INTRODUCTION

INTRODUCTION

1. Definition and Nomenclature

Research in the field of liquid crystals has been passing through various phases of activities since it was first identified by Reinitzer in 1888(1). During the last few years, interest in liquid crystals has intensified, primarily as a result of its wide commercial applications.

The matter generally exists in one of the three states i.e. solid, liquid or gas. The melting point of normal solids, occuring abruptly, involves the collapse of the overall positional order of the lattice array and marks the onset of essentially free rotation of the particles. Two intermediate phases of matter have been identified where only one or the other of these two freedoms (freedom of position or freedom of rotation) has been at least partially obtained. These are liquid crystals and plastic crystals. These mesophases do not satisfy all the criteria for either a true solid or a true liquid and exhibit many physical properties that are characteristic of both, for example, liquid crystals flow, but their optical properties are those usually expected only of regular solids. Although the molecules within plastic crystals maintain solid condition, have rotational diffusional mobilities as found in liquid phase. In liquid crystals the molecules are free to move at will but their rotational mobility is restricted whereas in plastic crystals the molecules are free to rotate in place and to some extent change lattice sites, but they still form a regular crystalline superstructure.

The phenomenon of mesomorphism is fundamentally a consequence of molecular shape. A necessary (but not sufficient) condition for the formation of mesophase is that the molecules comprising the system be either (a) elongated and in some cases also flat (possibility of liquid crystallinity) or (b) approximately spheroidal (possibility of plastic crystallinity). A primary determining factor of mesomorphism is probably the length to width ratio of the molecular frame, which we denote by R. If $R \gg 1$, there is a possibility of liquid-crystal formation. If $R \triangleq 1$, a plastic crystal phase might occur. Other qualities entering into or preventing the formation of a mesophase are considered in detail later.

Reinitzer (1), an Austrian botanist, for the first time observed the phenomenon of liquid crystallinity in the case of cholesteryl benzoate. Lehmann (2), however, was the first to carry out the systematic study of such compounds and coined the term liquid crystal or crystalline liquid to describe this phenomenon. Friedel (3) and Friedel and Friedel (4) who studied liquid crystals in more detail proposed the term 'mesomorphism' as this phase is neither a true liquid nor a true solid but finds place between a crystalline solid and an isotropic liquid. This term and the associated terms mesomorph, mesogens, mesoform and mesomorphism are widely used in the literature.

Rinne (5) has criticised both these terminologies on the basis that they did not carry any structural meaning. He classified matter as either ataxy (a disordered or amorphous structure) or eutaxy (an ordered structure). Thus the classification is :

1. Atactites - Isotropic liquids, gases and other amorphous matter.
2. Eutactites - (a) Crystals-three-dimensional order.
    (b) Paracrystals-one-or two-dimensional order.

Though merits of terms 'liquid crystals' and 'mesomorphism' are much debated, these terminologies are widely accepted in scientific world. Brown and Shaw (6) have used 'mesomorphism' as the title for their review.

Liquid crystals are classified into two major groups on the basis of the manner in which they are obtained. One of these is identified as thermotropic liquid crystals indicating that liquid crystal phase is obtained by the application of heat. Lyotropic liquid crystals constitute the second major group where liquid crystal phase is obtained by mixing two or more components in suitable solvent. Eventhough the terms thermotropic and lyotropic are widely used Gray and Winsor (7) prefer the terms amphiphilic and non-amphiphilic. The amphiphilic mesogens are called lyotropic while the non-amphiphilic mesophases are commonly called thermotropic.

2. Thermotropic Liquid Crystals

Soon after the initial discovery of liquid crystals by Reinitzer (1), Lehmann (8,9), Gattermann and Ritschke (10), and Vorlander (11) prepared hundreds of organic compounds which exhibited liquid crystallinity. The common feature found in all these compounds was their elongated rod shaped molecules having polar and polarizable groups.

In the early stage of the development of liquid crystals a number of workers objected this phenomenon (12-14) and suggested that the properties observed in such compounds might either be due to the minute crystalline impurities in isotropic liquid or it might be due to the emulsion of liquids. However later experiments of Bredig and Von Schukowsky (15), Coehn (16) and A.C. de Kock (17) have supported the view that crystalline liquid is a homogeneous phase and not an emulsion of two liquids. Mauguin (18) and Friedel and Grandjean (19) from their study proved beyond any doubt that liquid crystal state is a truely physical state, intermediate between the crystalline solid and the isotropic liquid.

The liquid crystalline molecules are long and rod-shaped possessing one or more dipolar groups. This type of structure favours the parallel alignment of the molecules. In the crystalline state of a mesogen the bonding forces exist between the molecules. However, thermal agitation disturbs these bonds and on heating weaker bonds break first leaving the solid with some degree of relative movement before sufficient thermal energy has been acquired to overcome, in any great degree, the tendency for them to set themselves parallel to one another. Thus the solid melts to a fluid but remains mesomorphic because of the preferred orientation of the molecules. On further heating the thermal vibrations are increased to a greater extent and the isotropic liquid is obtained. The gradual thermal break-down in liquid crystalline compounds may be expressed as under :

$$\text{Crystalline state} \xrightarrow{t_1} \text{Liquid crystalline state} \xrightarrow{t_2} \text{Isotropic liquid state}$$

$$\xrightarrow{\text{Increasing temperature}}$$

In most of the solid crystalline substances, heating breaks down their ordered structure and the solid is transformed into an isotropic liquid, whose state of order shows no preferred direction at its melting point. However, if the conditions are favourable for mesomorphism, the order breaks down in stages, first passing into liquid crystalline state at temperature t_1. This state has certain degree of order and hence acquires anisotropic properties. Further heating to t_2 destroys the orientation of the molecules and the mesophase finally changes to isotropic liquid. Thus the action of controlled heat is responsible for breaking down the alignment in stages. The classification of matter into three state in the case of such mesogens should be inadequate and hence a modified way may be as follows :

$$\begin{array}{c}\text{Crystalline}\\\text{solid}\end{array} \overset{t_1}{\rightleftarrows} \begin{array}{c}\text{Liquid}\\\text{crystal}\end{array} \overset{t_2}{\rightleftarrows} \begin{array}{c}\text{Isotropic}\\\text{liquid}\end{array} \overset{t_3}{\rightleftarrows} \begin{array}{c}\text{Vapour or}\\\text{gas}\end{array}$$

The transitions t_1 and t_2 take place at definite temperatures and are precisely reversible. But the reversal from the liquid crystalline state into the crystalline state is usually accompanied by supercooling. The transition t_2 is precisely reversible that is, there is no detectable supercooling. This type of transition in which t_2 is at a higher temperature than t_1 is termed enantiotropic transition and the phase obtained is known as an enantiotropic mesophase. However, a mesophase may be monotropic in nature. For example, a mesogen may melt at t_1 to give an isotropic liquid but when the isotropic liquid is cooled, supercooling may occur and the temperature may fall considerably below t_1

and mesophase may appear at t_2 before crystallization occurs. The mesophase obtained this way is termed monotropic mesophase and is observed only on cooling. The monotropic temperature t_2 is also reversible and on raising the temperature before crystallization isotropic liquid is obtained at t_2 itself. The sequence of changes of state for a compound exhibiting monotropic mesophase may be represented as under :

$$\begin{tikzcd}
\text{Crystalline state} \arrow[rr, "t_1"] & & \text{Isotropic liquid state ,} \arrow[dl, shift left] \\
& \text{Mesophase} \arrow[ul] \arrow[ur, shift left, "t_2"'] &
\end{tikzcd}$$

3. Smectic, Nematic and Cholesteric Liquid Crystals

Friedel (20) carried out detailed optical studies of liquid crystals and conveniently divided them into three types - smectic, nematic and cholesteric. Most of the liquid crystalline substances which have been studied are exclusively either smectic, nematic or cholesteric. Some compounds, however, exhibit both types of mesophases i.e. smectic and nematic or smectic and cholesteric and they have always definite transition temperatures defining the stability of different mesophases. The change with increasing temperature may be represented as :

$$\begin{tikzcd}
\text{Crystalline solid} \arrow[r, shift left, "t_1"] & \text{Smectic Mesophases} \arrow[l, shift left] \arrow[r, shift left, "t_2"] & \text{Nematic or Cholesteric Mesophase} \arrow[l, shift left] \arrow[r, shift left, "t_3"] & \text{Isotropic liquid} \arrow[l, shift left]
\end{tikzcd}$$

There are also a number of mesogens possessing more than one smectic phase, the phenomenon is known as polymorphism of smectic mesophase. In this case also the temperature range and the stability of the different mesophases are sharply defined.

$$\text{Crystalline solid} \overset{t_1}{\rightleftarrows} \text{Smectic II} \overset{t_2}{\rightleftarrows} \text{Smectic I} \overset{t_3}{\rightleftarrows} \text{Nematic or Cholesteric} \overset{t_4}{\rightleftarrows} \text{Isotropic liquid}$$

3.1 Smectic Liquid Crystals

The smectic mesophase is turbid viscous state, with certain properties reminiscent of those found for soaps. The term 'Smectic' is in fact derived from the Greek word, 'Smectos' meaning soap-like and has no special significance. It was first used for ammonium oleate, a soap salt, it being the first substance known.

Smectic liquid crystals have their molecules arranged in definite layers. These layers can slide over one another because the molecules are free to move from side to side, or backward and forward, but not up and down. The molecules in their turn may or may not be arranged in regular rows, but have their long axes perpendicular to the plane of the layer (Fig. 1).

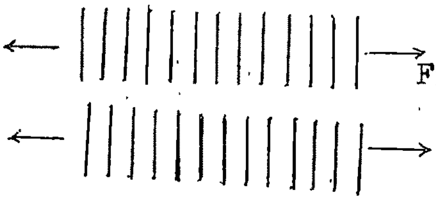


Fig.1. A section representing the molecular arrangement in two plane smectic strata

A film of smectic phase stretched over a small hole in a plate gives the condition of parallel sheets. The resulting structure is optically extinct and is said to be homeotropic. An interesting feature of the homoeotropic structure is the formation of series of strata or terraces. These terraces are called the Grandjean terraces after their discoverer Grandjean (21). The stratified structure of the smectic phase was inferred from the formation of stepped drops observed under microscope and has been further confirmed by X-ray analysis (22).

When the smectic phase is formed on cooling the isotropic liquid, it first appears frequently in the form of non-spherical characteristic elongated birefringent bodies which are known as batonnets. They increase in number as the temperature falls, coalesce and show evidence of a focal conic structure, so named, after their shape. The focal conic structure is an important means of detecting the smectic mesophase. It extends all over the specimen and when examined in polarized light it gives a fan-like appearance and has its origin in lack of common orientation of the smectic sheets as they form.

When focal conic texture is observed under the microscope a number of fine dark lines are seen. The shape and the arrangement of these lines are like those of ellipses and hyperbolae. The study and explanation of the focal conic structure are largely due to G.Friedel (20). The polygonal texture is generally obtained when the preparation is fairly thick and not too viscous. Bragg (23) has given an excellent account of the focal conic structure and the geometry involved, which furnishes further evidence for the layer theory of the smectic structure.

Saupe (24) proposed a subdivision of smectic phase into two groups following the proposal of Herrmann (25)- smectic phase with unstructured layers and smectic phase with structured layers. Much work on the classification of smectics has been done by Sackmann and Demus (26). They examined a number of pure compounds and their mixtures with one another and assigned structures to the smectic mesophase. They classified smectic phase according to the textures observed (Table 1).

<u>Table 1</u>

<u>Scheme of texture classification of smectic liquid crystals</u>(26)

Smectic A :	(a) Simple fan-shaped texture		
	(b) Simple polygon texture		
Smectic C :	(a) Broken fan-shaped texture		Schlieren texture
	(b) Broken polygon texture		
Smectic B :	(a) Fan-shaped texture	With decreased number of lines	
	(b) Polygon texture		
	(c) Mosaic texture		

Sackmann and Demus (26) have proposed seven smectic phases, A through G. These are identified by miscibility studies. However, de Vries (27) has classified the smectics into three main classes α, β and γ on the bases of X-ray studies. The class α contains smectic types A, C, F and D ; class β contains the smectic type B and class γ contains the smectic type E, G and H.

3.2 (a) Nematic Liquid Crystals

The term nematic meaning thread like (Greek nema, thread) is used because of the mobile thread-like lines which are observed in nematic mesophase. The optical effects of the nematic threads have been studied by Zocher and Birstein (28). It seems the threads are lines of discontinuities in the structure and correspond to the ellipses and hyperbolae in smectic phase. As there being no stratification in the medium like the one in the smectic phase, no definite geometrical law can be applied. Frank (29) has named these lines as disclinations.

The molecules in the nematic phase are arranged with their long axes parallel but they are not separated in layers and can be compared with a long box of round pencils. The molecules in the nematic phase exist in the form of groups, each group containing about 100,000 parallel molecules. These groups are referred to as swarms, and the theory known as the 'Swarm Theory' was first proposed by E.Bose (30) in 1909, to explain the molecular arrangement and order in the nematic phase. Zocher (31) proposed the distortion hypothesis which is now referred to as the continuum theory of liquid crystals. Luckhurst (32) applied both the swarm and distortion theories of the nematic mesophase to the study of magnetic resonance experiments and has shown that they lead to isomathematical conclusions.

The properties of nematic structure indicate that the molecules are parallel or nearly parallel to one another but are not in layers. A schematic representation of the order in a nematic phase is shown in the figure (Fig.2.).

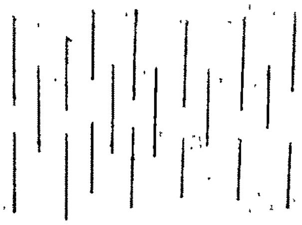


Fig.2. Molecular arrangement in the nematic phase.

A nematic liquid crystal on cooling from the amorphous isotropic liquid gives at first circular birefringent areas (droplets). The appearance of the textures which are formed after the completed transition often depends considerably on the layer thickness. Thicker nematic layers may show the typical threaded texture. The well - defined thread-like structure may move and float around in the nematic liquid. The term nematic refers to these features.

In thinner layers the threaded texture changes to the schlieren texture with point-like disclinations. The appearance between crossed polaroids is characterized by dark brushes which start from points in which the direction of extinction is not defined. Usually points with two or four dark brushes can be observed. By suitable surface treatment it is possible to obtain films with uniform molecular alignment. With untreated surface the surface effect may produce an irregular texture reminding one of polished marble (the marble texture).

3.2 (b) New types of Nematic Phases

Common nematogenic materials consist of rod-like molecules whose longest axes tend to be parallel in the nematic phase as discussed earlier. Alben (33), Onsagar (34) and Deyer (35) suggested that in addition to such positive nematics, it is reasonable to expect that there might be 'negative' nematics with planar molecules aligned with their shortest axes parallel.

Recently Chandrasekher et al., (36) have reported that thermotropic mesomorphism has been observed in pure compounds consisting of simple disc like molecules, viz. benzenehexa-n-alkanoates. They have suggested the structure which has transitional periodicity in two dimensions and liquid like disorders in the third. Another new type of nematic mesophase has been discussed by Zimmer and White (37) obtained during the process of coking and carbonization. The mesophase trans-formation usually occurs in the range of 400 to 500°C. This mesophase has been termed the carbonaceous mesophase.

Recently number of workers have reported metastable re-entrant nematic phase below the smectic mesophase in number of system (38a,38b,39,40) e.g. in the mixture, at high pressure and at atmospheric pressure in pure compound. The common feature of compounds exhibiting this phenomenon is a cyano end group that they possess.

3.3 Cholesteric Liquid Crystals

The cholesteric mesophase is found in the melts of several compounds mainly having sterol type of skeleton. Initially they were cholesterol derivatives from which it derives the name. However, the chiral nematogenic molecules also exhibit cholesteric mesophases.

Cholesteric mesophase has certain characteristic properties of its own which are markedly different from the smectic and nematic mesophases. The most striking property of the cholesteric mesophase is the scattering of light to give vivid colours when illuminated by white light. The colour of the scattered light at a particular angle to the surface of the film is dependant on (a) the substance, (b) the temperature and (c) the angle of the incident beam.

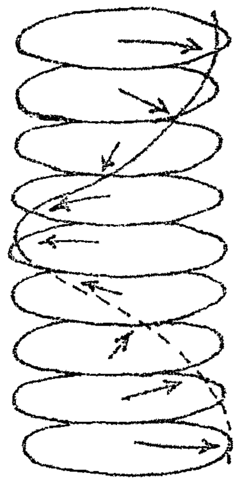
Daniel Berg (41) is of the opinion that the molecules in the cholesteric liquid crystals are aligned to each other within the planes but with respect to the next plane there is a slight twist. So as one goes up the axis from one cholesteric plane to the next, the cholesteric molecules are spiral, the repeat distance being of the orders of 1000 A° (Fig.3.). This repeat distance gives the cholesteric phase its peculiar optical properties of scattering the light and appearing highly iridescent. Cholesteric liquid crystals can occur in three textures (24).

(i) Focal conic texture

When an isotropic liquid is cooled the texture obtained is focal conic. The focal conic texture derives its name from the conic sections that are sometimes readily visible, as in the case of smectics. The focal conic texture nucleates in discrete points from where it grows in all directions, forming circular areas, until finally the whole film is covered.

(ii) Planar or Plane texture

The focal conic texture of cholesteric changes to the plane texture when the cover glass is shifted.



PROBABLE ORGANIZATION OF THE CHOLESTERIC PHASE

FIG. 3.

In this texture the sample is uniformly aligned with the twist axis perpendicular to the plane of the film. There are, however, often alignment discontinuities which can show reflection colours. For perpendicular incidence the wavelength of the light at the centre of the reflection band is equal to the length of the pitch multiplied by refractive index.

(iii) Blue phase (Isotropic texture or Blue apparition).

On cooling an isotropic liquid some cholesteric compounds such as cholesteryl nonanoate exhibit a phase, which is visible to the eye in reflected light, but not visible microscopically in transmitted light using crossed polarisers. The phase is known as a blue phase. This phase on further cooling changes to a birefringent texture. Due to this, the transition temperatures on cooling isotropic cholesteric liquid are not readily observed optically and one gets the impression that supercooling is occuring. At present the knowledge regarding blue phase is scanty (42-47). Detail study of more such compounds would only help to understand blue phase.

4. Plastic Crystals

In contrast to liquid crystals, which are solid-like liquids, plastic crystals are liquid-like solids. The basic difference between a liquid crystal and a plastic crystal on a molecular scale is largely one of geometry.

Whereas liquid crystal molecules are generally long and rigid, plastic crystal molecules are usually compact and globular. Plastic crystals were first recognized by Timmermanns (48). Plastic crystals are neither true liquids nor true solids but constitute a further mesomorphic state of matter equivalent in status to the liquid crystals (49).

5. Lyotropic Liquid Crystals (Amphiphilic Compounds)

Mesomorphism formed by the effect of solvent on amphiphilic compounds is referred to as lyotropic liquid crystals. Those compounds which possess two groups which differ largely in their solubility properties are characterized as amphiphilic (50). These are (a) a hydrophilic group which tends to be water soluble and hydrocarbon insoluble and (b) a lipophilic group which tends to be hydrocarbon soluble and water insoluble. McBain (51) has discussed the forms of mesomorphism in soap solution. A number of cationic and nonionic detergents have also been shown to give anisotropic phases when they are treated with solvents and in particular with water (52,53,54). A close relationship obviously excisting between these liquid crystalline states and the truely colloidal states, has been discussed by Ostwald (55). Robinson (56) has reported lyotropic phase having properties similar to thermotropic cholesteric phase.

Lyotropic systems are also thermotropic and it is the cooperative action of the temperature and the solvent which enables them to pass successively from the solid crystalline state to the liquid crystalline state and to the isotropic liquid or the dissolved state. Recently Gray and Winsor (57) have discussed constitutional analogies between thermotropic liquid crystals, plastic crystals and lyotropic liquid crystals.

6. Mesomorphism in Biological Systems

Liquid crystals play an important role in nature. Brown and Shaw (6) have pointed out that the mesomorphic modifications are of important biological significance, as slight changes in composition and in physical and chemical properties can materially affect the formation, continuation or cessation of the mesomorphic state, a delicate balance characteristic also of many biological processes. Catalytic processes in biological systems could readily find a favourable environment in the structure of the mesomorphic state. As Bowden (58) has put it, this state seems to be especially suited to biological functions and may possibly be the basis of vital activity.

Living sperms composed in part of protein, nucleoproteins and albumins, have been shown to possess a mesomorphic state (59,60). Fergason and Brown (61) have reviewed the liquid crystals in living systems.

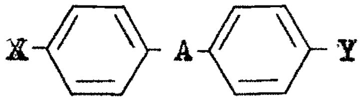
Stewart (62) mentions that there are several good theoretical reasons why matter in the liquid crystalline state should play a part in the structure of living tissues and gives a number of examples where mesomorphism is observed in biological systems. Chapmann (63) describes the essential components of membranes of living cells and connective tissues and the significance of liquid crystals therein.

7. Chemical Constitution and Mesomorphic State

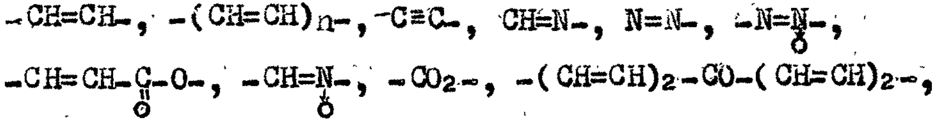
Vorlander from his study of a large number of organic compounds pointed out that a close relationship exists between the symmetry of the molecule and its capacity to form liquid crystals. In general the molecules of a liquid crystalline compound are elongated, rod- or lath-shaped and possess middle and terminal polar groups.

Intermolecular cohesive forces between molecules are required for the formation of liquid crystals. However, the intermolecular attractions should not be so strong that the melting point of the compound is very high. At high temperature the thermal motion prevents the existence of an ordered phase. If the intermolecular forces are very weak, the crystals may melt at lower temperature but the cohesive forces may again be weak to maintain the molecules in the ordered state. Thus for the formation of liquid crystal, the cohesive forces operating between elongated molecules must be both anisotropic and of suitable magnitude (64). Another criterion for the formation of liquid crystals is rigidity of the elongated molecules. If the molecules lack rigidity, flexing may occur along its length and this may prevent the formation of liquid crystals. For example, long chain n-alkanoic acids are non-mesomorphic because the alkyl chains are flexible and these may coil and bend. The introduction of unsaturation in the chain however makes the molecules more rigid due to Sp^2 hybridization and thus alkane - 2,4-dienoic acids are mesomorphic.

The majority of the thermotropic liquid crystals are aromatic in nature. Aromatic nuclei are polarizable planar, rigid and can give rise to mesomorphism if the substituents are placed in proper positions. For benzene nuclei the substituents must occupy p-position and be of such a kind that they link up at least one other benzene ring which also carries a p-substituent. It is preferable that the linking group between the two benzene nuclei should also be of a rigid nature. This can be represented as :

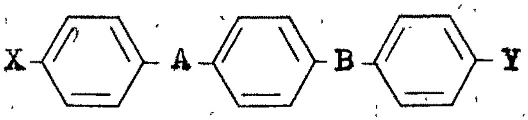


where X and Y are the terminal substituents and A is the central linkage. The usual central linkages are



$-CH=CH-$, $-(CH=CH)_n-$, $-C\equiv C-$, $CH=N-$, $N=N-$, $-N=\underset{O}{\underset{\downarrow}{N}}-$,
$-CH=CH-\underset{O}{\underset{\|}{C}}-O-$, $-CH=\underset{O}{\underset{\downarrow}{N}}-$, $-CO_2-$, $-(CH=CH)_2-CO-(CH=CH)_2-$,
$-CH=N=N=CH-$, $-CH_2-CH_2-$, $-O-CH_2-CH_2-O-$, $(-CO_2H)_2$ etc.

When more than two benzene rings are linked through more than one central group the liquid crystalline properties are enhanced.



The linkage of benzene rings through o- or m- position is not favourable to the liquid crystal formation because the molecules then become non-linear. The benzene ring plays an important role in the formation of mesomorphic compounds. The increase in the number of aromatic rings increases the stability of the mesophases.

Dewar and Goldberg (65) in their studies have shown that the replacement of aromatic rings by saturated alicyclic rings gives marked reduction in thermal stabilities of the mesophase indicating that linearity is essential for a compound to exhibit mesomorphism. Dewar and Riddle (66) from their studies of number of potentially mesomorphic esters and thioesters suggest that the geometry is the most important factor in determining the stabilities of the nematic mesophases the essential requirement being a linear rod-shaped molecule of more or less uniform cross-section.

Dewar and Griffin (67) thermodynamically studied the role of the central group on the stability of nematic liquid crystals. They suggest that polarity in the central part of the linear molecule might reduce the nematic-isotropic transition temperature through a reduction in the effective symmetry number, eventhough polarity of the terminal groups favours the nematic stability. They also suggest that the ideal structure for a nematic molecule seems to be a linear non-polar cylinder of uniform cross-section with polar ends. Recently Billard(68) and Eidenschink et al., (69) have reported number of 1,4-trans cyclohexane derivatives exhibiting mesomorphism. Mesomorphic compounds contaning a heterocyclic ring have been reported by a number of authors (70-72). Nash and Gray (73) have discussed the liquid crystalline behaviour of heterocyclic compounds.

7.1 The effect of terminal substituents on liquid crystalline behaviour

In majority of the cases, the terminally substituted compounds exhibit more stable mesophase compared to unsubstituted mesogenic compounds ; however for smectic liquid crystals certain terminal substituents reduce the thermal stability. Gray (64) obtained group efficiency order in nematic and smectic systems. Gray (74) and Dave and Vora (75) have studied the effect of substitution in cholesteryl benzoates ; and obtained a group efficiency order for the different substituents in the cholesteric systems.

Most of the terminal alkyl groups found in mesogenic compounds are unbranched. It is found that branching produces a decrease in the thermal stability of the mesophases. When the branching occurs at the first carbon atom of the chain, the effect on liquid crystal thermal stability is the greatest. Branching at any point appears to have greater effect on the nematic than on the smectic thermal stability. Movement of the point of branching away from the first carbon atom of the chain towards the end of the chain causes the transition temperature to rise again (64).

From the view point of applications of liquid crystals, the end group has become quite important. A highly dipolar end group, whose dipole works across the long axes of the molecules endows the mesophase with a negative dielectric anisotropy whereas if the dipole is acting along the long axes of the molecules, then it exhibits positive dielectric anisotropy. Consequently many mesogenic compounds having cyano, nitro and halogen as lateral or end groups are synthesized (76-78).

Schroeder et al., (79) reported some mesogenic compounds with a free phenolic and amino end groups. The mesogenic compounds with phenolic and amino end groups are rare, as intermolecular hydrogen bonding raises the melting point which in turn does not allow compounds to melt in stages (80). Recently Vora and Gupta (81) have reported first extensive homologous series having a phenolic end group and opened up new avenues in liquid crystal research.

7.2 The effect of lateral substituents on liquid crystalline behaviour

The lateral substituents may force apart the molecules and may thus reduce the intermolecular lateral cohesions but at the same time the side substituent may increase the molecular polarizability which in turn may increase the intermolecular attractions. Normally the first effect predominates i.e., a lateral substituent decreases the mesophase thermal stabilities. However, if the substituent does not have fullest breadth increasing effect as in the case of 5-substituted-6-n-alkoxy-2-naphthoic acids (82) then the second effect predominates i.e., the thermal stabilities of substituted mesogens increases. An order of the substituent effect for the lateral substitution is given by Gray (64) as :

Smectic order : $H < F < Cl < Br = NO_2 < Me < I$

Nematic order : $H < F < Me < Cl < Br < I = NO_2$

Wiegand (83) studied liquid crystalline properties of 2,6-, 1,5-, and 1,4-anisylidene diamino naphthalenes. Gray and Jones (82) studied a number of substituted alkoxy naphthoic acids. Dave and co-workers studied mesogenic naphthalene Schiff bases (84) and esters of 1,5- and 1,4-dihydroxy naphthalene with p-n-alkoxybenzoic acids (85,86). These studies show that the order of liquid crystal thermal stability in naphthalene ring substitution is as under :

2,6- > 1,5- > 1,4-

Gray and co-workers (64) studied a number of lateral substituted biphenyls at 2- or 2'-positions. These substituents in addition to increasing the breadth of the molecule, increase the thickness by imposing a steric effect on the system. It is found that the effect is more pronounced on the smectic thermal stabilities than on the nematic thermal stabilities.

7.3 Mesomorphism in Homologous Series

The relationship between transition temperatures and increase in the alkyl chain length of mesomorphic compound is quite interesting. A number of homologous series exhibiting mesomorphism have been synthesized by various workers in the field. When the mesomorphic transition temperatures e.g., nematic-isotropic, smectic-isotropic, cholesteric-isotropic, smectic-nematic, smectic-cholesteric or smectic-smectic, for the homologous series are plotted against the number of carbon atoms in the n-alkoxy groups, smooth curves may be drawn through points for like or related transitions. Usually the melting points (crystal-smectic, crystal-nematic or crystal-cholesteric) do not exhibit the regular trends. The nematic-isotropic, smectic-isotropic and cholesteric-isotropic temperatures alternate typically ; these lie on two falling curves the upper one for even and the lower one for odd number of carbon atoms in the n-alkoxy chain. For a system with n-alkyl group attached direct to the ring the reverse situation arises because the oxygen of the ether link in the alkoxy group is equivalent stereo-chemically to a methylene unit (64).

The odd-even effect becomes less marked as the series is ascended and the two curves merge later in the series. The smectic-nematic temperatures usually do not alternate and lie on a smooth curve which rises steeply at first, then levels out and merges with the falling nematic-isotropic curve. However, there are cases in which the smectic-nematic transition curve does not merge with the falling nematic-isotropic transition curve and the last members of the series exhibit nematic mesophase along with the smectic mesophase. There are also cases in which the smectic-nematic and smectic-cholesteric temperatures alternate. These are dealt with in greater detail in the discussion part.

8. Mixed Mesomorphism

Just as the melting points of the solids are depressed by the additions of other substances, so also are the transition temperatures of liquid crystals are lowered by the addition of foreign substances. When a mesomorphic compound is mixed with another mesomorphic or non-mesomorphic component, the solid-mesomorphic and mesomorphic-isotropic transition points may get depressed and the degree of depression will depend upon the concentration of the added component in the mixture.

Bogojawlensky and Winogradow (87) have reported the formation of mixed liquid crystals from pairs of substances one or even both of which were not giving normal liquid crystals. Vorlander and Gahren (88) and Bennett and Jones (89) also observed that binary mixtures in which both the components were non-mesomorphic, gave rise to liquid crystals within a certain concentration range when they were melted. Dave and co-workers (90) studied a number of binary systems in which one component was nematogenic and the other non-mesomorphic and derived orders of end group efficiency in the nematic mesophases. Recently Dave and Vora (91) reviewed these order of end group efficiency in the nematic mesophase as under :

$NO_2 > OEt > OMe >$ n-Pro $> NMe_2 > Me = Cl > F = Br > H$

Sackmann and Demus (26) identified smectic mesophases on the basis of miscibility criteria and texture phenomenon. Dave, Patel and Vasanth (92) have studied binary systems comprising a smectogenic and a polymesogenic (Smectic-Nematic) and non-mesogenic compounds. They found that in the binary mixtures comprising NO_2 group in the non-mesogenic component, the smectic and nematic mesophases show an enhancement in the thermal stability. Domon and Billard (93) and Hulme and Raynes (94) have used a numerical technique to predict the eutectic composition of some liquid crystalline mixtures.

A single liquid crystal does not satisfy all the requirements of technological applications. Hence, recently many mixtures have been reported where a mesogen or other compounds are added to the low melting mesogen, either to decrease the melting point, or to increase the mesophase range or for the change in electric conductivity and dielectric anisotropy (95 - 100).

9. Physical Properties

In recent years a large amount of work is being done on the physical properties such as X-ray studies (101,102), spectroscopic studies (103 - 105), magnetic resonance (106,107), mossbauer effect (108), Viscosity

(109,110), surface tension (111,112), ultrasonics (109,113,114), dielectric constant (115), magnetic susceptibilities (116,117), chromatography (118,119) and calorimetric studies of liquid crystals (120 - 126).

Liquid crystals are anisotropic melt and the availability of room temperature liquid crystals has opened up new avenues of research in physical chemistry. A number of books and reviews have discussed the physical studies of mesogens and their uses in different fields (74,127 - 137). Due to the sharp changes in molecular orientation at phase transitions the viscosity and surface tension studies are providing interesting observations. Gas chromatography studies and specific volume studies help to evaluate order parameters of liquid crystals. Nuclear magnetic resonance studies of many compounds have been carried out by using liquid crystal as solvent. Now the availability of a mesogen with less unsaturation (aromatic to alicyclic) would be preferred as solvent in IR and UV studies. Recent report of a mesogen having a ferrocene moiety would be quite helpful in mossbauer spectroscopic study (138). Dielectric studies have become more important as the dielectric anisotropy decides about the field of application for the liquid crystal compounds. Ultrasonic studies, magnetic susceptibility etc. are of interest due to the ordered nature of the mesophase.

Calorimetry

Calorimetry is a valuable method for the detection of phase transitions. Calorimetric measurements have been made, using adiabatic calorimetry, differential scanning calorimetry (DSC) and differential thermal analysis (DTA). Adiabatic calorimetry has greater precision although various calculation methods can introduce a considerably larger uncertainty and the technique is quite time consuming. The differential methods are more rapid, but precision is comparatively lower with the larger errors at the lower transition heats.

The most significant thermodynamic studies have been reported in an important series of papers by Arnold and co-workers (120 - 123). They use the method of adiabatic calorimetric measurements for the determination of heat capacities and latent heats. Calorimetric measurements using DTA and DSC methods have been reported by Barrall et al., (124) and by Ennulat (125).

Brown et al., (126) have compared the (thermotropic calorimetric) results of different workers. They suggest that the rather large discrepancy in these values is an indication of the uncertainty of the DTA method and hence the caution should be exercised in the interpretation of results based on this method.

10. Applications of Liquid Crystals

Characteristic optical and physical properties of liquid crystals enthused technologists to find their practical applications. Cholesteric liquid crystals have the property of reacting to the temperature changes by change of colours and find use in medicine and in industry. They are used for measuring local rises in skin temperature (139), to outline tumours, to pinpoint the location of placenta, in non-destructive testing of materials, in analytical tool to detect the presence of small amounts of gases or solvent vapours (140), in liquid crystal thermometers (141) and in publicity materials and toys.

Recently nematic and nematic-cholesteric mixtures of substances have stimulated progress in electronic research and industry. In the liquid crystalline state, compounds with nematic mesophase possess the ability to scatter light on the strength of an applied electric field. This property is employed to convert information from an electrical form to an optical form.

10.1 Liquid crystal display devices (142 - 145)

In recent years a large number of devices utilizing nematic and cholesteric liquid crystals are produced. A liquid crystal device differs fundamentally from an electronic display device such as cathode ray tube, a liquid crystal device generates no light of its own but it scatters light. Such a device offers two advantages (1) since it reflects light instead of generating it, can be viewed under a wide range of light conditions including direct sunlight or a flood light, (2) since the liquid crystal devices do not emit light, it should require relatively little power.

A liquid crystal device (cell) is made by sandwitching a liquid crystal mixed with some dopent between two glass plates which are coated by some electrically conducting transparent material such as tin oxide. By applying the electric current (10-300 volts) to the plates the liquid crystalline molecules can be oriented in the desired manner and cell becomes opalescent. When the field is switched off, the cell generally becomes transparent again within microsecond. Some liquid crystal systems remain opalescent even after the electric field is switched off. The opalescent system become transparent when a high frequency voltage is applied. This phenomenon is used to produce memory storage devices. Liquid crystals may be used to provide a thin screen television display.

New uses for liquid crystal displays are rapidly emerging in all areas of application related technology. A large volume of published materials is available on the application of liquid crystals (64,135 - 137,145).