

## : LIQUID CRYSTAL :

### 1.1 Introduction :

The term 'Liquid crystal' seems to be a paradox. After all, liquids and crystals are quite different forms of matter. They have nothing in common. As we know that generally, there are three states of matter solid, liquid and gas. Plasma is supposed to be the fourth state of matter.

A Liquid state is described as a free flowing substance that has viscosity and no shape of its own, shape of liquid is that of its container. It has surface tension, its own boiling point, and if heated further converts into gaseous state. Liquid has no crystalline nature. Particles in a liquid move in a totally random manner, flow around and over each other quite easily.

A solid state is described to have its own particular shape, have no viscosity but has elasticity, rigidity. Solids may be either crystalline or amorphous. Crystalline solid state is rigid state of matter consisting of regularly spaced particles in three dimensional matrix. These particles move but only

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within the region of their sites in the crystal lattice. The particles are held together by forces within the solid. Crystalline solid has its own melting points.

Then what are liquid crystals? As the name suggests, they are states of matter intermediate between the solid and liquid state. Liquid crystals have some properties characteristics of liquids and some others characteristics of crystalline solids. The liquid crystals can flow, pour and take the shape of any container they are poured into, but their particles do something we ordinarily think of only in solids.

The interconversion of phases at well defined temperatures near melting point of crystalline solid, particularly in case of organic corespounds, was observed by an Austrian botanist Reinitzer (1) in 1988. While synthesising cholesteryl benzoate it was found that it has two melting points. The solid melted at  $145^{\circ}\text{C}$  to give a turbid liquid, which changed sharply to clear liquid at  $179^{\circ}\text{C}$ . The subsequent studies of Lehmann (2) Schenk (3) Vorlander (4) and Friede (5) established that the intermediate phases between crystalline solids and isotropic liquids form mesophases called liquid crystalline states. Lehmann (2) showed that the turbid liquid is birefringent and hence anisotropic.

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The theoretical study of this special phase poses certain intriguing and unsolved problems and calls for a new understanding and development of statistical theories. The behaviour of liquid crystals and exhibition of colour patterns has triggered the experimental efforts in this novel field. The liquid crystals have unusual physical and optical properties and have number of important technological and commercial applications. They are already being used in digital watches, digital readouts, memory systems, display devices, disposable thermometers, leather industry and pharmaceuticals. As a result, the liquid crystals have excited general interest and popular appeal and an extensive study is being pursued in various laboratories all over the world.

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## 1.2 Classification of Liquid Crystals :

The liquid crystals can be classified on the basis of methods of their formation. There are two recognized classes of liquid crystals. First Thermotropic liquid crystals and second Lyotropic Liquid crystals.

Thermotropic liquid crystals are formed when the temperature of some crystalline solids of rod

like molecules is varied. The intermediate phase between crystalline solid and isotropic neat liquid serves as thermotropic liquid crystal. If a thermotropic liquid crystal can be formed by both the cooling and heating processes, then the phase is known as 'enantiotropic'. Those thermotropic liquid crystals which are obtained only when the substance is supercooled are called 'monotropic'. There are some 5000 organic compounds which yield these thermotropic liquid crystal phases.

Lyotropic liquid crystals are formed when certain compounds are treated with a highly polar solvent such as water. One of the compounds is usually amphiphilic containing a polar head group attached to one or more hydrocarbon chains. The second compound is usually water or heavy water. The typical hydrophilic groups in the amphiphilic compounds forming lyotropic liquid crystals (6) are  $--OH$ ,  $--O(CH_2-C(CH_3)_2)_nH$ ,  $--COOH$ ,  $--COONa$ ,  $--SO_3Na$ ,  $--SO_3K$ ,  $--NMe_3Br$ ,  $--PO_4$ ,  $--CH_2-CH_2-NH_3^+$  and typical lipophilic groups are  $--C_nH_{2n+1}$  and  $--O_2C--CH--CH_2COOC_nH_{2n+1}$  etc.

### 1.3 Classification of Thermotropic liquid-Crystals :

Thermotropic liquid crystals are classified in three main classes (7), namely 1) Smectic, 2) nematic

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and 3) Cholesteric. Each of these exhibits characteristic optical patterns or textures observed in thin Films ( 0.3 mm) under a polarizing microscope.

1) Smectic :

Smectic Means soap like; many common soaps exhibit smectic phases at elevated temperatures ( $200^{\circ}\text{C.}$ ) or in the presence of water. This mesophase has the highest crystalline order. Molecules in this mesophase are arranged in layers with their long axes parallel to each other. (Fig. 1.1). However, there is a significant scatter of the long molecular axes from the perfect parallel arrangement due to thermal fluctuations. It may be mentioned that various types of smectic phases are known depending upon the molecular arrangements within the layers (B). Smectic liquid crystals have relatively high viscosity and have not found as many applications as the other classes mentioned below. The centre of mass of the molecules is in a plane which is perpendicular to the optic axis of the molecules. The fluidity of the phase comes from the flexibility and the gliding ability of the layers over each other. Different smectic liquid crystals are mentioned as smectic A, Smectic B, Smectic C.....  
.....Seven types at different temperatures.

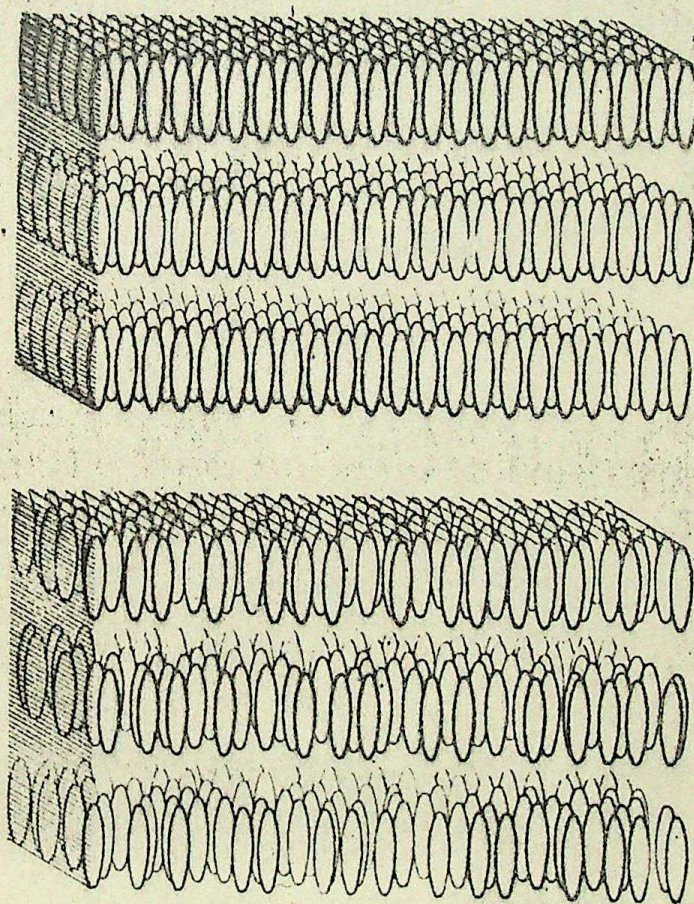
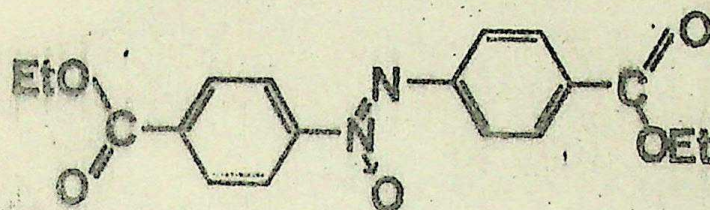


Fig. 1.1

## 2. Nematic :

Nematic means thread like, exhibits a lower degree of a molecular order than smectic liquid crystals, as the molecules are not separated into layers, although they are aligned parallel to each other. (Fig. 1.2). In this phase molecules have a greater mobility. This mesophase have been most extensively used for structural studies in NMR experiments. For substances exhibiting both the smectic and the nematic phases, the smectic always occurs at a lower temperature. The constituent molecules in this phase are usually long rod like structures and the ordering consists of a preferred parallel arrangement of the long axes of larger group of molecules. When a nematic liquid crystal is examined under polarized microscope, tiny thread-like structures are visible called textures. These structures seem to be the boundaries between the regions of different molecular orientation. Optically, a nematic behaves as uniaxial material with the centre of symmetry. The existence of centre of symmetry is also supported by the absence of ferro-electric and Second harmonic generation in light scattering Phenomenon. Nematic is optically strongly birefringent or doubly refracting, the refractive index being

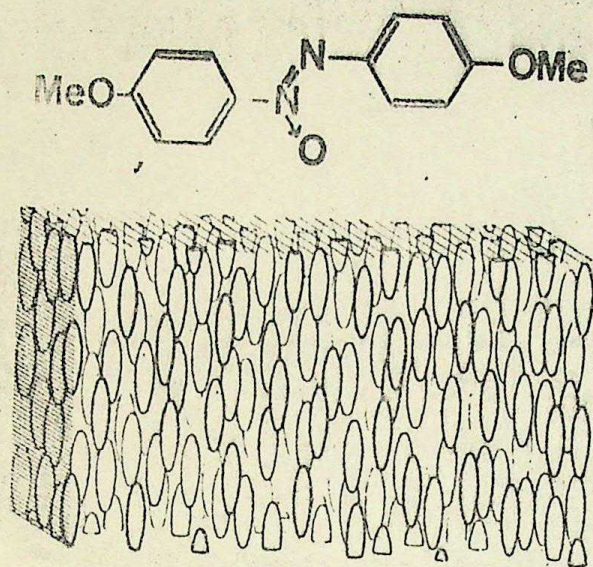


Fig. 1.2

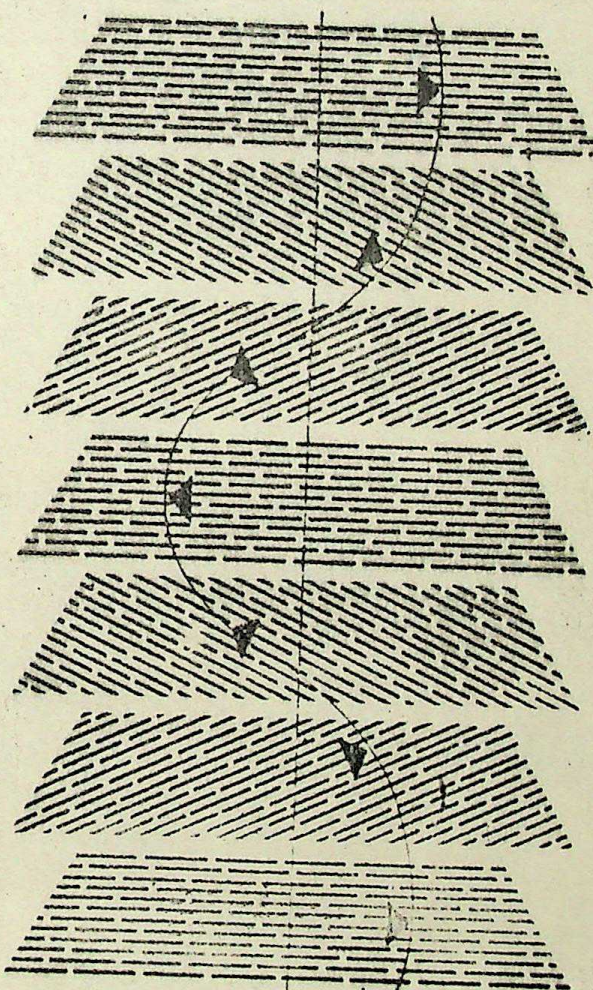
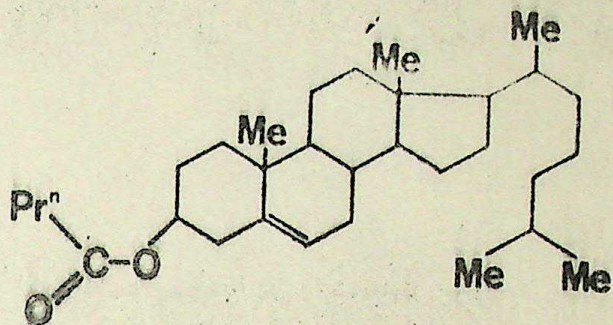


Fig. 1.3

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different for light polarized parallel and perpendicular to the director axis. Nematics show anisotropies in diamagnetic and dielectric properties. Pure nematics are good insulators, but when doped with ionic impurities it becomes conducting.

It may again be emphasized that the parallel arrangement of molecules is not at all as perfect due to thermal fluctuations. A measure for the fluctuations give the degree of order defined by the average value.:

$$S = \frac{1}{2} \langle 3\cos^2\theta - 1 \rangle$$

Where  $\theta$  :- is the momentary angle between the long axis of the molecule and the axis of preferred orientation. For isotropic arrangement, i.e. random orientation of the axes,  $S=0$  and for perfect parallel alignment  $S=1$  (i.e.  $\theta=0$ ).

### 3) Cholesteric :

The name arises from the fact that most compounds exhibiting this phase a skeleton similar to the steroid cholesterol. The cholesteric phase is a special type of the nematic phase and is formed by optically active compounds. In this mesophase, the molecules are

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separated into layers and within one layer they are arranged parallel to each other, whereas between two successive layers the direction of longest molecular axis is slightly displaced. This displacement follows a helical path (Fig. 1.3). The helix can be right or left handed depending upon the sense of displacement. The pitch of the helix changes critically with small variation of temperature, pressure, etc. resulting in changes of the reflecting properties. Such substances have found applications in temperature sensing devices.

The presence of the helical distortion makes cholesteric phases unsuitable for high resolution NMR studies. As the cholesteric phase is of the most optically active compounds; a compensated mixture of d-rotatory and l-rotatory cholesteric liquid crystal changes into nematic mesophase and can be used in NMR experiments for structural studies (9).

The molecular structure of a cholesteric liquid crystal is delicately balanced and is easily disturbed. These small disturbances interfere with the weak forces between molecules and have the effect of slightly changing the molecular structure of the substances. But such a structural change also changes the optical properties of liquid crystal which give

them potentials of technical applications in detection of toxic chemicals, thermography or surface temperature mapping, light modulating devices such as light valves, memory circuits, rear projection screens, display panels of digital readouts, watches.

1.4 Lyotropic liquid crystals : Lyo- means containing water. As stated above Lyotropic liquid crystals are formed by mixing two or more components in solvents generally polar type.

The molecular packing in the Lyotropic liquid crystals is explained as follows:

The soaps are amphiphiles, meaning compounds which have a hydrophilic ( an affinity for water ) polar group attached to a long hydrophobic ( water-repellent ) hydrocarbon chain. The amphiphilic compounds are characterised by having in the same molecule two parts with greatly different solubility properties. One part of the molecule is hydrophilic (an affinity for water) which tends to be soluble in water and insoluble in hydrocarbons and the other is lipophilic (insolubility in water) which has reverse solubility characteristics. As the concentration of soap increases, the hydrophobic paraffin chains tend

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to associate preferentially with one another, since they are quite insoluble in water. At the concentration known as the critical micelle concentration, aggregates of the alkylsalphate ions form stable entities known as micelles. The non-polar hydrocarbon chains occupy the interior of the micelles with the ionic head groups on the surface where they can interact efficiently with the solvent (Fig. 1.4). This type of behaviour is typical not only for soaps but also for naturally occurring materials such as phospholipids. The critical micelle concentration and the aggregation number depends on many factors -- the nature of the polar head group and of the hydrocarbon chain and the presence or absence of electrolytes etc.

As the concentration of the soap increase an anisotropic liquid crystalline material may be formed, which has a lamellar structure as shown in Fig. 1.5. The hydrocarbon chains form the superstructure with the polar groups lying along the interface with water. The arrangement is such that the hydrocarbon chains are perpendicular to the interface and each layer is approximately two hydrocarbon chain lengths thick.

Irradiation with high Frequency sound converts a lamellar phase into isotropic solution. The sonication does not destroy the lamellar structure, but causes the formation of closed bilayeres called vesicles (Fig. 1.6).

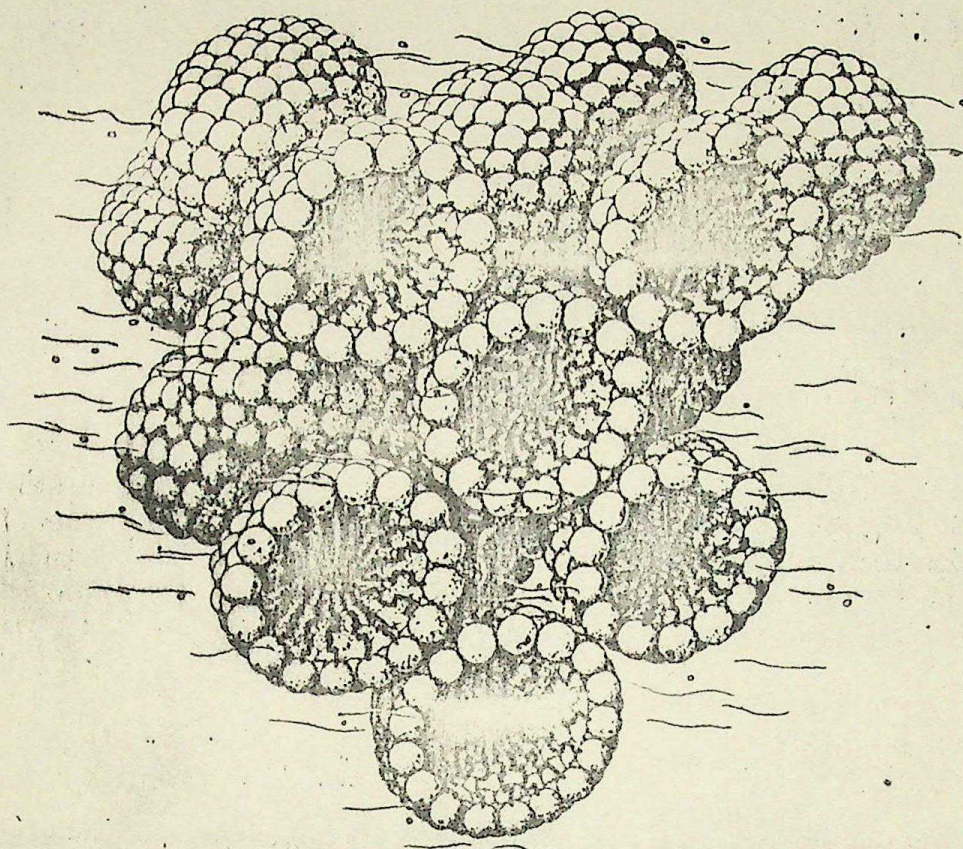
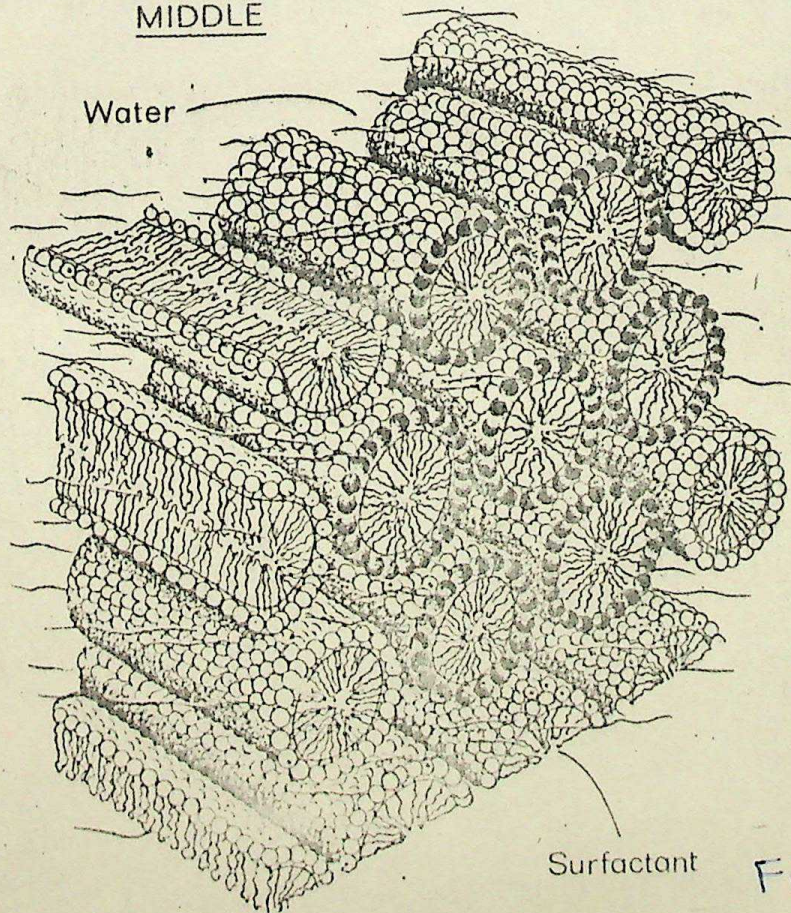


Fig. 1.4

MIDDLE



Surfactant

Fig. 1.7

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They are spheroidals in shape and enclose a volume of water dependent on the diameter of the vesicle and separated from the interstitial water.

With changing composition, the lamellar structure often becomes unstable and cylidrically shaped aggregates may form a hexagonal packed structure (Fig. 1.8). The polar head groups in this case lie on the surface of the cylinder with the hydrocarbon chains in the interior (middle Soap). The hexagonal and the lamellar anisotropic liquids are by far the most common Lyotropic phases. However, many other types of phases like cubic, reversed micellar and reversed hexagonal may occure under different conditions.

Sometimes nematic lyotropic liquid crystals capable of being oriented by magnetic fields may also be formed. The exact structure of such phases is not yet well established, though they are assumed to have a cylindrical superstructure resembling the hexagonal phase. Such nematic lyotropic liquid crystal phase have enormous use as orienting media in NMR experiments.

#### 1.5 Liquid crystals as NMR solvents :

Saupe and Englert in 1963 (10) for the first time demonstrated the use of thermotropic nematic

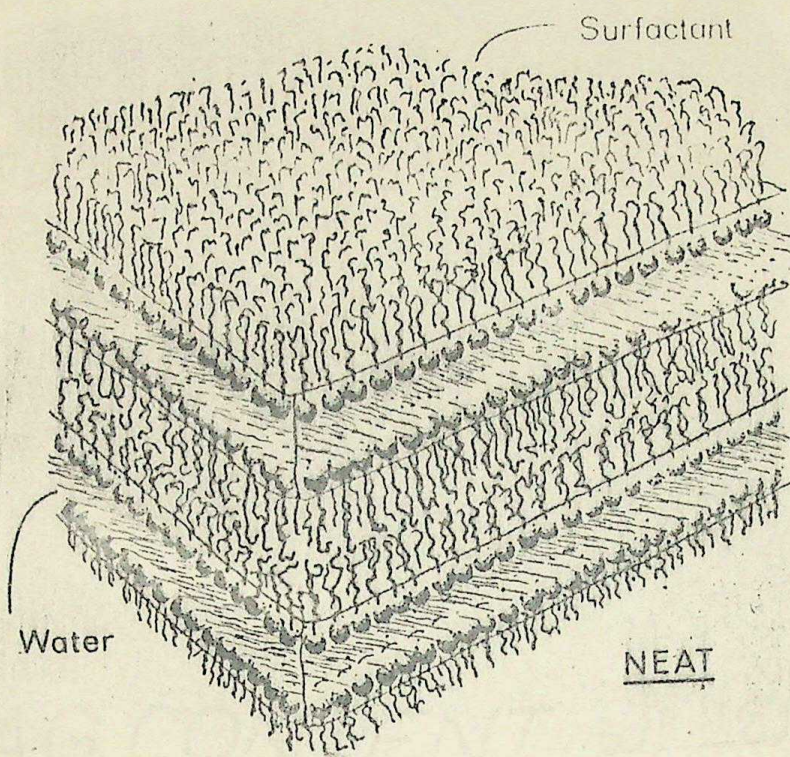


Fig. 1.5

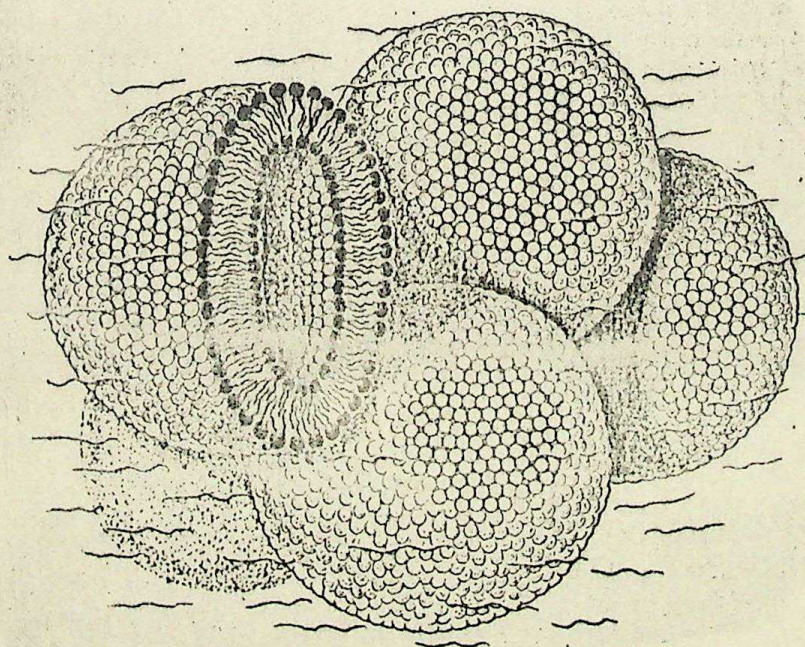


Fig. 1.6

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liquid crystal as very useful solvent for studying different solutes by NMR spectroscopy. The solute molecule gets oriented in nematic liquid crystal solvent which is a new technique for the determination of the relative arrangement of nuclei of the solute. The scope of this technique is quite broad and the precision compares well with that obtainable from other available methods. NMR spectroscopy in liquid crystal solvents is the most recent addition to other different techniques such as X-rays, microwave, I.R., neutron diffraction, electron diffraction, electron spin resonance to study the molecular structure of a compound. This is the only technique among those mentioned above where the material is studied in the liquid phase. In the favourable cases it gives a precision of about 1 part in  $10^4$  in the relative bond distances and the bond angles (11).

Out of different types of thermotropic liquid crystals, only the nematic liquid crystals are extensively used as solvents for NMR spectroscopy. Very few cholesteric liquid crystals of compensated mixtures with opposite types of optical activity converts cholesteric into nematic mesophase and can be used in NMR experiments for structural studies(9). Smectic

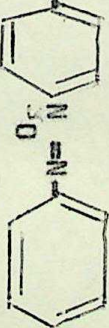
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liquid crystals also serve as solvents for NMR spectroscopy giving large line width and hence very few times used as solvents.

Lyotropic liquid crystals of nematic nature was for the first time used as solvent in NMR spectroscopy by Lawson and Flaut (12) in 1967. It has its own particular mixture of different ingredients. Since then several other lyotropic phases have been used in NMR experiments and the results have been summarised (13) in detail.

The use of lyotropic liquid crystal solvents in NMR experiments for the study of molecular structure is much less than that of thermotropic probably because the formation of the lyotropic nematic phases depend critically on the concentration and purity of the ingredients used (14), and it takes much longer time to get proper orientation. However, their use as the orienting media has certain advantages over the thermotropic liquid crystals. These phases are more sensitive to solvent-solute interactions, have low line width as compared with thermotropic solvents and relatively low molecular order of the dissolved species which simplified the analysis of the spectra.

Following are the commonly used thermotropic nematic liquid crystal solvents for NM R spectroscopy (15), with the nematic range of temperature in pure form.

| Sr.No. | Name                                                                        | Commercial name.                                                                                              | Structure.                                                                            | Nematic range °C |
|--------|-----------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|------------------|
| I.     | N-(p-Methoxybenzylidene)-<br>-p-n-butylaniline.                             | M.B.B.A.                                                                                                      |  | 10-48            |
| II.    | N-(p-Ethoxybenzylidene)-<br>-p-n-butylaniline.                              | E.B.B.A.                                                                                                      |   | 32.5-81          |
| III.   | p-n-Butyl-p'-methoxy-<br>-ozoxybenzene.                                     | Merck's<br>Phase IV                                                                                           |    | 16-76            |
| IV.    | 65 mole % Merck's phase IV<br>+ 35 mole %<br>p-ethyl-p'-methoxyazoxybenzene | Merck's<br>Phase V                                                                                            |    | -5 to 75°C       |
| V.     | Nematic Mixture                                                             | Estman kodak<br>Nematic Mixture.                                                                              | undisclosed                                                                           | -1 to 105        |
| VI.    | P-cyano-p-n-pentylbiphenyl                                                  | P.C.P.B.                                                                                                      |    | 22.5-35.         |
| VII.   | ZLI 1167<br>ZLI 1165                                                        | These commercial nematic liquid crystals<br>produced by Merck Germany are also in<br>use at room temperature. |                                                                                       |                  |

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Following Lyotropic Nematic Liquid crystal solvents are in use for NMR spectroscopy.

- 1) An 8:1:1:10 mixture (by weight) of sodium  $C_8$  or  $C_{10}$  alkylsulphate, the corresponding alcohol, sodium sulphate and water ( $D_2O$ ). by Lawson and Flaut (12).
- 2) A 14:1:1:20 mixture (by weight) of sodium dodecylsulphate, decanol, sodium sulphate and water ( $D_2O$ ) by Khetrapal et.al.(16).
- 3) A 7.5 1.5:1:15 mixture (by weight) of potassium laurate, decanol, potassium chloride and water ( $D_2O$ ) by Long Jr.(17).
- 4) A 10:1:20:1 mixture (by weight) of decylmanium chloride, decanol, water ( $D_2O$ ) and Ammonium chloride, Amonium chloride in this phase may be replaced by other salts by Reeves et.al. (18). This phase has superstructure carrying a positive charge.
- 5) Lyotropic phase in which the ions form the phase itself provide high resolution NMR spectra, have also been used. by Reeves et.al. (19-21).
- 6) For specific purpose polypeptides also serve as lyotropic liquid crystal phase such as poly- $\gamma$ -benzyl-L-glutamate (P.B.L.G.) etc. by Iizuka, E.et.al.(22-24).

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