Unit III

Surface and interfacial phenomenon

Measurement of surface and interfacial tension:

A number of methods are available to determine surface and interfacial tensions. Some of these methods are:

- Capillary rise
- Tensiometer
- Bubble pressure
- Drop method(count, weight)

Capillary Rise Method:

This is a good method because the parallel walls of the test tube allow better viewing of the two meniscuses that need to be seen. Consider the simple situation as depicted in Fig, in which the end of a capillary tube of radius r, is immersed in a liquid of density ρ. For sufficiently small capillaries, one observes a substantial rise of liquid up to height h, in the capillary as the force exerted on the liquid due to surface tension. The balance point can be used to measure surface tension. The surface tension acting along the inner circumference of the tube exactly counterbalances the weight of the liquid. The surface tension at surface of the meniscuses is due to the force acting per unit length at a tangent. If θ is the angle between capillary wall and the tangent, then the upward vertical component of the surface tension is $\gamma \cos \theta$. The total surface tension along the circular contact of meniscus is $2\pi r$ times $\gamma \cos \theta$. Therefore,

<p style="text-align:center">Upward force = $(2\pi r \gamma) \cos \theta$</p>

Since, for most liquids θ is equal to zero, then cos θ = 1, and upward component reduces to 2πrγ. The liquid is pulled downward by the weight of the liquid column. Thus,

Downward force = Weight = Mass × g = $h\pi r^2 \rho g$

At balance point, upward force is equal to downward force,

Upward force = Downward force

Substituting values of above 2 equations, we get,

$(2\pi r \gamma) \cos \theta = h\pi r^2 \rho g$

where, r is radius of capillary, h is the capillary rise, ρ is liquid density, g is acceleration due to gravity and γ is the surface tension of the liquid.

Rearrangement of above equation gives a simple expression for surface tension:
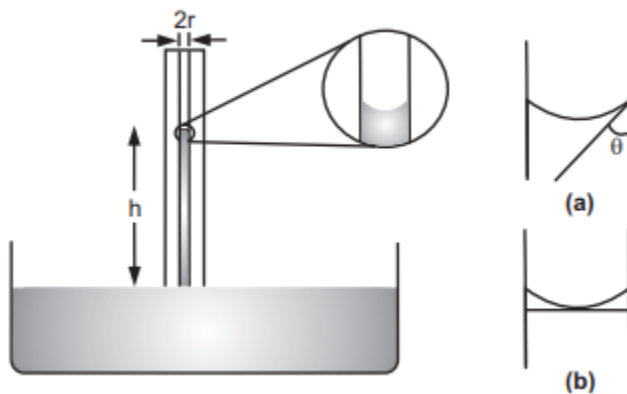
$\gamma = \rho \, grh \, / \, 2$

Figure: Rise in a Capillary Tube due to Surface Tension: (a) Contact Angle between Surface of Liquid and Capillary Wall (b) Mass of Liquid above Meniscus

In the Fig, the meniscus boundary shows that the liquid surface in the tube is not perfectly flat. Instead it curves-up (or sometimes down, for example, mercury) at the wall to form a meniscus. The material in this region also contributes to the force of gravity, so one often finds correction to above equation to yield

$$\gamma = \frac{\rho g r \left(h + \frac{r}{3}\right)}{2}$$

where, the contact angle (the angle between the surface of the liquid and the inner wall of the glass of capillary) has been assumed to be zero.
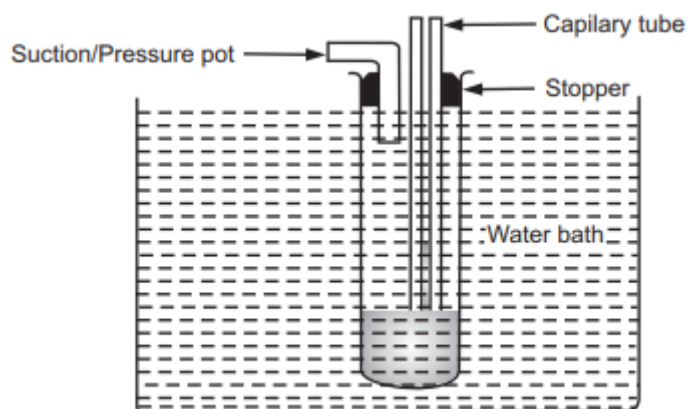

Figure: Schematic of the Device for Measuring Capillary Rise

By this method surface tension against the air is determined. The liquid in the capillary must be raised and lowered several times before making the first reading. To get good results the cleaned capillary should be soaked in nitric acid for several minutes, following by washing with deionized water. When not in use, the capillary should be stored in polyethylene bottle containing deionized water. The apparatus is shown in Fig. A test tube is fitted with a two-hole stopper. Through one hole the capillary tube is fitted. The tube is fitted through a glass slave and held in place by a piece of rubber tubing. In the second hole another tube is fitted through which pressure or suction can be applied. This whole apparatus is immersed in a water bath to allow control of temperature as change in temperature causes rapid disturbance in the liquid level. The apparatus is calibrated by determining capillary rise of deionized water, for which the temperature dependent surface tension is well known.

Tensiometer:

      Tensiometers are used to determine surface or interfacial tension with the help of an optimally wettable probe suspended from a precision balance. The probe is either a ring or a plate. A height adjustable sample carrier is used to bring the liquid to be measured into contact with the probe. A force acts on the balance as soon as the probe touches the surface. If the length of the plate or circumference of the ring is known, the force measured can be used to calculate the surface or interfacial tension. The probe must have a very high surface energy. The ring is made of platinum iridium alloy and plate is made of platinum.

DuNouy RingTensiometer:

      Historically the ring method was the first to be developed; hence many of the values for interfacial and surface tension given in the literature are the results of the ring method. In this method, the liquid is raised until contact with the surface is observed. The sample is then lowered again so that the liquid film produced beneath the ring is stretched as shown in Fig.
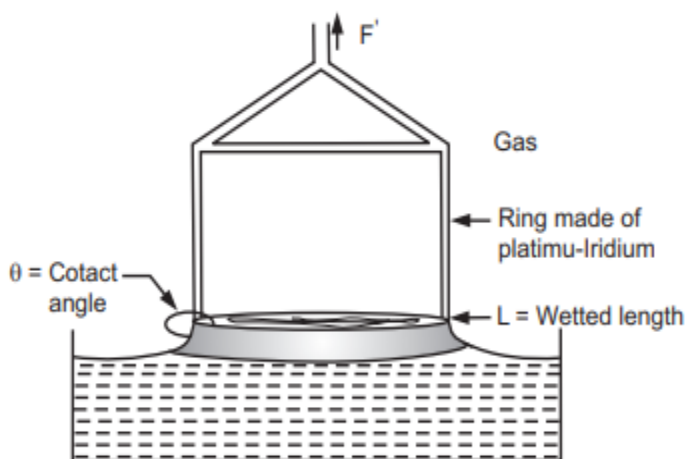

Figure: Schematic Diagram of the Ring Method

As the film is stretched, a maximum force is experienced; this is recorded in the measurement. At the maximum, the force vector is exactly parallel to the direction of motion; at this moment, the contact angle θ is zero. The illustration in Fig shows the force change as the function of distance of ring from the surface of liquid.
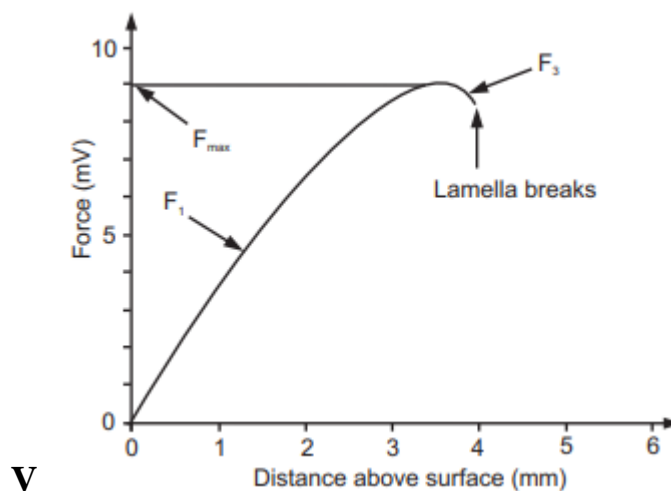

Figure: Change of Force with Ring Distance

In practice the distance is first increased until the area of maximum force has been passed through. The sample trough containing the liquid is then moved back so that the maximum point is passed through a second time. The maximum force is only determined exactly on this return movement and used to calculate the surface tension. The following equation is used for the calculation;

$$\gamma = \frac{[Fmax - Fv]}{L \times \cos\theta}$$

where, γ is surface or interfacial tension, F_{max} is maximum force, F_v is weight of volume of liquid lifted, L is wetted length and θ is contact angle. The contact angle decreases as the extension increases and has the value zero degree at the point of maximum force, this means that the term cos θ has the value equal to 1.

Correction for the ring method:

The weight of the volume of the liquid lifted beneath the ring, expressed by the term F_v, must be subtracted from measured maximum force (F_{max}) as it also affects the balance. The curve of the film is greater at the inside of the ring than at outside. This means that maximum force (at contact of angle = 0°) is reached at different ring distances for the inside and outside of the ring; thus, the measured maximum force does not agree exactly with the actual value.

Harkins and Jordan, have a drawn-up tables of correction values by determining different surface tensions of standard liquid with rings of different diameters. Zuidema and Waters scientists also obtained correction values for small interfacial tensions by extrapolating data given by Harkins and Jordan to cover the range of tensions accurately.

Advantages:

➢ Many values in the literature have been obtained with the ring method; this means that in many cases the ring method should be preferred for comparison purposes.

➢ As the wetted length of the ring is high it leads to a higher force on the balances so there has a better accuracy.

➢ Small interfacial tensions can be obtained more accurately.

➢ Cationic surfactants, which show poor wetting properties on platinum, the surface line between ring and liquid is more than that of plate.

Disadvantages:

➢ Corrections are required for volume of liquid lifted beneath the ring.

➢ Densities of the liquids are to be known.

Wilhelmy plate method:

In the Wilhelmy plate method the liquid is raised until the contact between the surface and the plate is observed. The maximum tension acts on the balance at this instance; this means that the sample does not need to be moved again during the measurement. Fig shows the illustrative diagram of Wilhelmy plate. Following equation makes the surface tension calculation

$$\gamma = F / [L \cos \theta]$$

Where,

γ is surface or interfacial tension,

F is force acting on the balance,

L is the wetted length and θ is contact angle.

The plate is made of roughened platinum and is optimally wetted so that contact angle is virtually a 0°. This means the term cos θ has a value of approximately the measured force and the length of plate need to be taken into consideration. Correction calculations are not necessary with plate method.
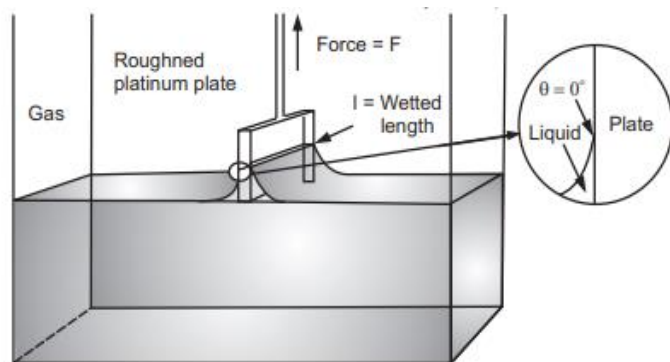

Figure: Schematic Diagram of a Wilhelmy Plate Method

Advantages:

1. No correction is required for measured values obtained by this method. 2. The densities of the liquids don't have to be known.

3. In an interfacial tension measurement, the surface is only touched and not pressed into or pulled out of the other phase; this avoids the phases becoming mixed.

4. This method is used for static measurement i.e. the plate does not move after the surface or interface has been detached. The surface or interface renewal and ultimately measurement failure is avoided.

Disadvantages:

1. The wetted length surface is small, so small force is required leading to variation in results.

2. Not suitable for cationic surfactants as platinum has poor wetting properties.

Drop weight method:

Stalagmometer is a glass tube, widened in the middle part. Its volume is calibrated by the scale on the tube, or by the top and bottom lines. The bottom part of stalagmometer is modified such that the liquid flowing through its smaller diameter forms drops.

The drop of a mass m gets released when its weight G= mg is equal or greater than the surface force at the end of tube:

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

Above equation suggests, that the surface tension σ can be calculated from the known water mass (m) and the radius of stalagmometer tube (r). However, it was shown experimentally, that only about 2/3 of the drop volume gets released. In addition, this portion is not constant

for all the drops.

On the other hand, the ratio of the mass and surface tension is constant for all the liquids:

$$\frac{m_1}{\gamma_1} = \frac{m_2}{\gamma_2}$$

Where m_1 and m_2 are the masses of drop 1 and 2 respectively, and γ_1 and γ_2 are the surface tensions corresponding to these liquids.

If the liquid with known surface tension is used for one of them, the surface tension of the other liquid can be calculated from the equation:

$$\gamma = \gamma_{water} \frac{m}{m_{water}}$$

It is a good practice to measure the mass of several drops in order to increase the precision of the calculation using the above equation.

Experimental procedure:

1. Mount the clean and dry stalagmometer on the vertical stand.

2. Weigh the mass of the empty weighing bottle (m_0).

3. Fill the beaker with distilled water. Mount the tubing with balloon on the top end of stalagmometer. Immerse the bottom end of stalagmometer into water and fill it up, such that the water level is above the wide part of stalagmometer.

4. Remove the balloon and collect 20 water drops into the weighing bottle.

5. Weigh the mass of the weighing bottle with the drops ($m_0 + m_{water} = m_{total}$) and from this equation determine the mass of 20 drops (m_{water}).

6. Empty the weighing bottle and stalagmometer, dry them and prepare for the next measurement.

7. Repeat steps 2-6 for the other liquids with unknown surface tension. Total mass is equal ($m_0 + m_{Liquid} = m_{total}$). Determine mass of the drops m_{Liquid}.

8. Write the results of the measurements.

9. Measure the laboratory temperature, find the corresponding water surface tension) according and calculate the surface tensions of studied liquids.

Determination of the surface tension by the drop counting method:

There are two marks (lines) on the stalagmometer: the top line above the wide part and the bottom line bellow it. The volume between these two lines is (V), and the liquid, with density (ρ) contained in this volume, has a mass (m):

$$m = \rho V$$

This volume (V) corresponds to n drops, which are released from the stalagmometer upon the decrease of liquid level from top to bottom line mark. Here, the average mass of one drop is:

$$\frac{m}{n} = \frac{\rho V}{n}$$

Substituting the mass (m) in the equation with the mass of one drop then yields:

$$\gamma = \gamma_{water} \frac{\rho_L n_{water}}{\rho_{water} n_L}$$

where n_L is the number drops of the liquid and n_{water} is the number drops of water.

Experimental procedure:

1. Fill the stalagmometer up to the top mark with distilled water.

2. Release the water to the weighing bottle and count how many drops it takes to decrease the water level in stalagmometer down to the bottom mark.

3. Write down the number of drops n_{water}.

4. Empty and dry the weighing bottle and stalagmometer, and prepare it for the next measurement.

5. Repeat steps 1 – 3 for liquids with the unknown surface tension.

6. Write down the densities of studied liquids according to the notes on bottles, and density of distilled water at the actual laboratory temperature.

7. Using equation, calculate the surface tension for all the studied liquids.