$-8\pi\gamma r dr = -4\Delta P \pi r^2 dr$

$$\Delta P = \frac{2\gamma}{r}$$

$4\pi\gamma r^2 - 8\pi\gamma dr = 4\Delta P \pi r^2 - dr$

radius of bubble ↓
pressure air inside ↑
relative to out side

$-8\pi\gamma dr = -4\Delta P\pi r^2 dr = 4\pi r_?$

$= -4\pi r$

(6)

__Measurement of Surface tension & Interfacial tension :-__

capillary rise method } → only surface T
max Babble Pressure "

necessary Drop method " } → Both ST & IT
to control wihelmy plate "
temp while measuring ST/IT DU-Noy ring "

Selection of method depends on
→ Whether to determine ST/IT
→ Convenience desired
→ size of sample available
→ whether to study effect of time on ST
→ ST of liq ↓ with ↑ of Temperature ↑ K.E
→ region of critical temp, ST of liq zero
PBu → water ST 0°C 75.6, 25°C 63.5 dynes/cm, 20°C 72.8

__Capillary rise method__

When a capillary tube - placed in liquid contained in a beaker, liq rises to certain height

b/z adhesion b/n glass & liq > cohesion b/n liquid

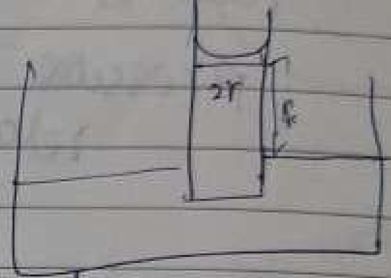
liquid wet capillary wall

→ Spreading over it & rising the tube

→ By measuring the rise in capillary possible to measure surface tension.

→ Consider capillary tube radius r immersed

liquid – wets surface



due to ST liq rises

two forces – ST
– wt of column of the liquid in tube

Force due to surface tension
at any point
$r\cos\theta$

θ – contact angle b/n surface of liquid / capillary wall

total upward force along – inside circumference of capillary is given by

θ – contact angle b/n surface of capillary wall

$2\pi r\gamma\cos\theta$

For water $\theta = 0$ $\cos\theta = 1$

$S_T = 2\pi r\gamma$

Counter balancing force – weight of the liq. column → gravity (mass × acceleration)

Counteracting force

πr^2 – cross sectional area

h – height of rise of liq column

w – weight of liquid above h

ρ - density of liq ρ_0 - density of vapour
g

$\pi r^2 h(\rho-\rho_0)g + w$

w, ρ_0, disregarded.

$\rho >> \rho_0$
w is negligible

At equilibrium $2\pi r \gamma = \pi r^2 h \rho g$

$\gamma = \frac{1}{2} r h \rho g$

$\pi r^2 h(\rho-\rho_0)g + w$

capillary rise — Pressure difference

Pressure on concave side > convex side

Pressure in liquid immediately below meniscus is less than outside tube at same height
liquid moves up — hydrostatic head - equals until

pressure drop

height - travelling microscope

d - SPG bottle

$\Delta P = \frac{2\gamma}{r} = h\rho g$

$\gamma = \frac{1}{2} h\rho g r$

precautions:-

→ outer vessel - large diameter
→ capillary tube - uniform diameter
→ meniscus better to allow meniscus to fall than to rise
→ height - accurately
→ Temp - constant

described above. Similarly water is taken in the pipette and the weight of one drop of water (w_w) is obtained. The relative surface tension of the liquid

$$= \frac{\text{Surface tension of the liquid}}{\text{Surface tension of water}}$$

$$= \frac{w_l/2\pi r}{w_w/2\pi r}$$

$$= \frac{w_l}{w_w} \qquad \text{... (13)}$$

Drop count method

In this method, the given liquid is sucked into the drop pipette upto the mark A. Keeping the pipette vertically, the number of drops formed when the liquid level falls from mark A to B is noted.

We know that

$$\gamma = \frac{\text{weight of one drop of liquid}}{2\pi r}$$

$$= \frac{mg}{2\pi r \times n}$$

where m = mass

g = gravitational force

n = number of drops

$$\text{Also, } \gamma = \frac{\upsilon dg}{2\pi r \times n}$$

where υd = volume × density = mass (m)

For relative surface tension of a liquid, the number of drops of water (n) formed for the same volume (A to B) is found out. Then, the relative surface tension of the liquid is given by

$$= \frac{\text{Surface tension of liquid}}{\text{Surface tension of water}}$$

$$= \frac{\upsilon d_l g/2\pi r n_l}{\upsilon d_w g/2\pi r n_w}$$

$$= \frac{d_l/n_l}{d_w/n_w}$$

$$= \frac{d_l}{d_w} \times \frac{n_w}{n_l} \qquad \text{... (14)}$$

When the interfacial tension is determined, the drops are formed within the other immiscible liquid. It is important to make sure that the tip of the pipette is completely wetted by one of the two immiscible liquids.

Precautions

1. The tip of the pipette should have no imperfections in the outer circumference.
2. The drops should be formed slowly.
3. About 20 to 30 drops should be collected and from this average weight is determined.
4. Temperature should be maintained constant.

2.4. Wilhelmy Plate Method

It provides for the direct measurement of force exerted on a piece of thin platinum foil at the interface between two immiscible liquids or surface of a liquid. The force exerted is equal to the

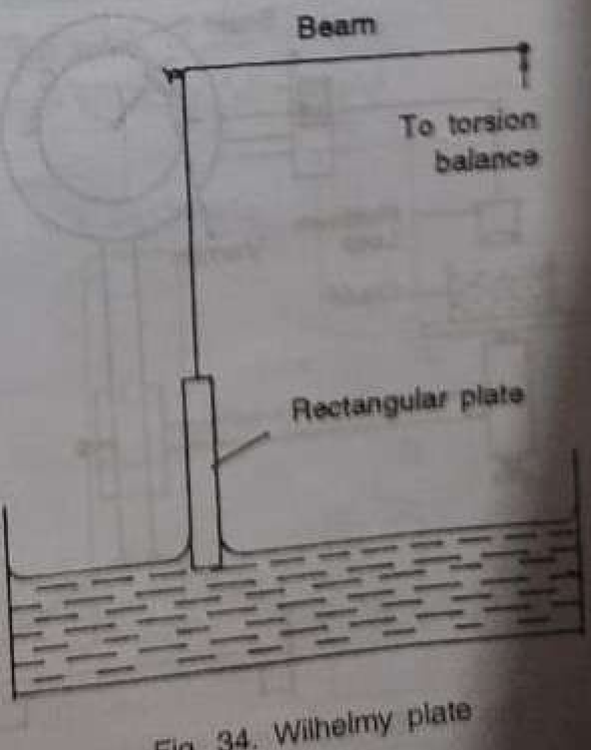


Fig. 34. Wilhelmy plate

surface tension multiplied by the perimeter of the foil.

A thin rectangular plate of platinum (or mica) is suspended vertically from a beam attached to a torsion balance (Fig. 34). The liquid whose surface tension is to be measured is taken in a dish and this is raised under the plate until the bottom edge of the plate just comes in contact with the surface of the liquid. When the plate touches the surface, the surface forces will drag the plate downwards and this force exerted around the perimeter of the plate is measured by the rotation of the torsion wire required to restore the plate to its original position (i.e. when the edge of the plate is coincident with the plane of the free liquid surface).

If the liquid completely wets the plate, the force exerted in terms of weight is given by

$$W = 2(L + T)\gamma$$

$$\gamma = \frac{W}{2(L + T)} \quad \text{... (15)}$$

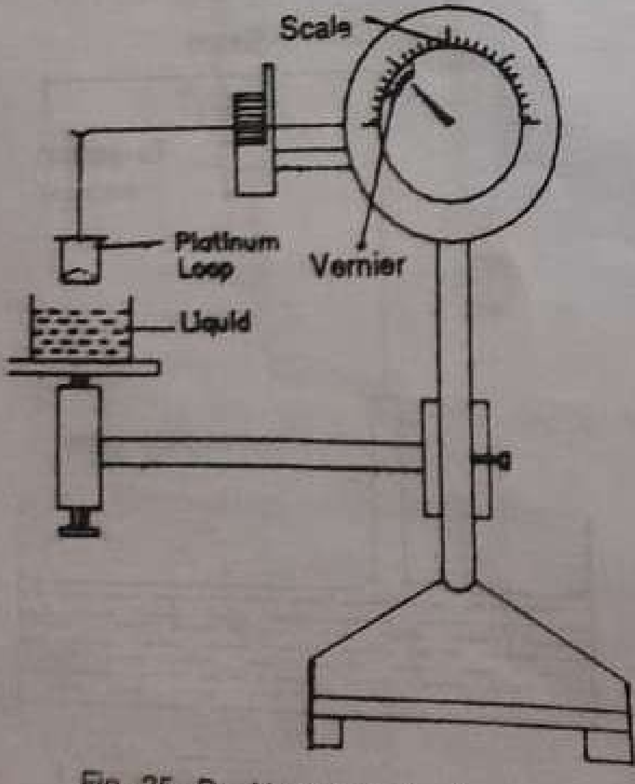


Fig. 35. Du Nuoy ring tensiometer

where L and T are the length and thickness of the plate on the horizontal plane respectively and $2(L + T)$ represents the perimeter of the rectangular plate.

2.5. Ring detachment method (Du Nuoy Ring Tensiometer)

The principle involved in *Du Nuoy* tensiometer is that the force needed to lift a wire ring from the surface or between two immiscible liquids is proportional to the surface or interfacial tension respectively.

The apparatus is also called *Torsion balance* or *Du Nuoy's* balance which is shown in Fig. 35.

A platinum wire ring of about four centimeter in circumference is suspended from the loop attached to a scale through a torsion wire. The liquid is taken in the pan and the position of the pan is adjusted so that ring just touches the surface of the liquid. The torsion on the wire is increased gradually so that the ring just detaches from the surface of the liquid. The force required (to detach) is read in dynes on the graduated disc which is directly proportional to the surface tension

$$P = w = 2\pi(r_1 + r_2)\gamma$$

$$\text{or } \gamma = \frac{P}{2\pi(r_1 + r_2)} \quad \text{... (16)}$$

where P is the pull exerted through torsion wire on the ring and is read on the scale, where $w =$ force in terms of weight and r_1 and r_2 are inner and outer radii of the ring

Introducing a correction factor (c.f), the equation becomes

$$\gamma = \frac{P}{2\pi(r_1 + r_2)} \times \text{c.f.} \quad \text{... (17)}$$

If the radius of the wire is small and that $r_1 = r_2$

$$\gamma = \frac{P}{4\pi r} \times \text{c.f.} \quad \text{... (1}$$

The correction factor (c.f.) is introduced to compensate for variables in the radius of the ring, radius of the wire used to form the ring and for the volume of the liquid raised out of the surface.

For the determination of interfacial tension, the ring is detached from the interface between two immiscible liquids. The ring should be preferentially wetted by the denser liquid.

Experimental Precautions

1. The ring should lie in a flat plane
2. The plane of the ring must be horizontal
3. The vessel (pan) containing the liquid should have wider diameter.
4. Temperature control should be adequate.

3. Spreading coefficient:

When oleic acid is dropped on to water, it spreads immediately on the surface of water. In this case, oleic acid is considered as the spreading liquid (L) and the water as the sublayer liquid (S).

In general, spreading occurs when the adhesive forces exceed the cohesive forces.

The work of cohesion (w_c) may be considered as the surface free energy increase produced by separating a column of pure liquid into two halves (Fig. 36).

The free energy increase on increasing the surface area has already been given as $\gamma\Delta A$

Then,

$$w_c = \gamma_L \Delta A + \gamma_L \Delta A$$

$$= \gamma_L(\Delta A + \Delta A)$$

Considering a column of liquid with a cross sectional area of 1 cm^2, the equation is

$$w_c = \gamma_L(1 + 1)$$

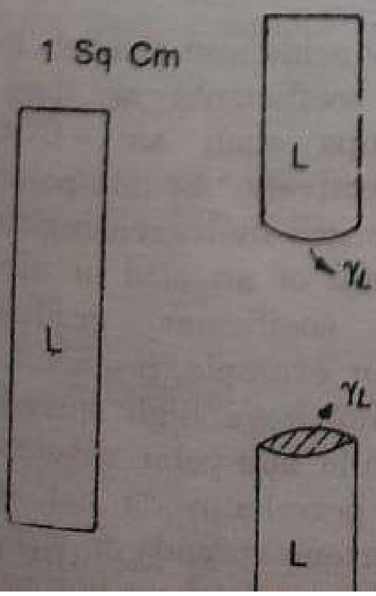
$$w_c = 2\gamma_L \quad \text{... (19)}$$

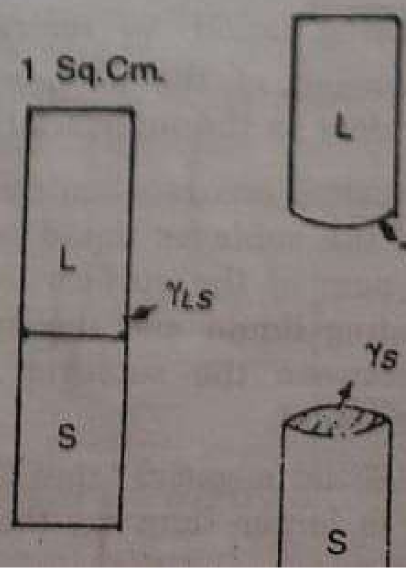
(When these two newly created surfaces are brought together to form a column of liquid, again an equal and opposite amount of energy will be released)

The work of adhesion (w_a) may be considered as the free energy increase produced by separating a column of two immiscible liquids at the boundary (at the interface) into two sections (Fig. 37).

The work of adhesion is

$$w_a = \gamma_L \Delta A + \gamma_S \Delta A - \gamma_{LS} \Delta A$$





The apparatus is assembled as shown in Fig. 31.

The stopcock is opened. The mercury is allowed to drop down from the reservoir slowly till the bubbles come out from the wider capillary (*B*). The maximum pressure required for this is noted from the manometer. The apparatus is reset and the stopcock of capillary *B* is closed so that bubbles will form only from the smaller (thinner) capillary. The pressure is noted. The experiment is repeated. The difference between these pressures will give the value of *P*. Substituting these values in the formula, the surface tension is obtained.

2.3. Drop Method

When a liquid is allowed to fall through a capillary tube, it forms a drop which increases in size and detaches from the tip of the tube when the weight of the drop of the liquid just equals the total surface tension at the circumference of the tube (Fig. 32).

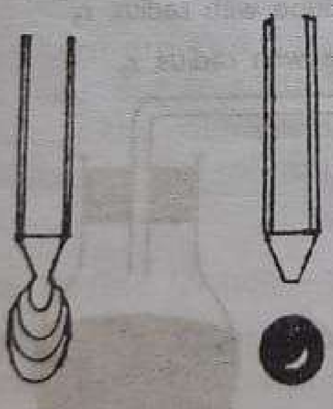


Fig. 32. Formation of a drop from the tip of capillary tube

Expressing mathematically

$$w = 2\pi r\gamma \quad \text{... (12)}$$

where w = weight of one drop of the liquid

r = radius of the capillary

γ = surface tension of the liquid.

Determination of surface tension can be undertaken in two ways by using a drop pipette (**Stalagmometer**)

1. Drop weight method
2. Drop count method

Drop weight method

The stalagmometer (Fig. 33) consists of a glass tube with a bulb blown approximately in the middle of the tube. There are two markings *A* and *B* as shown in the figure. The tip of the stalagmometer is capillary.

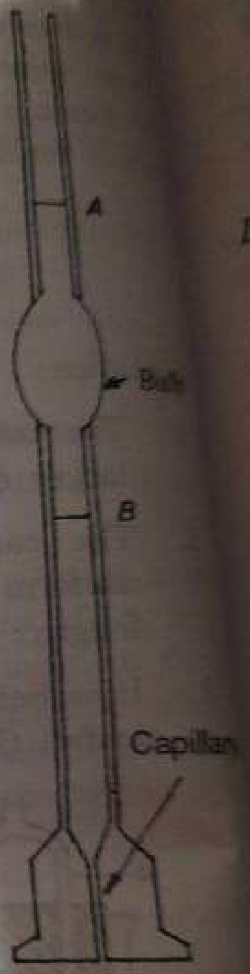


Fig. 33. Stalagmometer (or) Drop pipette

The given liquid is sucked into the drop pipette upto the marking *A*. Then the liquid is allowed to drop slowly from the tip of the pipette. Twenty to thirty drops are collected from the pipette kept vertically into a clean tarred beaker and the weight of one drop of the liquid is found out (w). The surface tension of the liquid is, then given by

$$w = 2\pi r\gamma$$

$$\gamma = \frac{w}{2\pi r}$$

It is usual to report relative surface tension of a liquid with respect to water. For this, the liquid is first taken in the pipette. The weight of one drop of the the liquid (w_l) is found out a