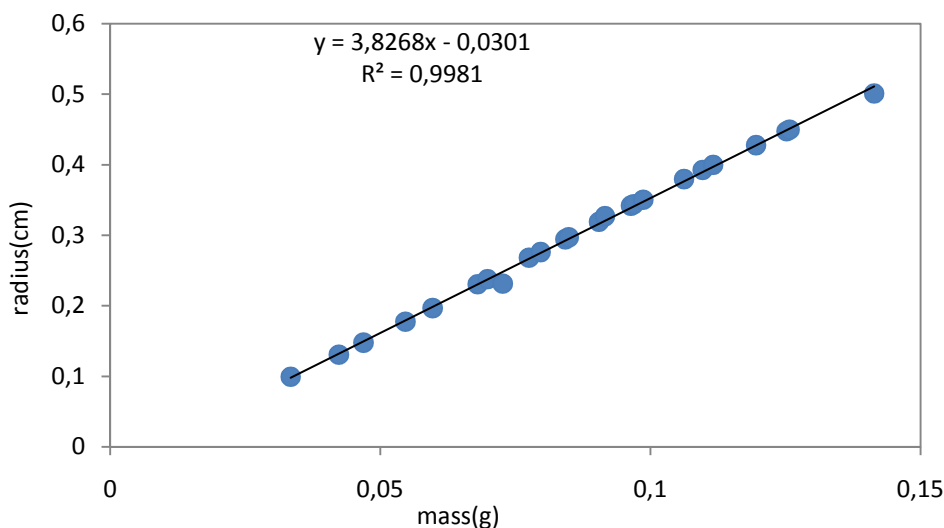


Figure 2. Relationship between the radius and mass of a drop of water.

The relationship obtained is:

$$r(\text{cm}) = 3.83 \times m(\text{g}) - 0.03 \quad (1.4)$$

1.2.3. Determination of surface tension

-Prepare solutions of SDS (sodium dodecyl sulfate) with the following concentrations: 1.0 mM; 3.0 mM; 5.0 mM; 7.0 mM; 9.0 mM, 11.0 mM; 15.0 mm; 18 mM and 20.0 mM from a stored concentrated solution.

-Put the liquid in a burette keeping the bench free of vibrations, as shown in Figure 3:

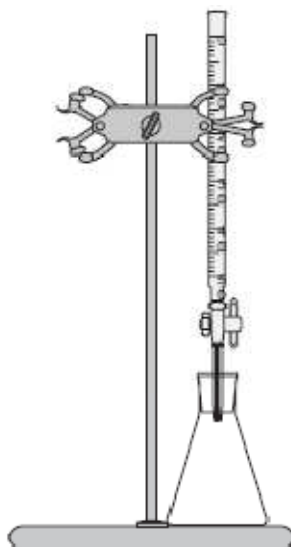


Figure 3. Experimental set-up

-Collect 10 drops of liquid in the flask (already weighed). Take note of the mass and calculate the corresponding volume of the collected drops (start by pure water and then, by order, from less concentrated solution to more concentrated solutions; adjust to approximately 1 drop per minute).

-Calculate the surface tension of the various solutions.

1.3. Additional notes

Cleanliness is essential in the measures of surface tension. Small amounts of impurities affect the surface properties. Therefore, thoroughly clean the material to be used in the experiment. If the liquid is volatile it is necessary that the droplets are collected in closed containers. In addition, the first drop should be knocked over for about 5 minutes so that the container becomes saturated in the vapors of the liquid. In this case, it is also necessary to make two measures, one with approximately 15 drops and another with 5 drops. The weight difference between the two measures will give the weight of the drops free of the weight of the steam.

1.4. Treatment of results

Represent the surface tension as a function of the concentration of solute and graphically determine critical micelle concentration (CMC) of this surfactant.

2. Adsorption isotherm

2.1. Introduction

When contact occurs between two condensed phases there is usually an increase or decrease in the solute concentration at the interface. This phenomenon is called adsorption. There are two main types of adsorption on solids: physical adsorption and chemical adsorption. In physical adsorption molecules attach themselves on the surface of the adsorbent by van der Waals forces (physical bonds) and can form several layers, while the chemical adsorption is a chemical bonding between the molecules of the condensed phase and the solution. Freundlich, studying the adsorption phenomenon empirically, arrived to the following equation:

$$\log\left(\frac{x}{m}\right) = \log k + \left(\frac{1}{n}\right) \log C \quad (2.1)$$

Where x is the amount of adsorbed solute by the mass m of the solid adsorbent, C is the equilibrium concentration and k and n are empirical constants. For physical adsorption of acid in coal, n has values between 0.1 and 1.0 depending on the nature of the system. For a given system the amount of adsorbed solute is a function of the concentration of the adsorbate, the surface area of the adsorbent (solid phase) and temperature. Thus, when measured (x/m), by adsorption, is represented as a function of concentration, at a fixed temperature, we obtain an adsorption isotherm.

2.2. Experimental part

2.2.1. Material

- Erlenmeyer flasks of 250 mL
- 50 mL burettes
- 10 mL, 25 mL and 50 mL pipettes,
- 100 mL volumetric flasks
- Goblet of 250 mL
- Funnel
- Filter paper
- 0.5 M Acetic Acid
- 0.5 M sodium hydroxide
- Activated carbon
- Phenolphthalein.

2.2.1. Experimental procedure

-Put 10 g of activated charcoal in a goblet and wash with distilled water; filter and put in the oven at 120° C for one hour. Remove and allow cooling in a desiccator under vacuum.

-Prepare 200 mL of a 0.5 M acetic acid solution and standardize by titration with 25 mL of a 0.5 M NaOH solution, using phenolphthalein as indicator. With the rest of the standardized solution prepare 5 acid solutions of 100 mL, in the range of concentrations 0.25 to 0.01 M.

- Weigh 5 Stopped Erlenmeyer flasks and 5 coal samples of 0, 25 g each (do the weighing quickly, to avoid adsorption of moisture from the atmosphere). Transfer the prepared solutions for Erlenmeyer flasks containing activated carbon and note the time.

-Keep the mixture while stirring for 45 minutes. Then leave the coal decant and filter (Figure 4)

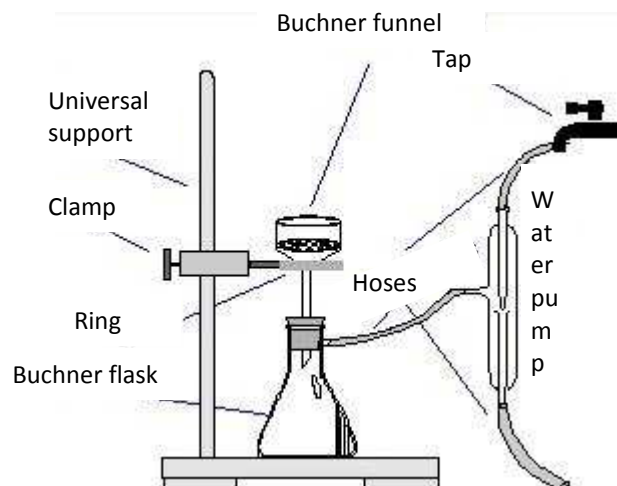


Figure 4. Experimental set-up for filtration.

-Use 10 mL of each sample and titrate with 0.5 M sodium hydroxide, using phenolphthalein as indicator.

2.3. Treatment of results

Based on the results obtained apply the Freundlich equation and calculate the parameters k and n .

3. Viscosity of macromolecules

3.1. Introduction

The intrinsic viscosity measurement has been used for the characterization of macromolecules. Is one of the simplest methods for determining molar mass of polymers, but also allows obtaining information regarding structure and polymer-solvent interactions. The difference between a dilute solution viscosity η and the solvent viscosity, η_0 , is a measure of the effect of individual molecules of solute on the viscosity of the system. The relationship between this difference and the viscosity of the solvent provides specific viscosity η_{sp} :

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{\eta}{\eta_0} - 1 \quad (3.1)$$

where the ratio of viscosities of the solution and solvent is called relative viscosity, η/η_0 . In a capillary viscometer, the viscosity of liquid is proportional to its density and time of flow, that is:

$$\eta = k\rho t \quad (3.2)$$

where k is a constant of the viscometer, ρ is the density and t the time of flow. To determine the relative viscosity, it is not necessary to know the viscometer constant, once for a dilute solution, we can assume that the density of the solution is of the same order of magnitude of the solvent density and relative viscosity is simply the ratio between the flow time of the solution and that of the pure solvent. The viscosity increases with the concentration of solute and the ratio η_{sp}/c is called reduced viscosity, η_r . The extrapolation of η_r to null concentration allows us to obtain the intrinsic viscosity $[\eta]$, which is a measure of the hydrodynamic volume of macromolecules in solution. The $[\eta]$ gives information regarding the size of macromolecules and type of solvent. The relation between intrinsic viscosity and molar mass is given by the equation of Mark and Houwink:

$$[\eta] = K \cdot M^\alpha \quad (3.3)$$

The constants K and α can be determined experimentally and are constant for a given polymer solvent system at a given temperature. Therefore, from the intrinsic viscosity is possible to determine the molar mass.

3.2. Experimental part

3.2.1. Material

- 25 mL volumetric flasks
- Pipettes
- Capillary Viscometer
- Stopwatch
- Polyacrylamide Solution

3.2.2. Experimental procedure

- Prepare a polyacrylamide solution in water.
- From the above solution prepare, by dilution, 25 mL of 5 different concentrations (between 5×10^{-4} and $25 \times 10^{-4} \text{ g.mL}^{-1}$).
- Wash the Capillary Viscometer with a mixture of hydrogen peroxide and ammonia and then several times with distilled water. For this type of solutions is appropriate a Ubbelohde viscometer (Figure 5):



Figure 5. Experimental set-up of viscometer.

- Measure the time of flow for the pure solvent and for solutions while maintaining the temperature constant at $\approx 30^\circ \text{ C}$.

3.3. Treatment of results

Calculate the relative viscosity and specific viscosity for each solution.

Calculate the average molar mass of the polymer. For polyacrylamide in water at 30° C , the constants in the equation of Mark and Houwink are: $K = 6.31 \times 10^{-3} \text{ mL/g}$ and $\alpha = 0.80$.

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