Chapter –IV
Liquid State

Contents:

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Introduction:

Three different phases of matter are familiar to us - solid, liquid and gas. Liquids and gases flow while a solid under normal conditions does not. A solid retains its shape while a fluid (a collective name for gases and liquids) will take the shape of the containing vessel. In other words a solid is rigid while fluids do not possess the property of rigidity. The same material can exist either as a solid, a liquid or a gas, under different conditions of temperature and pressure. This is a matter of common observation. For example, when water, which is a liquid at room temperature, is cooled below O°C at atmospheric pressure, it becomes solid ice. Heating water to 100°C at atmospheric pressure converts it to steam. Such a transition of matter is called a phase transition. Intermolecular forces are stronger in liquid state than in gaseous state. Molecules in liquids are so close that there is very little empty space between them and under normal conditions Liquids are denser than gases. Because molecules do not separate from each other. However, molecules of liquids can move past one another freely, therefore, liquids can flow, can be poured and can assume the shape of the container in which these are stored. In the following sections we will look into some of the physical properties of the liquids such as vapor pressure, surface tension and viscosity. The liquid state of matter is of great practical importance. The arrangement of atoms in a liquid is more disordered than in a crystal.

A liquid is made up of tiny vibrating particles of matter, such as atoms, held together by intermolecular bonds. Unlike a gas, a liquid does not disperse to fill every space of a container, and maintains a fairly constant density. A distinctive property of the liquid state is surface tension, leading to wetting phenomena. When a liquid is heated, the atoms or molecules gain kinetic energy . If the temperature becomes sufficiently high, the liquid becomes a gas , or it may react with chemicals in the environment. Water is an example of a liquid that becomes gaseous when it is heated gradually. When a liquid is cooled, the atoms or molecules lose kinetic energy. If the temperature becomes low enough, the liquid becomes a solid. Water is a good example. If cooled down, it freezes into ice.

Intermolecular forces:

Intermolecular forces are the forces of attraction and repulsion between interacting particles (atoms and molecules). This term does not include the electrostatic forces that exist between the two oppositely charged ions and the forces that hold atoms of a molecule together i.e.,covalent bonds.

Attractive intermolecular forces are known as van der Waals forces, in honor of Dutch scientist Johannes van der Waals (1837-1923), who explained the deviation of real gases from the ideal behavior through these forces. vander Waals forces vary considerably in magnitude.

There are **three types of Intermolecular forces** which are,

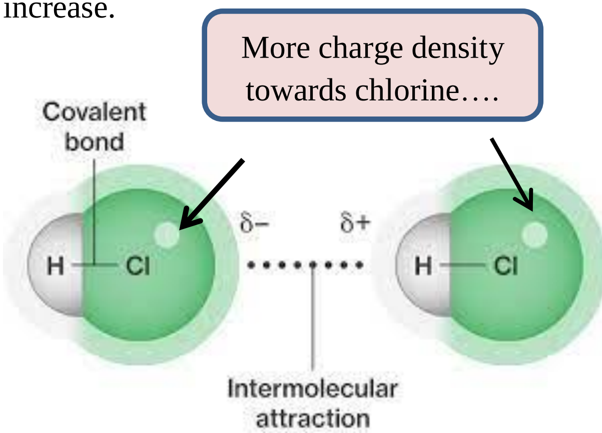
1. Dipole-dipole forces or interactions.
2. Dispersion forces or London forces.
3. Dipole-induced dipole forces.

A particularly strong type of dipole-dipole interaction is hydrogen bonding. Only a few elements can participate in hydrogen bond formation, therefore it is treated as a separate category. It is important to note that attractive forces between an ion and a dipole are known as ion-dipole forces and these are not van der Waals forces.

1) Dipole-dipole forces or interactions:

- Dipole-dipole forces act between the molecules possessing permanent dipole.
- Ends of the dipoles possess "partial charges" and these charges are shown by Greek letter *delta* (d). Partial charges are always less than the unit electronic charge (1.6×10^{-19} C). The polar molecules interact with neighboring molecules.
- Fig 4.1 shows electron cloud distribution in the dipole of hydrogen chloride and Fig. 4.2 shows dipole-dipole interaction between two HCl molecules.
- This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved. These interactions are about 1% strong as a covalent bond.
- The attraction between opposite charge is greater than repulsion between the like poles.
- The attractive force decreases with the increase of distance between the dipoles. As in the above case here also, the interaction energy is inversely proportional to distance between polar molecules.

- Dipole-dipole interaction energy between stationary polar molecules (as in solids) is proportional to 1/*r*3 and that between rotating polar molecules is proportional to 1/*r* 6, where *r* is the distance between polar molecules.
- Besides dipole dipole interaction, polar molecules can interact by London forces also. Thus cumulative effect is that the totals of intermolecular forces in polar molecules increase.



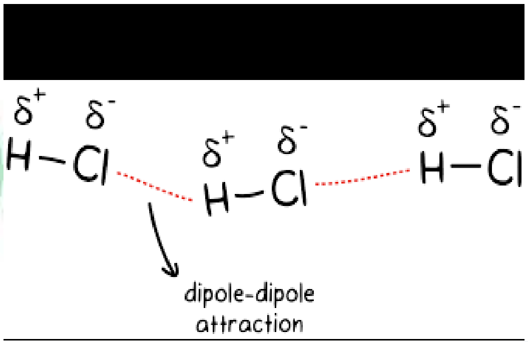

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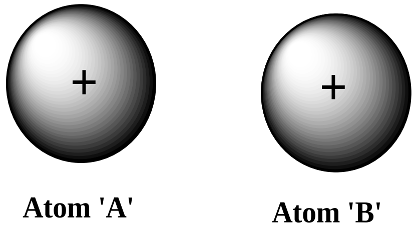
Fig.4.1 Distribution of electron cloud in HCl, a polar molecule.

Fig.4.2 Dipole-dipole interaction between two HCl molecules.

Dispersion forces or London forces:

- Atoms and nonpolar molecules are electrically symmetrical and have no dipole moment because their electronic charge cloud is symmetrically distributed. But a dipole may develop momentarily even in such atoms and molecules.
- This can be understood as follows. Suppose we have two atoms ‘A’ and ‘B’ in the close vicinity of each other (Fig. 4.3). It may so happen that momentarily electronic charge distribution in one of the atoms, say ‘A’, becomes unsymmetrical *i.e.*, the charge cloud is more on one side than the other (Fig. 4.4 and 4.5).



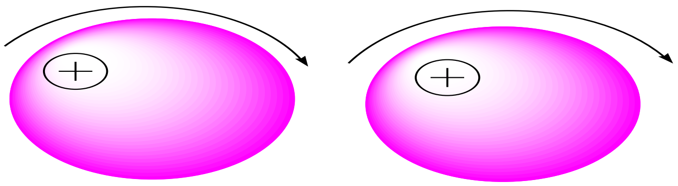


Fig.4.3 Symmetrical distribution of electronic charge cloud

Fig.4.4 (A) Atom ‘A’ with instantaneous dipole, more electron density on the right hand side.
Fig.4.4 (B) Atom ‘B’ with induced dipole.

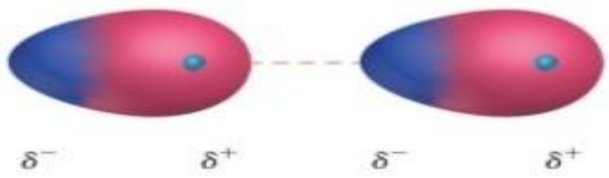


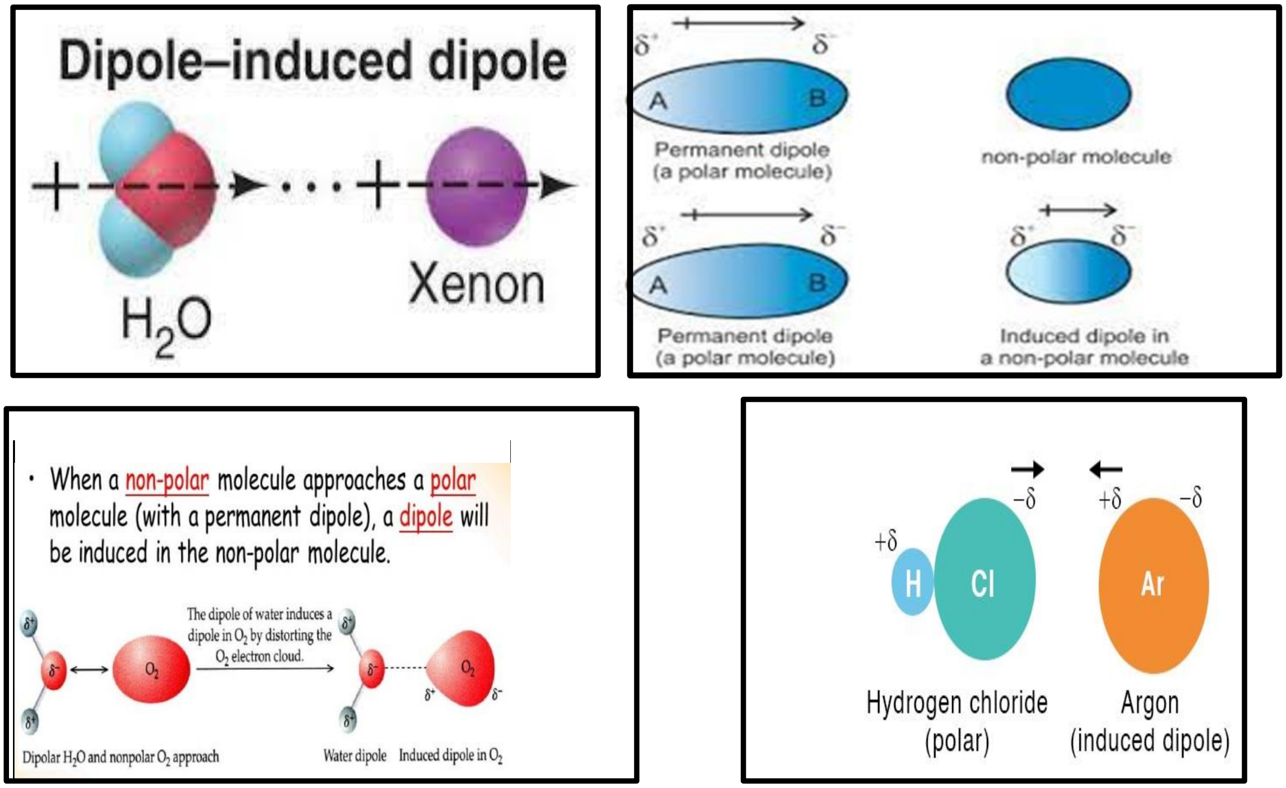
Fig.4.5 (A) Atom 'A' more electron density on the left hand side
Fig.4.5 (B) Atom 'B' with induced dipole.

- This results in the development of instantaneous dipole on the atom 'A' for a very short time. This instantaneous or transient dipole distorts the electron density of the other atom 'B', which is close to it and as a consequence a dipole is induced in the atom 'B'.
- The temporary dipoles of atom 'A' and 'B' attract each other. Similarly temporary dipoles are induced in molecules also.
- This force of attraction was first proposed by the German physicist Fritz London, and for this reason force of attraction between two temporary dipoles is known as London force. Another name for this force is dispersion force.
- These forces are always attractive and interaction energy is inversely proportional to the sixth power of the distance between two interacting particles (i.e., $1/r^6$ where r is the distance between two particles).
- These forces are important only at short distances (~500 pm) and their magnitude depends on the polarisability of the particle.

Dipole-induced dipole forces:

- This type of attractive forces operates between the polar molecules having permanent dipole and the molecules lacking permanent dipole.
- Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electronic cloud (Fig. 5.3). Thus an induced dipole is developed in the other molecule.
- In this case also interaction energy is proportional to $1/r^6$ where r is the distance between two molecules. Induced dipole moment depends upon the dipole moment present in the permanent dipole and the polarisability of the electrically neutral molecule.
- We have known that molecules of larger size can be easily polarized. High polarisability increases the strength of attractive interactions.

- In this case also cumulative effect of dispersion forces and dipole-induced dipole interactions exists.



- When a non-polar molecule approaches a polar molecule (with a permanent dipole), a dipole will be induced in the non-polar molecule.

The dipole of water induces a dipole in O_2 by distorting the O_2 electron cloud.

Fig.4.6 Dipole - *induced dipole interaction between permanent dipole and induced dipole.*

Hydrogen bonding:

- This is special case of dipole-dipole interaction. The molecules in which highly polar N–H, O–H or H–F bonds are common. But Cl may also participate in hydrogen bonding.
- The electrostatic force of attraction that occurs between molecules when one molecule contains hydrogen covalently bonded to a highly electronegative atom is called Hydrogen bonding.
- For. e.g. The H_2O molecule is electrically neutral, but the positive and negative charges are not distributed uniformly. This charge displacement constitutes an *electric dipole*, represented by the arrow at the bottom.(Fig.4.7)

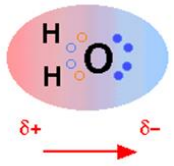


Fig.4.7 Unequal distribution of charges in water.

- Energy of hydrogen bond varies between 10 to 100 kJ mol^{-1}. This is quite a significant amount of energy; therefore, hydrogen bonds are powerful force in determining the structure and properties of many compounds,
- For example hydrogen bonding in proteins and nucleic acids.
- Strength of the hydrogen bond is determined by the columbic interaction between the lone-pair electrons of the electronegative atom of one molecule and the hydrogen atom of other molecule.
- The strength of this *dipole-dipole attraction* is less than that of a normal chemical bond. Notice that the hydrogen bond (shown by the dashed green line) is somewhat longer than the covalent O—H bond. It is also *much weaker*, about 23 kJ mol^{-1} compared to the O–H covalent bond strength of 492 kJ mol^{-1}

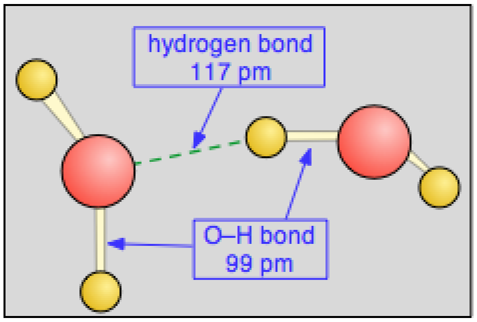


Fig.4.8 Hydrogen bond distance between water.

- ✓ A hydrogen bond in water occurs between the hydrogen atom of one water molecule and the lone pair of electrons on an oxygen atom of a neighboring water molecule.
- ✓ Water freezes into ice in which the hydrogen bonds form a rigid and stable network.

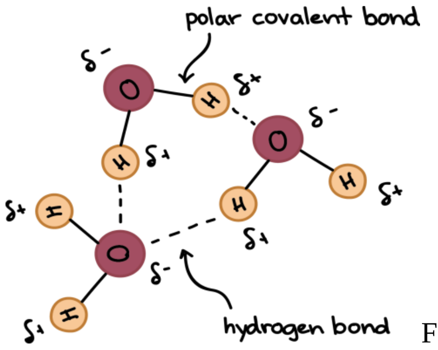


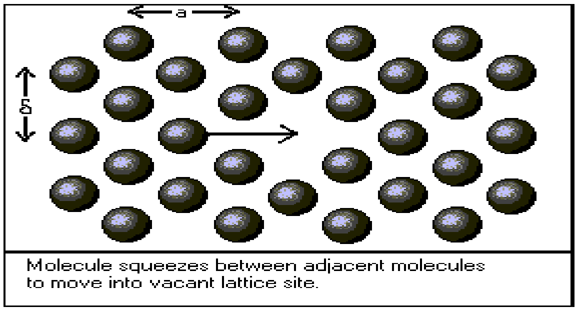
Fig.4.9 Hydrogen bonding in water.

- Intermolecular forces discussed so far are all attractive.
- Molecules also exert repulsive forces on one another.
- When two molecules are brought into close contact with each other, the repulsion between the electron clouds and that between the nuclei of two molecules comes into play.
- Magnitude of the repulsion rises very rapidly as the distance separating the molecules decreases.
- This is the reason that liquids and solids are hard to compress. In these states molecules are already in close contact; therefore they resist further compression; as that would result in the increase of repulsive interactions.

Structure of liquids (a qualitative description):

- It is assumed that a short range intermolecular force exists while the long range forces are negligible. Therefore, liquids have structure similar to that of crystal.
- The difference is that, the ordered arrangement of molecule extends over a short region instead of over the whole mass. This is called short range order or long range order. The short range order in a liquid structure is continuously changing due to the thermal motions.
- In X-ray diffraction, instead of getting harp lines a few broad bands are observed. This indicates regular order.
- As the temperature of the liquid is raised the bonds become less pronounced (not definite) and the pattern resembles those of a gas.
- Henry Eyring, in 1933, suggested vacancy model for a liquid. According to him, in the liquid most of the space is occupied by the molecules and only a small fraction of the total liquid is free. This void space is called free volume.
- The vapors contain an only a few molecules moving randomly and thus have large free volume.
- With rise in temperature, the vaporized molecule increases causing an increase in the vacancies of the liquid.

- Density of vapor increases while that of liquid decreases. At critical temperature density of vapor and liquid becomes equal.
- According to Eyring, the free volume is distributed randomly and the vacancies are approximately of molecular size.
- Molecules adjacent to a vacancy possess gas like property. While molecule away from the vacancy would be having solid like property.



Molecule squeezes between adjacent molecules to move into vacant lattice site.

Fig.4.10 Eyring's model.

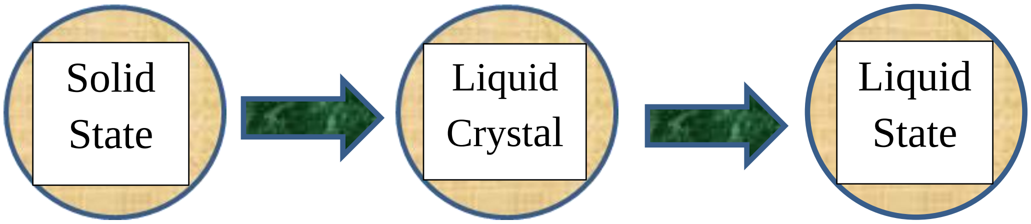
Difference between solids, liquids and gases:

Sr. No	Basis for comparison	Solid	Liquid	Gas
01	**Meaning**	Solid refers to a form of matter which has structural rigidity and has a firm shape which cannot be changed easily.	Liquid is a substance that flows freely, having a definite volume but no permanent shape.	Gas refers to a state of matter, do not have any shape but conform to the shape of the container, completely, in which it is put in.
02	**Shape and Volume**	Fixed shape and volume.	No fixed shape but has volume.	Neither definite shape nor volume.
03	**Energy**	Lowest	Medium	Highest
04	**Compressibility**	Difficult	Nearly difficult	Easy
05	**Arrangement of molecules**	Regular and closely arranged.	Random and little sparsely arranged.	Random and more sparsely arranged.
06	**Fluidity**	Cannot flow	Flows from higher to lower level.	Flows in all directions.

07	**Molecular motion**	Negligible molecular motion	Brownian molecular motion	Free, constant and random molecular motion.
08	**Intermolecular space**	Very less	More	Large
09	**Intermolecular attraction**	Maximum	Medium	Minimum
10	**Sound speed**	Fastest	Faster than gas but slower than solid	Lowest among all
11	**Storage**	Don't need container, for storage.	Cannot be stored without container.	Needs closed container for storage.
12	**Density**	Very high	Lower than solid but higher than gases	Very low density.
13	**Diffusion**	Can diffuse into liquids	Diffusion is higher than solids	Highly diffusible as particles move randomly at high speed.
14	**K.E. of particles at a given temp.**	Least energy	Higher than solids	Maximum energy
15	**Inter particle space**	Least	Lesser	More than others.
16	**Expansion on heating**	Low	More than solids	More than liquids.
17	**Particle motion**	Only vibrates thus only vibratory motion	Transversal, rotational and vibrational motion	Large transversal, rotational and vibratory motion.
18	**Direction of motion of particles**	About fixed position	Move around each other.	Move quickly in all directions.

Liquid Crystals/ Mesomorphic states:

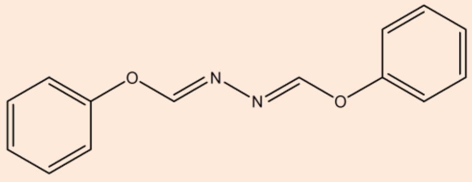
- Liquid crystals (LCs) are a state of matter which has properties between those of conventional liquids and those of solid crystals. For instance, a liquid crystal may flow like a liquid, but its molecules may be oriented in a crystal-like way.
- When a solid melts, the vibration of its constituent particles acquires such magnitude that they lapse into translator motions. However, in some cases molecular or ionic clusters do not lose their identity beyond the melting point of the solid.
- In such a solid, the breakdown of clusters in some directions is very slow and they yield very viscous cloudy liquids at a more or less sharp characteristics temp. known as transition point.
- If the temp.is increased beyond the transition point, the cloudiness disappears again sharply at a new temp., known as melting point of solid.
- Beyond the M.pt., the substance usually behaves as an ordinary liquid, between the temp. i.e. transition point and M.P. ,the cloud liquid shows double refraction, a behavior usually exhibited by crystalline solids.
- On this account the cloudy liquid state sometimes called Mesomorphic state or regarded to be made up of liquid crystals. (made up of liquid and crystals)
- Actually they are more like liquids in having properties such as mobility, surface tension, viscosity etc.
- For example 1) Liquid crystal 5-chloro -6-n-heptyloxy-2-naphthoic acid exists in ordinary crystalline form, on heating to 438.5 K the crystal fuses sharply yielding turbid liquid.
- If this is spread on flat plate, one may see steps or ridges; it is birefringent (double refraction) showing coloured areas under polarized light and having different optical properties parallel and perpendicular to the plate. Thus it shows, anisotropic behavior (they have different properties in different direction) the turbid liquid is termed as liquid crystal.



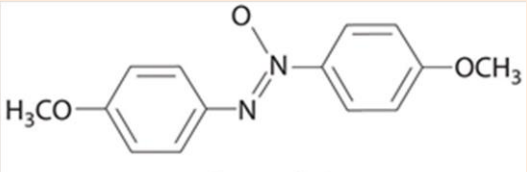
- Example 2) para-cholesteryl benzoate

para-cholesteryl benzoate (Solid) ⇨ **Para-cholesteryl benzoate (Mesomorphic state)** ⇨ **para-cholesteryl benzoate (Liquid)**

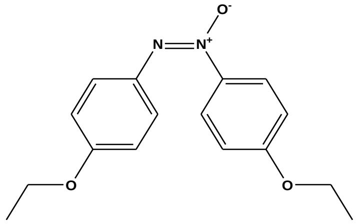
Some other typical compounds showing liquid crystal are-



Anisaldazine



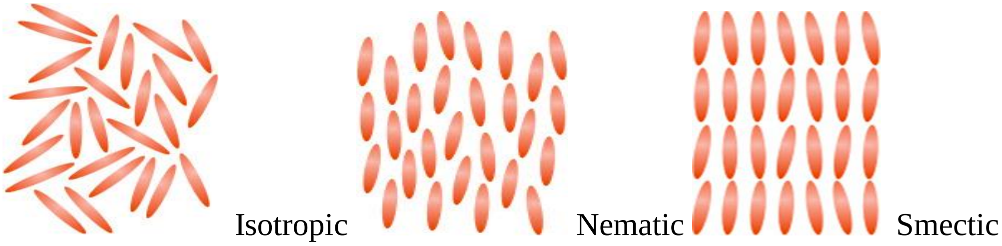
***p*-Azoxyanisole**



4,4' azoxy diphenetole

Classification of liquid crystal: An essential condition for liquid crystals to occur is that the molecule must be highly geometrically anisotropic,usually long and relatively narrow.Depending on detail molecular geometry the system may pass through one or more mesophases before it is transformed into the isotropic liquid. Transitions to these intermediate states may be brought about by purely thermal process (thermotropic liquid crystals) or by the influence of solvents (Lyotropic liquid crystals).

Thermotropic liquid crystals are further classified into nematic,cholesteric and smectic liquid crystals.

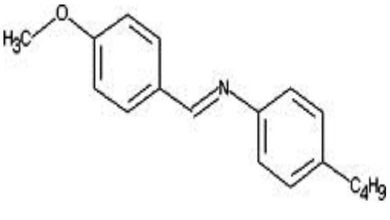


Isotropic Nematic Smectic

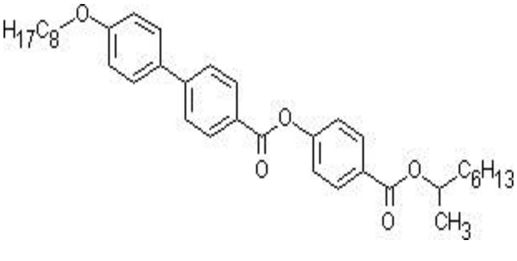
Structure of nematic phases:

- In the nematic phase all molecules are aligned approximately parallel to each other. In each point a unit vector can be defined, parallel to the average direction of the long axis of the molecules in the immediate neighborhood. This vector, known as the director, is not constant throughout the whole medium, but is a function of space.
- The figure below shows the molecular structure of a typical rod-like liquid crystal molecule. It consists of two or more ring systems connected by a central linkage group.

- The presence of the rings provides the short range molecular forces needed to form the nematic phase, but also affects the electrical and elastic properties.
- The chemical stability of liquid crystals, their resistance to e.g. moisture or ultraviolet radiation, depends strongly on the central linkage group.
- Compounds with a single bond in the center are among the most stable ones. At one side of the rings there is a long side chain which strongly influences the elastic constants and the transition temperature of the liquid crystal phases.
- At the other end, a terminal group is connected, which determines the dielectric constant and its anisotropy. A few examples of molecules that exhibit a liquid crystal phase are shown below.



MBBA



MHPOBC

Ex. 1. *N*-(4-methoxybenzylidene)-4-butylaniline (MBBA)

2. 4-(1-methylheptyloxycarbonyl) phenyl4-octyloxybiphenyl-4-carboxylate (MHPOBC)

Structure of cholestric phases:

- In some liquid crystals such as in cholesteryl crystals some colour effect under polarised light is observed.
- Due to optically active molecules the choleseric state has a spontaneous twist about an axis normal to the director.
- The molecule should have long and stringly attractive groups should be present to promote adhesion between adjacent molecules.
- A cholestric liquid crystal display (ChLCD) is a display containing a liquid crystal with a helical structure and which is therefore chiral.
- Cholestric liquid crystals are also known as chiral nematic liquid crystals.
- They organize in layers with no positional ordering within layers, but a director axis which varies with layers.
- The variation of the director axis tends to be periodic in nature.
- This has intermolecular forces that favor alignment between molecules at a slight angle to one another.
- The structure can be visualized as a stack of very thin 2-D nematic-like layers with the director in each layer twisted with respect to those above and below forming a continuous helical pattern about the layer normal.
- They organize in layers with no positional ordering within layers, but a director axis which varies with layers.
- The variation of the director axis tends to be periodic in nature.
- The period of this variation (the distance over which a full rotation of 360° is completed) is known as the pitch. This pitch determines the wavelength of light which is reflected.

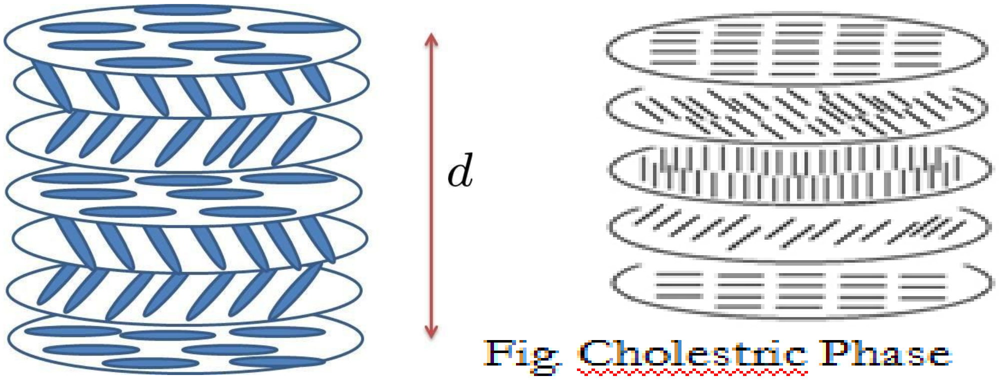


Fig. Cholestric Phase

Applications of Liquid Crystals:-

1. Research on optical & electrical properties of these unique compounds attracted very much by scientific and industrial community. Later, research at a number of industries, universities and government laboratories began to focus on their applications, which exploited the electro-magneto-optic characteristics and photoelectric properties of nematic and cholesteric type liquid crystals.
2. Cholesteric liquid crystal substances, when applied to the surface of the skin, have been used to locate veins, arteries, infections, tumors and the fetal placenta which are warmer than the surrounding tissues.
3. Nematic liquid crystals are useful research tools in the application of magnetic resonance. Molecules that are dissolved in nematic liquid crystal solvents give a very highly resolved NMR spectrum exhibiting intermolecular dipole-dipole fine structures. Analysis of the spectra of molecules in liquid crystal solvents yield information regarding the anisotropy of chemical shifts, direct magnetic dipole-dipole interaction, indirect spin-spin couplings, bond angles, bond lengths, molecular order and relaxation process.
4. Liquid crystals have been used in chromatographic separations138 as solvents to direct the course of chemical reactions and to study molecular arrangements and kinetics and as anisotropic host fluid for visible, UV and IR spectroscopy of organic molecules.
5. Liquid crystals are widely used in cosmetic industry in manufacturing of liquid crystal makeup removers, lipsticks and lip glasses containing cholesteric liquid crystals.
6. Liquid crystals are using extensively in pharmaceutical industries.
7. Liquid crystal displays are common in calculators, digital watches, oscillaographic systems; television displays using L.C.D. screens have also been developed. Cholesteric liquid crystals have also been used for novelty items such as toys and decorative materials.
8. Liquid crystal polymers also gained much interest on industrial applications. Polyester liquid crystals were developed for fire resistant, and are used as coating for multifiber, optical cables due to good surface roughness, low coefficient of friction. Polyesters are used for moldings with improved elastic modulus. Ferroelectric liquid crystals, Mesomorphic free radicals are used for EPR study and colorless large pitch cholesteric’s has been developed.

Bharat Shikshan Sanstha's
Shri Chhatrapati Shivaji College, Omerga
Tq. Omerga Dist. Osmanabad - 413606 (MS), India
(Affiliated to Dr. Babasaheb Ambedkar Marathwada University, Aurangabad) | NAAC Reaccredited 'B' Grade

DEPARTMENT OF CHEMISTRY

Question Bank

Class: B.Sc. Semester –II
Title of Paper: Physical Chemistry (Paper –IV) CHE-204
Title of Chapter: Liquid State.

Questions:

1. Define liquid crystals. Discuss their characteristics.
2. What are liquid crystals? How they classified?
3. What are Nematic liquid crystals?
4. Differentiate between Nematic and Cholestric liquid crystals?
5. Discuss briefly the general properties of liquids?
6. Differentiate between solid, liquid and gases.
7. What are intermolecular forces?
8. Describe the structure of liquids.
9. Explain the Eyring vacancy model of liquid structure.
10. Write notes on following:
    A) Dipole –dipole interactions
    B) London forces
    C) Hydrogen bond in liquids.
    D) Dipole-induced dipole forces

Multiple choice questions:

1. What is the boiling point at pressure 1 atm known as?
    a) Standard boiling point
    b) Normal boiling point
    c) Van der Waal boiling point
    d) saturated boiling point

2. Viscosity of liquid __________ with rise in temperature.

a) Increases

b) Decreases

c) Remains constant

d) Is independent

Explanation: As there is a rise in temperature the viscosity of liquid increases while the viscosity of gas decreases. In liquids, due to rise in temperature, molecules have high thermal energy so they can overcome intermolecular attractions.

3. What is S.I. unit of Surface Tension?

a) Dyne/meter

b) Newton-meter

c) Newton/meter

d) Dyne-meter

Explanation: Surface Tension is the tendency of a fluid to occupy least surface area as possible. It is defined as the force per unit distance. So, the units of surface tension are Newton/meter in S.I. the system, Dyne/cm in C.G.S system.

4. A water drop is spherical in shape due to _____________

a) Viscosity

b) Poise

c) Surface tension

d) Reflection

Explanation: Surface Tension is the tendency of a fluid to occupy least surface area as possible. It is defined as the force per unit distance. So, the spherical shape that is acquired by a water drop is due to surface tension.

5. Conversion of a liquid to a gas at all temperatures is called..

a) sublimation b) evaporation c) condensation d) boiling

6. The molecules of liquid which escape first have

a) highest kinetic energy b) lowest kinetic energy moderate

c) kinetic energy d)infinite kinetic energy

7. The pressure that vapors apply on the surface of the liquid at equilibrium is called

   a) torr b) vapor pressure c) liquid pressure d) condensation

8. At Mount Everest, the water boils at….

   a) 100 °C b) 90 ° C c) 80 °C d)70 °C

9. If the liquid is heated to increase the kinetic energy then the liquid will

   a) evaporate slowly b) evaporate faster c) not evaporate d)boil

10. Lipids flow because

    a) The intermolecular forces between molecules are weak enough to allow the molecules to move around.

    b) The intramolecular forces between molecules are weak enough to allow the molecules to move around.

    c) The intermolecular forces between molecules are weak enough to allow atoms to form different types of molecules.

    d) The intramolecular forces are weak enough to allow atoms to form different types of molecules.

11. Which of the following do liquids and gases have in common..

    a) Both liquids and gases have the ability to flow.

    b) Neither liquids nor gases have a fixed shape.

    c) Both liquids and gases have weaker intermolecular forces than solids.

    d) All of the answers are correct.