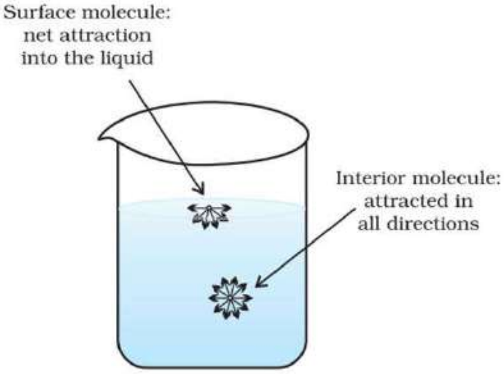
# The Liquid State

A molecule in the bulk of liquid experiences equal intermolecular forces from all sides. The molecule therefore does not experience any net force. But for the molecule on the surface of liquid, net attractive force is towards the interior of the liquid (see Fig.), due to the molecules below it. Since there are no molecules above it.



*Forces acting on a molecule on liquid surface and on a molecule inside the liquid*

Thus, liquids tend to minimize their surface area. The molecules on the surface experience a net downward force and have more energy than the molecules in the bulk, which do not experience any net force. Therefore, liquids tend to have minimum number of molecules at their surface. If surface of the liquid is increased by pulling a molecule from the bulk, attractive forces will have to be overcome. This will require expenditure of energy. The energy required to increase the surface area of the liquid by one unit is defined as surface energy.

**Surface Tension:** The force that tends to contract the surface of a liquid known as surface tension. Surface tension, represented by the symbol **γ**, is measured in force per unit length. Its SI unit is newton per meter but the cgs unit of dyne per centimeter is also used. The surface tension of water is 72.8 dyne/cm at 20$^{o}$C.

Surface tension is responsible for the shape of liquid droplets. Although easily deformed, droplets of water tend to be pulled into a spherical shape by the cohesive forces of the surface layer.

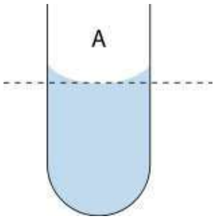
## Capillary Action

**Cohesion:** The attraction between the like molecules in liquid is known as cohesion.

**Adhesion:** The attraction between the liquid and walls of the capillary is known as adhesion.

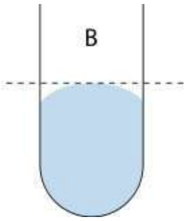
**Case A: if, adhesion > cohesion**

The liquid is said to wet the wall. This is happen in case of water and many other liquids. The meniscus is concave.



**Case B: if, adhesion < cohesion**

The liquid does not wet the wall. This is happening in case of mercury. The meniscus is convex.



**Surface active agents (Surfactants)**: The substance which lowers the surface tension of the liquid is known as surface active agents. Exa: Soaps, detergents, shampoo etc.

**<u>Effect of Temperature on Surface Tension:</u>** From the Eotvos equation: $\boldsymbol{\gamma(M/\rho)^{2/3} = k(Tc-T)}$

Where M is molar mass, ρ is density, Tc is critical temperature and k is constant. From the equation, it is clear that surface tension decreases with increase in temperature. This decreasing phenomenon occurs due to lowering of intermolecular force of attraction or cohesive force between liquid molecules as temperature increases.
When **T = Tc, γ = 0, i.e. at critical temperature surface tension of liquid is zero.**

**<u>Interfacial Tension</u>**: If two immiscible liquids are present one above the other in a vessel. Then, the force acting per unit length along the interface is called interfacial tension.

Surface tension of a liquid is the force acting along the surface of separation between the liquid and its vapour. However, interfacial tension is the force acting along the surface of separation of two immiscible liquids contact to each other.

**<u>Methods of Surface Tension Measurements:</u>** The following methods are used for surface tension measurements.

1. Capillary rise method
2. Stallagmometer method – drop weight method
3. Torsion method by Tensiometer

**1. <u>Capillary rise method:</u>** suppose a liquid of density ρ, rises in a capillary of radius r through a height h.

The total force (F) due to surface tension raising the liquid upward = γ x inside circumference of capillary = $2\pi r\gamma$ ------(1)

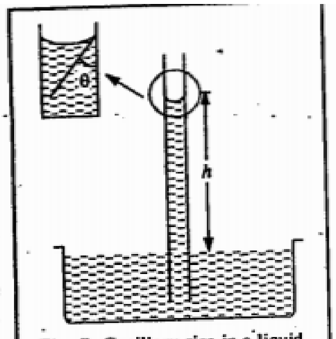


**Fig. 7. Capillary rise in a liquid.**

Downward gravity force = $mg = V\rho g = \pi r^2 h\rho g$ ---(2) (Volume $V = \pi r^2 h$)

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

$\boldsymbol{\gamma = rh\rho g/2}$ ------(3)

This equation is valid when contact angle θ = 0,

if the contact angle is not zero then upward force will be $2\pi r\gamma\cos\theta$. In this case the surface tension would be

$\boldsymbol{\gamma = rh\rho g\cos\theta/2}$ --------(4)

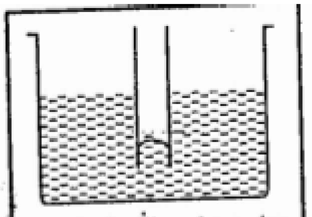


**Fig. 8. Capillary depression in mercury**

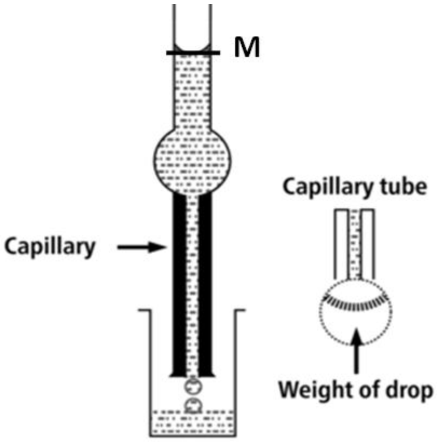
If capillary is dipped in mercury, mercury does not rise in it. The meniscus is lowered by the height –h. this is because of the contact angle θ between glass and mercury is $180^o$. so, $\cos 180^o = -1$, hence according to equation (4) h would be negative.

**Question:** If water at $25^oC$ rises through 6.36 cm in a capillary of radius 0.2 mm. What will be the surface tension at that temperature? (Density of water = $0.997x10^3$ $kgm^{-3}$)

**Answer: $\gamma = rh\rho g/2 = (.02 \text{ cm x } 6.36 \text{ cm x } 0.997 \text{ gcm}^{-3} \text{x } 981 \text{ cms}^{-2})/2 = 62.20$ dyne/cm**

**2. <u>Stallagmometer method – drop weight method:</u>** The stalagmometric method is one of the most common methods used for the surface tension determination. In this method the surface tension of unknown liquid is compared to a reference liquid of known surface tension (typically water). Liquid is filled up to the mark M and the number of falling drops counted of both liquids.

The drop falls when its weight w just exceeds the force of surface tension. At equilibrium



$w = mg = 2\pi r\gamma$ (m is the mass of one drop, r is the radius of drop at the end of capillary tube)

For drop of two liquids (one is water and other is unkown)

$w_1 = m_1g = 2\pi r\gamma_1$ (for first liquid i.e. water)

$w_1 = m_2g = 2\pi r\gamma_2$ (for second unknown liquid)

Hence $\frac{w1}{w2} = \frac{\gamma 1}{\gamma 2}$

Let $n_1$ and $n_2$ be the numbers of drops formed from the same volume V of the two liquids. Then,

Mass $m_1$ of a single drop of liquid 1 = $\frac{V\rho 1}{n1}$

Mass $m_2$ of a single drop of liquid 2 = $\frac{V\rho 2}{n2}$ , $\rho_1$ and $\rho_2$ is density of liquids

Then $w_1 = V\rho_1 g/ n_1$

Then $w_2 = V\rho_2 g/ n_2$

$$\frac{w1}{w2} = \frac{\gamma 1}{\gamma 2} = \frac{V\rho 1gn2}{V\rho 2gn1}$$

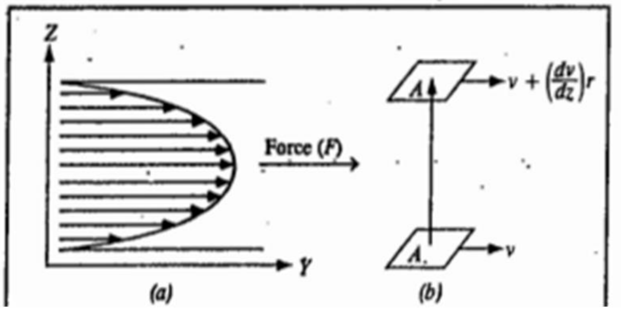
$$\frac{\gamma 1}{\gamma 2} = \frac{\rho 1n2}{\rho 2n1}$$

Determined the relative density of liquids and number of drops the surface tension $\gamma_2$ of unkown liquid can be calculated.

# Viscosity

**Viscosity may be defined as the force of friction between two layers of a liquid moving past one another with different velocities.**

Consider the laminar flow of liquid in y direction. The layer in contact with the wall of the tube is stationary. However, the velocity of the successive layers increases as move away from the surface. If the distance between two layers is r and *v* is the velocity of slow moving layer. As a result velocity gradient is set up along z-direction.



The velocity profile during flow of a liquid in a glass tube.

If we want to maintain the velocity gradient, we must apply an external force along y-axis. This force (*F*) is proportional to common area of two layers (A) and velocity gradient.

$$F \propto A(dv/dz) = -\eta A(dv/dz)$$

Where the proportionality constant η is coefficient of viscosity, $\frac{dv}{dz}$ is velocity gradient. The minus sign shows that the viscous force on faster layer is in opposite direction to its motion. The reciprocal of viscosity is called **fluidity**. It is denoted by φ = 1/η

**Coefficient of viscosity (η):** If A = 1 $cm^2$, dv = 1 cm/s, dz =1 cm, then **F = η,** Coefficient of viscosity of a fluid is defined as the tangential force per unit area which is required to maintain a unit velocity gradient between its layers.

**Unit:** The SI unit of viscosity is the pascal-second (Pa·s), or equivalently kilogram per meter per second ($kg \cdot m^{-1} \cdot s^{-1}$). The CGS unit is the poise (P, or $g \cdot cm^{-1} \cdot s^{-1}$ = 0.1 Pa·s).

## Effect of Temperature on Viscosity of Liquid:

The relationship between the coefficient of viscosity and temperature is expressed as:

$$\boldsymbol{\eta = Ae^{Ea/RT}}$$

Where A is constant. Ea is called the activation energy for viscous flow. From the equation it is clear that the viscosity decreases with increase of temperature. Viscosity in liquid is mainly due to the cohesive force (inter molecular force of attraction). Increase in the temperature reduces the cohesive forces between the molecules of liquid and hence the viscosity decreases.

*In contrast to liquid the viscosity of gases increases with increasing temperature.*

**Determination of Viscosity by Ostwald Viscometer:** This method is based on Poiseuille's law. The rate of flow of a liquid through a capillary tube with the coefficient of viscosity of the liquid is expressed by the equation:

$\eta = (\pi r^4 tP)/8Vl$ ....*(1)*

*Where V is the volume in ml of the liquid flowing in t seconds through a narrow tube of radius r cm and length l cm under hydrostatic pressure P dynes per square centimeter and η is coefficient of viscosity in poises.*

*since,* $P = h\rho g$ *----(2)*

Then equation (1) becomes:

$\eta = (\pi r^4 th\rho g)/8Vl$ ....*(3)*

The fixed volume of liquid is filled in bulb A and sucked and then allowed to flow between the mark C and D.

For liquid 1: $\eta_1 = (\pi r^4 t_1 h\rho_1 g)/8Vl$ -----*(4)*

For liquid 2: $\eta_2 = (\pi r^4 t_2 h\rho_2 g)/8Vl$ -----*(5)*

The value of h is same in both cases since equal volume of both liquids are taken.

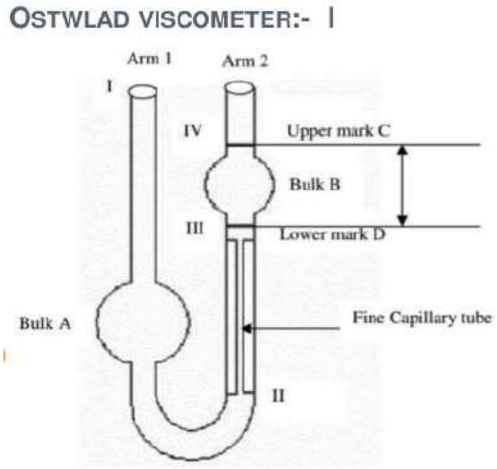


Fig. 1:- Ostwald Viscometer

Hence,

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2}$$

*Liquid 1 taken as water, by* knowing the *coefficient of viscosity of water ($\eta_1$) that of other liquid ($\eta_2$), can easily be calculated.*

**Question:** Benzene takes 46 s to flow through an viscometer while water takes 68 s, at the same temperature. The respective densities are 0.8 and 0.998 g/cm$^3$. Coefficient of viscosity of water is 1.008 centipoise. Calculate coefficient of viscosity of benzene.

**Answer:** Let $\eta_1$, $\eta_2$ coefficient of viscosity of benzene and water, respectively

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2} \text{ or, } \eta_1 = \frac{\eta_2 \rho_1 t_1}{\rho_2 t_2} = \frac{(1.008\ x\ 10^{-2} dynecm^{-2} s)(0.8 gcm^{-3})(46s)}{(0.998\ gcm^{-3})(68s)}$$

= 0.0065 dynecm$^{-2}$s = 0.0065 poise = 0.65 centipoise

# Liquid Crystals

## Introduction

The discovery of liquid crystals dates back to 1888 when Austrian botanist **Friedrich Reinitzer** observed unusual behaviour in cholesteryl benzoate. It melted at one temperature to form a cloudy liquid and cleared at a higher temperature. This intermediate phase was later identified as a liquid crystal.

Liquid crystals (LC) Def: "states of matter that possess symmetric and mechanical properties intermediate between crystalline solids and isotropic liquids". Also known as mesophase.

The unique properties of LCs arise from the **anisotropic nature** of their molecules, which are usually elongated or rod-like. These molecules interact in a way that produces collective alignment, making them sensitive to **external factors** such as temperature, pressure, electric, and magnetic fields. For example, applying an electric field can reorient LC molecules, altering their optical transmission.

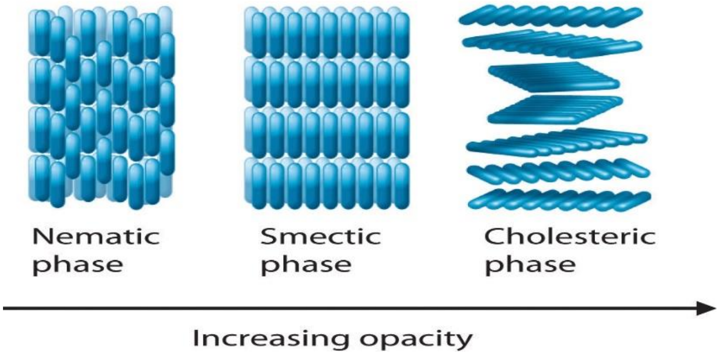
## Classification of Liquid Crystals

Liquid crystals are broadly classified based on the conditions under which they form and the type of molecular ordering they exhibit. The two main classes are **thermotropic liquid crystals** and **lyotropic liquid crystals**.

### A. Thermotropic Liquid Crystals

These are temperature-dependent and appear within a specific temperature range between solid and isotropic liquid states. They are further classified into:

1. **Nematic phase:**
    - Molecules are oriented in the same general direction (orientational order) but do not form layers.
    - They are fluid and easily reoriented by electric or magnetic fields.
    - Widely used in LCD technology.
2. **Smectic phase:**
    - Molecules have both orientational and positional order.
    - They are aligned parallel and arranged in layers, with different types (Smectic A, Smectic C, etc.) based on tilt.
3. **Cholesteric (Chiral Nematic) phase:**
    - Found in molecules derived from cholesterol.
    - The director (orientation axis) rotates helically, forming a periodic layered structure.
    - Responsible for selective reflection of light and vivid colours.



### B. Lyotropic Liquid Crystals

These are concentration-dependent and form when amphiphilic molecules (containing both hydrophobic and hydrophilic groups) are mixed with a solvent like water. Common examples are **soaps and detergents**.

- They self-assemble into micelles, hexagonal columns, or lamellar sheets depending on concentration.
- Important in biological systems (cell membranes) and drug delivery.

### Applications of Liquid Crystals

The most significant application of liquid crystals is in **Liquid Crystal Displays (LCDs)**, which are used in digital watches, calculators, mobile phones, televisions, computer monitors, and more.

### Working Principle of LCDs

LCDs exploit the ability of LC molecules to rotate the polarization of light. In a **twisted nematic (TN) LCD**, the liquid crystal layer is sandwiched between two glass plates coated with transparent electrodes and aligned at right angles. Without voltage, the molecules twist the plane of polarized light, allowing it to pass through a second polarizer, producing a bright pixel. When voltage is applied, molecules align with the field, blocking the rotation of light, and the pixel appears dark. This switching mechanism enables the creation of images with minimal energy consumption.

### Other Applications of Liquid Crystals

- **Thermometers and sensors:** Cholesteric LCs change colour with temperature, useful in thermography and fever indicators.
- **Optical devices:** Used in tunable lenses, polarizers, and shutters.
- **Medical field:** LCs are employed in drug delivery, bio-sensors, and non-invasive diagnostics.
- **Smart materials:** Applied in smart windows that control light transmission.
- **Decorative and novelty uses:** Toys, paints, and clothing with colour-changing effects.