<u>Liquid State</u> **S.Y.B.Sc**
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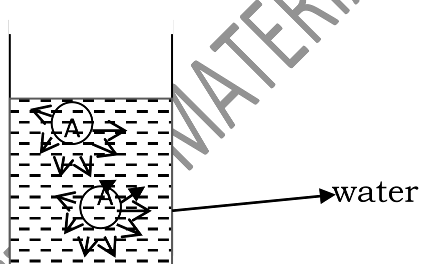
1	**Characteristics of the liquid state**.
	a) A liquid is made up of tiny particles called molecules or atoms (inert gas elements). b) A liquid has a definite volume but no definite shape. c) The intermolecular forces in liquid state are stronger than in gaseous state but weaker than in solid state. d) A liquid is not easily compressible nor it shows tendency to diffuse to a greater extent. e) The molecules in a liquid exhibit random motion.
2	**Properties exhibited by liquid state.**
	a) Surface tension b) Parachor c) Viscosity
3	**Surface tension:- It is defined as the force acting at right angles per unit length on the surface of liquid.**
4.	SI unit of surface tension = $\mathbf{Nm^{-1}}$
5.	**Development of surface tension:** A liquid is characterized by tiny particles called molecule. Consider a molecule A of a liquid (like water) lying inside the bulk of liquid as shown below:  The liquid molecule A is surrounded from all sides by other water molecules. Hence it experiences a balance force of attraction from all sides. When the same molecule reaches to the surface it experiences force of attraction from the molecules which lie below it. As a result, the molecule A experiences an inward force with is unbalanced. Thus every molecule at the surface of the liquid experiences such unbalance force which is called surface tension of the liquid. Thus the liquid remains under tension due to the unbalanced forces.
6	**Important features of surface tension**
	a) Surface tension of a liquid decreases with rise in temperature of the liquid b) Surface tension is maximum for viscous liquids than non viscous liquids. c) Surface tension tends to reduce surface area of a liquid to minimum. Because of this property, the drops of liquids flowing through a burette

and the gas bubbles in liquid appear spherical.

d) Surface tension is responsible for rise of liquid in capillary which wets the glass

e) Surface tension decreases by the addition of surface active agents in the liquid

7. Principle underlying surface tension.

Consider the flow of a liquid through a capillary of radius ‘r’. As the liquid drops come out of the capillary, two forces acts on them

i) Upward force f_1 due to surface tension given by $f_1 = 2\pi\, r\, \gamma \cos\theta$, where θ is angle of contact of liquid with capillary and γ – surface tension of the liquid

ii) Gravitational force f_2 acting downwards given by $f_2 = mg$, where m is the mass of the drop , g is acceleration due to gravity

At equilibrium,

$$f_1 = f_2 \text{ ie. } 2\pi_r \gamma \cos\theta = mg \qquad \text{---------------------(1)}$$

for liquids which wets the surface, θ = 0 , therefore cos θ = 1

hence, $$2\pi r\, \gamma = mg \qquad \text{---------------------(2)}$$

Thus from equation 2, one can determine surface tension of liquid if m and γ are known.

To simplify the process, if two liquids with surface tension γ_1 and γ_2 are taken and allowed to pass through the same capillary (at different time interval , then from equation 2 , we write,

$$\frac{2\pi_r \gamma_1}{2\pi_r \gamma_2} = \frac{m_1 g}{m_2 g}$$

i.e.

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

Thus measuring the masses m_1 and m_2 of two liquids experimentally, if γ_1 of one liquid is known then γ_2 of another liquid can be determined.

8 Drop number method of determination of surface tension of liquid.

Principle: - When two liquids of same volume with masses $\mathbf{m_1}$ and $\mathbf{m_2}$ respectively are allowed to flow through the same capillary, then the masses of two liquids is given by

$$m_1 = V.d_1 \text{ and } m_2 = V.d_2 \text{ ,}$$

where d_1 and d_2 are the densities of two liquids respectively but,

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2} \qquad \text{---------------------(1)}$$

Substituting m_1 and m_2 values in the above equation , we get,

$$\frac{\gamma_1}{\gamma_2} = \frac{V.d_1}{V.d_2}$$

Therefore ,

$$\frac{\gamma_1}{\gamma_2} = \frac{d_1}{d_2} \qquad \text{--------------------(2)}$$

If $n_1$and n_2 are the number of drops from a given volume V of liquid, then number of drops per ml for two liquids will be V/n_1 and V/n_2 respectively

Therefore, $m_1 = \frac{V}{n_1}.d_1$ and $m_2 = \frac{V}{n_2}.d_2$ ---------------------(3)

Substituting m_1 and m_2 in equation (1) we get,

$$\frac{\gamma_1}{\gamma_2} = \frac{\frac{V}{n_1}.d_1}{\frac{V}{n_2}.d_2}$$

$$\frac{\gamma_1}{\gamma_2} = \frac{n_2.d_1}{n_1.d_2} \qquad \text{----------------------(4)}$$

Thus γ_1 of one liquid is known , then one can find γ_2 of another liquid from equation (4)

9 Experimental measurement of surface tension by drop number method.

1)**Diagram**: For diagram, refer any text book

2) **Construction of stalagmometer** :- The apparatus used to measure surface tension is known as stalagmometer. It consist of a tube made up of glass with a bulb at the center. A capillary of uniform radius is fixed in the lower part of the tube through which the liquid flows. The upper and lower portions of the glass tube are graduated to measure fractions of drops and have been marked as A and B respectively, as shown in the figure. The upper portion of the stalagmometer is connected to a Y shape glass tube by rubber tubing. One arm of the Y shape tube is connected to a pinch cock while the other connected to a screw clamp.

Procedure:- The stalagmometer is first cleaned and dried. The screw clamp is first closed. The pinch cock is opened and given liquid is sucked till mark A. The pinch cock is now closed and the screw clamp is gradually opened to control the number of drops flowing out of the capillary. A fixed number of drops flowing per minute (**say 15 drops/min**) are allowed to fall and then the position of screw clamp is fixed.

The liquid is now again sucked by opening the pinch cock and the lower meniscus adjusted to mark A. The liquid is then allowed to flow from A to B and numbers of drops flowing are measured.

The above procedure is repeated by taking a reference liquid (usually water).

Thus by knowing n_1, n_2 ,d_1 and d_2 and γ_1, the surface tension γ_2 of the unknown liquid is then determined by the following formula:

$$\frac{\gamma_1}{\gamma_2} = \frac{n_2.d_1}{n_1.d_2}$$

VISCOSITY

10	**Viscosity**:- The resistance to flow of liquid is known as viscosity.
11	**Coefficient of viscosity (η)**:- It is defined as the force in Newton per unit area acting between two parallel layers of a liquid separated by a distance of 1m and flowing with a velocity difference of 1m/sec.
12	Unit of η:- $kg.m^{-1}s^{-1}$ or $Nm^{-2}s$ in SI system , $Dcm^{-2}s$ = 1 Poise in CGS system
13	Formula for **η** (**Poiseuille equation**) : $\eta = \frac{\pi P r^4 t}{8lV}$ Where, **P** is pressure under which the liquid flows through a capillary, **r** is the radius of the capillary ***l*** is length of the capillary **t** is time in seconds required for the liquid to flow through the capillary
14 Ans	**Derivation of the formula:** $\eta_l = \frac{t_i}{t_w} \times \frac{dl}{dw} \times \eta_w$ From Poiseulle's equation, $\eta = \frac{\pi P r^4 t}{8lV}$ --------------------(1) Let η_l and η_w represent the viscosities of liquid and water respectively. Then from equation (1) we get, $\eta_l = \frac{\pi P_l r^4 t_l}{8lV}$ and $\eta_w = \frac{\pi P_w r^4 t_w}{8lV}$ $\frac{\eta_l}{\eta_w} = \frac{P_l t_l}{P_w t_w}$ ---------------------(2) Where, t_l = time in seconds required for the liquid to flow t_w = time in seconds required for the water to flow But pressure = Force/Area = mg/A = volume x density x g / Area Therefore, P_l = V x d_l x g ------------------(3) P_w = V x d_w x g -----------------(4) As V is same for both the liquids, Substituting (3) and (4) in equation (2) we get, $\frac{\eta_l}{\eta_w} = \frac{V \times d_l \times g \times t_l}{V \times d_w \times g \times t_w}$ $\therefore \eta_l = \frac{d_l}{d_w} \times \frac{t_l}{t_w} \times \eta_w$ ----(5)
15	**Diagram of Ostwald's viscometer**:Please refer any text book

16 **Measurement of viscosity by Ostwald's viscometer**:

Construction of viscometer:

The viscometer consist of a U shape tube with one limb A having a bulb 'P' at lower end while the other limb B with a bulb 'Q' at the upper end. The limb B consist of a capillary fitted below the bulb 'Q' as shown in the figure. The bulb 'Q' consist of two mark a_1 and a_2 above and below it.

Working: A known volume of the experimental solution is poured through the limb **A** in the bulb **P**. The experimental solution is sucked from the upper end of limb **B** till it reaches above the mark $\mathbf{a_1}$ .The lower meniscus of the solution is adjusted to the mark $\mathbf{a_1}$ and the pressure is released. At the same time, stop clock is started. The time required for the experimental solution to flow from upper mark $\mathbf{a_1}$ to lower mark $\mathbf{a_2}$ is noted. The above procedure is repeated for distilled water. The average time required for the experimental solution and water is noted and substituted in the following equation:

$$\eta_l = \frac{d_l}{d_w} \times \frac{t_l}{t_w} \times \eta_w$$

PARACHOR

1 **Parachor and types of parachor.**

Ans. Parachor is defined as a molar volume of a liquid at a temperature at which its surface tension is unity.

The relationship between surface tension and density of the liquid and vapour was proposed by D.B.Mcleod and is given by equation,

$$\frac{\gamma^{1/4}}{\rho_l - \rho_v} = C \qquad \text{-----------------(1)}$$

Where **C** is constant of prop.

γ is surface tension of liquid

ρ_l is density of liquid

ρ_v density of vapour

Sugden modified equation (1) by multiplying it by mol. Wt. on both side

$$\frac{M.\gamma^{1/4}}{\rho_l - \rho_v} = M.C = cosnt = [P]$$

Here **[P]** is parachor

At ordinary temperature, ρ_v is much smaller than ρ_l . Therefore neglecting ρ_v in the above equation we get,

$$\frac{M.\gamma^{1/4}}{\rho_l} = P$$

$$\left(\frac{M}{\rho_l}\right)\gamma^{1/4} = [P]$$

But $\frac{M}{\rho_l}$ = Molar volume , therefore [P] = Molar volume x $\gamma^{1/4}$

When γ=1, [P] = Molar volume

Unit : m^3mol^{-1}

Types of parameters:

1) **Atomic parachor**:- It is the contribution made by each atom in the molecule.

2) **Structural parachor**:- It is the contribution made by various bonds and rings present in the molecule.

2 Evidences to support that parachor is an additive property.

Ans. The evidences to support parachor is an additive property are as follows:

a) The parachor values for isomeric compounds in the same family are same.

Eg. ester with formula $C_6H_{12}O_2$ has 4 isomers, all have same parachor

	Isomers	parachor
1	$H-C(=O)-O-C_5H_{11}$	293.6
2	$CH_3CH_2CH_2-C(=O)-O-C_2H_5$	293.6
3	$CH_3-C(=O)-O-C_4H_9$	295.0
4	$CH_3CH_2-C(=O)-O-C_3H_7$	295.0

b) The difference in parachor values of successive members in different homologous series are same

Ester	P	ΔP
$C_2H_4O_2$	138.1	----
$C_3H_6O_2$	177.3	39.2
$C_4H_8O_2$	216.1	38.8
$C_6H_{12}O_2$	293.8	38.8x2
$C_7H_{\cdot 4}O_2$	332.3	38.5

3 Determination of parachor values of individual atoms in a molecule

Ans. Consider the determination of parachor of carbon atom in CH_2 group.

The exp. det. Parachor for CH_2 is 39 while that of H is 17.1

As parachor is also an additive property

$$P_{CH_2} = P_C + 2P_H$$

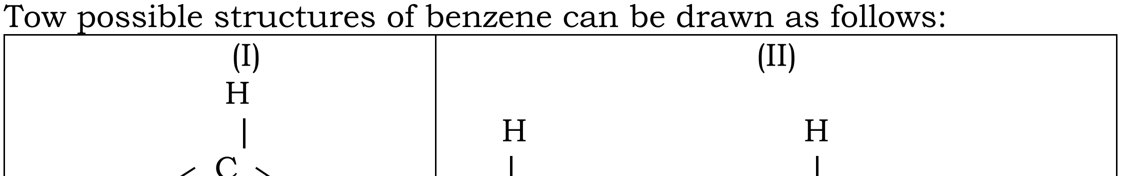
$$\therefore P_C = P_{CH_2} - 2P_H$$

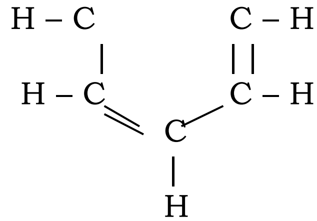
$$= 39 - 2*17.1 = 4.8$$

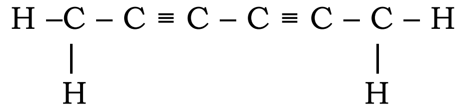
4 Use of parachors to determine structure of i) Benzene molecule ii) Quinone

Ans. i) Benzene:

Tow possible structures of benzene can be drawn as follows:





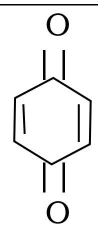


For structure (I)			For structure (II)		
6 C atoms	6 x 4.8 =	28.8	6 C atoms	6 x 4.8 =	28.8
6 H atoms	6 x 17.1 =	102.6	6 H atoms	6 x 17.1 =	102.6
3 double bonds	3 x 23.2 =	69.6	2 triple bonds	3 x 46.6 =	93.2
1 six membered ring	<u>1x 6.1 = 6.1</u>				224.6
		207.1			

Expt. det. value is 206.2 which confirms structure (I)

ii) **Quinone :**Mol formula $C_6H_4O_2$

(I)



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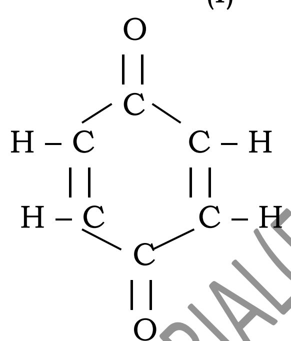
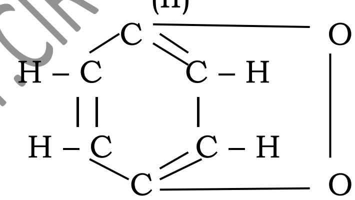


(II)



For structure (I)			For structure (II)		
6 C atoms	6 x 4.8	= 28.8	6 C atoms	6 x 4.8	= 28.8
4 H atoms	4 x 17.1	= 68.4	4 H atoms	4 x 17.1	= 68.4
2 O atoms	2 x 20	= 40.0	2 O atoms	2 x 20	= 40.0
4 double bonds	4 x 23.2 =	92.8	3 double bonds	3 x 23.2	= 69.6
1 six membered ring	<u>1 x 6.1 = 6.1</u>		2 six membered ring	<u>2 x 6.1= 12.2</u>	
		236.1			219.0

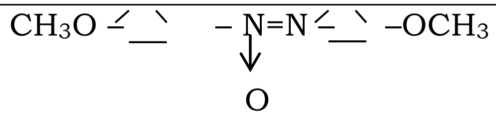
Expt. Det. Value is 231.8 which confirms structure (I)

Liquid Crystals

1 Liquid crystals and their classification

Ans. Liquid crystal represents a state of matter intermediate between a anisotropic crystalline solid and clear isotropic liquid. These crystals exhibit the fluidity property of liquid and optical property of a solid. According to Lehmann liquid crystals are defined as the milky and transparent substances produced before being transformed into clear liquids.

Eg. of liquid crystals p – Azoxy anisole



a) **Nematic (threaded like) liquid crystals**:- In these crystals the molecules lie parallel to each other but they are free to roll or slide over individually. They flow like liquids but due to their directional nature, they exhibit anisotropic properties.

Eg. N – paramethoxybenzylidine – p – butylamine
P – Methoxy annamic acid

b) **Smectic liquid crystals**: In these crystals , the molecules line up like soldiers or parade and form sheets (layers). Due to gliding layers of these crystals, they appear like soap structures. They do not flow as normal liquids (cell membranes are mainly composed of smectic liquid crystals) .

Eg. cholestoryl oleyl carbonate , Ethyl p-azoxy benzoate

c) **Cholesteric liquid crystals**: In these crystals parallel molecular layer exhibit in which the molecules in successive layers are slightly rotated with respect to the layers above and below so as to form spiral structure. These crystals have some characteristics of nematic and some of smectic crystals. The skeleton of structure passing through this state looks like cholesterol hence the name cholesteric crystals.

2 **Classification of liquid crystals on the basis of mode of preparation**.

Ans. On the basis of mode of preparation , they are classified as follows:

a) **Thermotropic liquid crystals:** These liquid crystals are observed over a short temperature range between solid and liquid states. They are highly viscous and can be either translucent or opaque. They find applications in watches, computer screens and thermometers.

Eg. **p – Azoxyanisole**

b) **Lyotropic liquid crystals**: These crystals are formed by the action of solvent on a solid. They are layered structures and are important for biological system.

Eg. aqueous solutions of detergent, lipids etc.

3 **Applications of liquid crystals**:

Ans. 1) Liquid crystals find application in ultra thin flexible computer and television display and fast reacting thermometer.

2) They find application in gas chromatography.

3) They are used as solvent for study of anisotropic molecular spectroscopy.

	4) Liquid crystals tunable filters are used as electro-optical devices . eg. hyper spectral imaging. 5) Polymer dispersed liquid crystals (PDPC) sheets and rolls are used as adhesive backed smart films which can be applied to windows and electrically switched between transparent and opaque to provide privacy .