Liquid State

Surface Tension: This property of liquids arises from the intermolecular forces of attraction. A molecule in the interior of a liquid is attracted equally in all directions by the molecules around it. A molecule in the surface of a liquid is attracted only sideways and toward the interior. The forces on the sides being counter balanced the surface molecule is pulled only inward the liquid. Thus there is a tendency on the part of the surface molecules to go into the bulk of the liquid. The liquid surface is, therefore, under tension and tends to contract to the smallest possible area in order to have the minimum number of molecules at the surface. It is for this reason that in air, drops of a liquid assume spherical shapes because for a given volume a sphere has the minimum surface area.

The surface tension (γ) is defined as : **the force in dynes acting along the surface of a liquid at right angle to any line 1 cm in length.**

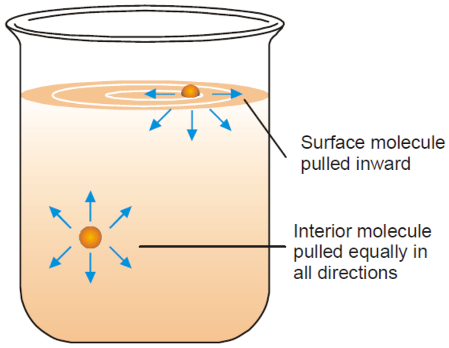

Fig 1. Surface tension is caused by the net inward pull on the surface molecules.

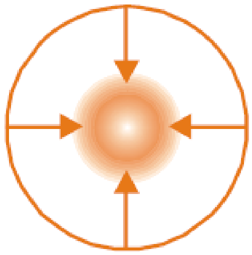

Fig 2. The inward forces on the surface molecules minimize the surface area and form a drop.

Units of Surface Tension: The unit of surface tension in CGS system is dynes per centimetre (dyne cm^{-1}). In SI system, the unit is Newton per metre (Nm^{-1}). Both these units are related as :1 dyne cm^{-1} = 1 m Nm^{-1}.

Effect of Temperature on Surface Tension:

A change in temperature causes a change in surface tension of a liquid. When temperature increases, there is an increase in kinetic energy of liquid molecules ($KE \propto T$), thereby decreasing intermolecular forces. It results in decrease in the inward pull functioning on the surface of the liquid. In other words, **surface tension decreases with increase in temperature.** W. Ramsay and J. Shields gave the following relationship between surface tension of a liquid and its temperature

$$\gamma\, (M/\rho)^{2/3} = k\,(t_c - t - 6) \quad ....(i)$$

where k is a constant (temperature coefficient), t_c is critical temperature and t any other temperature, $(M/\rho)^{2/3}$ represents molar surface energy of the liquid.

Table: Surface Tension of Some Liquids at Various Temperatures (dynes cm^{-1}):

Liquid	20°C	40°C	60°C	80°C
Water	72.75	69.56	66.18	62.61
Ethyl alcohol	22.27	20.60	19.01	–
Methyl alcohol	22.6	20.9	–	–
Acetone	23.7	21.2	18.6	16.2
Toluene	28.43	26.13	23.81	21.53
Benzene	28.9	26.3	23.7	21.3

Determination of Surface Tension:

The methods commonly employed for the determination of surface tension are:

Capillary-rise Method: A capillary tube of radius r is vertically inserted into a liquid. The liquid rises to a height h and forms a concave meniscus. The surface tension (γ) acting along the inner circumference of the tube supports the weight of the liquid column.

By definition, surface tension is force per 1 cm acting at a tangent to the meniscus surface. If the angle between the tangent and the tube wall is θ, the vertical component of surface tension is $\gamma \cos \theta$. The total surface tension along the circular contact line of meniscus is $2\pi r$ times. Therefore,

$$\text{Upward force} = 2\pi r\gamma \cos \theta$$

where r is the radius of the capillary. For most liquids, θ is essentially zero, and $\cos \theta = 1$. Then the upward force reduces to $2\pi r\gamma$.

The downward force on the liquid column is due to its weight which is *mass* × *gravity*. Thus,

$$\text{Downward force} = h\pi r^2 dg$$

where d is the density of the liquid.

But

$$\text{Upward force} = \text{Downward force}$$

$$\text{or } 2\pi r\gamma = h\pi r^2 dg$$

$$\gamma = hrdg/2 \text{ dynes/cm} \quad \ldots\ldots\ldots(1)$$

In order to know the value of γ, the value of h is found with the help of a travelling microscope and density (d) with a pyknometer.

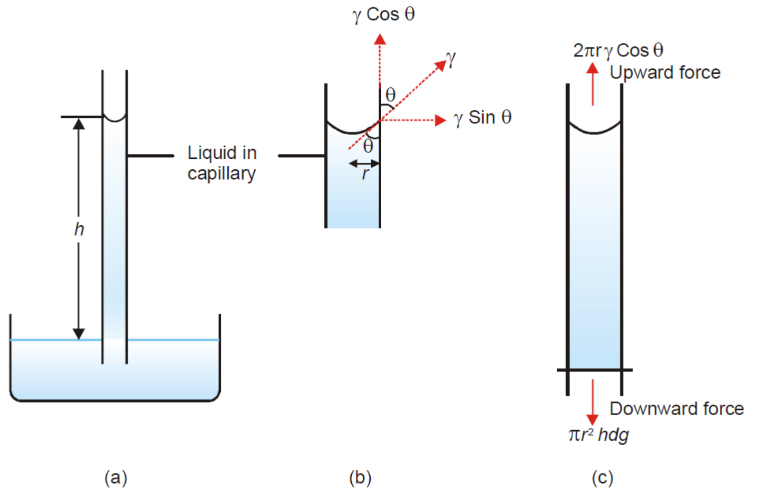

Fig. 3 (a) Rise of liquid in a capillary tube; (b) Surface tension (γ) acts along tangent to meniscus and its vertical component is γCosθ; (c) Upward force $2\pi r\gamma$ Cosθ counterbalances the downward force due to weight of liquid column, πr^2hgd.

2. Drop Formation Method: A drop of liquid is allowed to form at the lower end of a capillary tube (Fig.). The drop is supported by the upward force of surface tension acting at the outer circumference of the tube. The weight of the drop (mg) pulls it downward. When the two forces are balanced, the drop breaks. Thus at the point of breaking,

$$m\,g = 2\,\pi\,r\,\gamma \ \ldots(1)$$

where
- m = mass of the drop
- g = acceleration due to gravity
- r = outer radius of the tube

The apparatus employed is a glass pipette with a capillary at the lower part. This is called a **Stalagmometer** or **Drop pipette (Fig.).** It is cleaned, dried and filled with the experimental liquid, say upto mark A. Then the surface tension is determined by one of the two methods given below.

(i) **Drop-weight Method:** About 20 drops of the given liquid are received from the drop-pipette in a weighing bottle and weighed. Thus weight of one drop is found. The drop-pipette is again cleaned and dried. It is filled with a second reference liquid (say water) and weight of one drop determined as before.

Then from equation (1)

$$M_1\,g = 2\,\pi\,r\,\gamma_1 \ \ldots\ldots.(2)$$

$$m_2\,g = 2\,\pi\,r\,\gamma_2 \ \ldots\ldots(3)$$

Dividing (2) by (3)

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2} \qquad ...(4)$$

Knowing the surface tension of reference liquid from Tables, that of the liquid under study can be found.

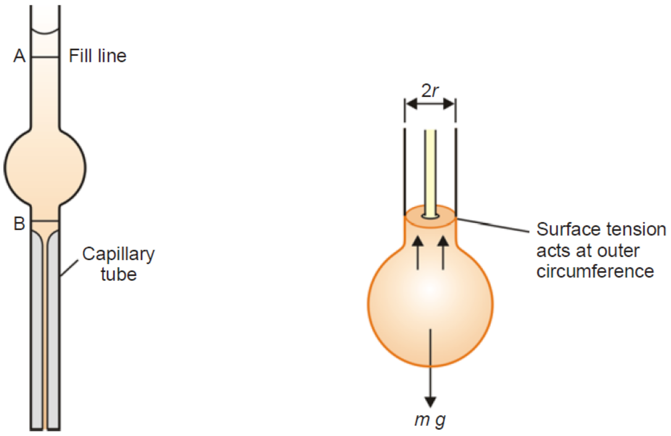

Fig. 4 A stalagmometer (left) A drop forming from a tube of radius r (right).

(ii) **<u>Drop-number Method</u>:** The drop-pipette is filled upto the mark A with the experimental liquid (No. 1). The number of drops is counted as the meniscus travels from A to B. Similarly, the pipette is filled with the reference liquid (No. 2) as the meniscus passes from A to B. Let n_1 and n_2 be the number of drops produced by the same volume V of the two liquids. Thus,

The volume of one drop of liquid 1 = V/n_1

The mass of one drop of liquid 1 = $(V/n_1)d_1$

where d_1 is the density of liquid 1.

Similarly,

The mass of one drop of liquid 2 = $(V/n_2)d_2$

$$\frac{\gamma_1}{\gamma_2} = \frac{(V/n_1)d_1}{(V/n_2)d_2} = \frac{n_2 d_1}{n_1 d_2}$$

The value of d_1 is determined with a pyknometer. Knowing d_2 and γ_2 from reference tables, γ_1 can be calculated.