Chapter 1

Introduction

1.1 Introduction:

Liquid crystal materials are generally organic compounds, which exhibit various degrees of translational and orientational order intermediate between the crystalline solids and those of isotropic liquids. This state of matter was discovered more than hundred years ago in 1888 by F. Reinitzer [1] while investigating the optical properties of some esters of cholesterol. O. Lehmann [2], a German Physicist, reaffirmed the observations made by Reinitzer and termed such materials as 'flowing crystals' in 1889, crystalline 'liquids' in 1890 and 'liquid crystals' in 1900. Georges Friedel [3,4] suggested the term "mesomorphic phase" or "mesophase", the state of matter observed between the isotropic liquid and crystalline solid. These materials provide new thermodynamically stable phases and are excellent systems for studying phase transitions and critical phenomena. Liquid crystals combine many of the physical properties of liquids such as fluidity with the anisotropic physical properties of crystalline solids. The combination of order, mobility and easy response of these materials to electric, magnetic and surface forces have generated many applications ranging from the familiar numeric displays, temperature sensors to high resolution TV displays, projection systems and optical computing.

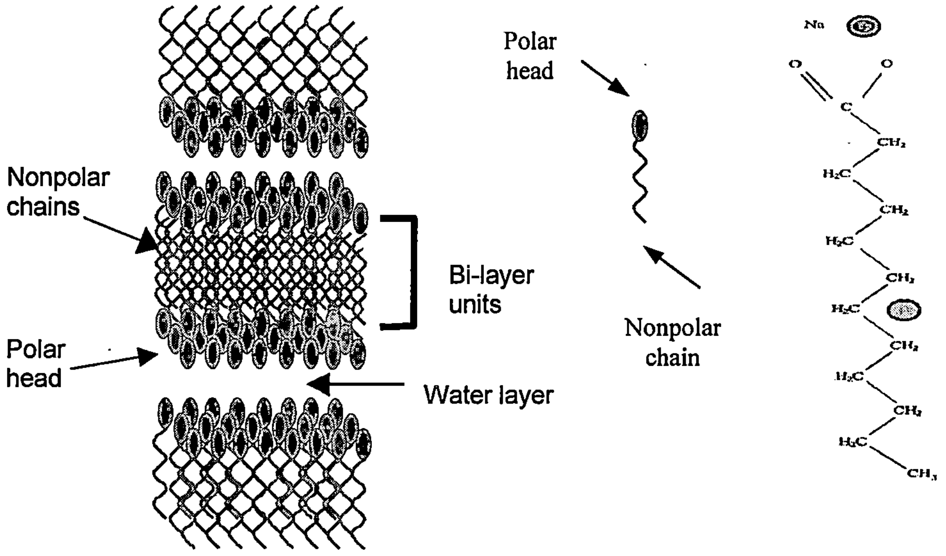
The molecules of the compounds showing mesophases are either anisometric molecules with a specific rod-like or disc – like shape or amphiphilic molecules or oligomers, polymers and dendrimers derived from these fundamental structures. Anisotropic dispersive forces between the molecules play a major role in the stabilization of these phases. There are several organic chemicals, which exhibit mesophases [5,6]; few organo-metallic [7,8] and inorganic chemicals [9] also show liquid crystalline properties as well. For general information on liquid crystals some books and reviews are listed in references [10-21]. Recent development in the field of liquid crystals and applications are also available in the literature [22-33].

1.2 Classification of liquid Crystals:

Liquid crystals are broadly classified into two types, viz. thermotropic and lyotropic.

1.2.1 Lyotropic liquid crystals:

Lyotropic liquid crystals belong to a class of substances called amphiphilic compounds (surfactant). One end of the molecule is polar and attracted to water (hydrophilic), while the other end is nonpolar and attracted to hydrocarbons, or lipophilic (figure 1.1(a)). The schematic diagram of sodium laurate, a common amphiphilic molecule is shown in figure 1.1(b).

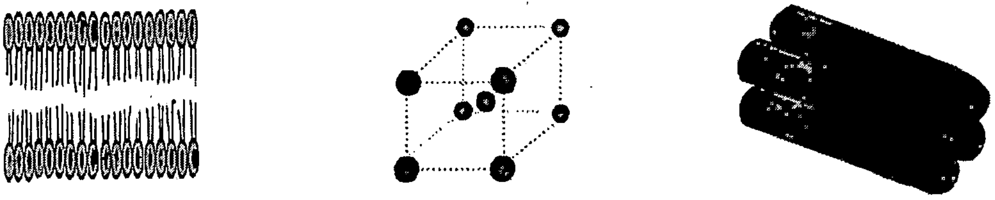


(a) **(b)**

FIGURE 1.1: Lyotropic liquid crystal molecules: Structure of the lamellar lyotropic liquid crystal phase **(a)** and Sodium laurate **(b)**

In solution, the molecules arrange themselves such that either the polar ends are dissolved in a polar solvent or the nonpolar ends are dissolved in a nonpolar solvent. The opposite end is kept isolated from the unlike solvent.

As the concentration of the molecules in solution increases, they take on different arrangements, such as – lamellar, cubic and columnar (figure 1.2).



Lamellar **Cubic** **Hexagonal**

FIGURE 1.2: Schematic representations of lamellar, cubical and hexagonal phases.

The amount of solvent is the controlling parameter for forming such mesophases. Solution of soap and water are typical examples of lyotropics and their mesomorphic properties appear both as function of concentration and temperature. Lyotropic liquid crystals have relevance to biological systems [27] as bio-membranes consist of lipids and water and usually also proteins, which have liquid crystalline properties.

Recently new types of mesophases been obtained with calamitic (rod –like) amphiphilic molecules carrying long lateral chain. Elongation of the lateral chains has led to different columnar phases in the sequence with space groups Colr/*c2mm* – Colsq/*p4mm* – Colr/*p2gg* – Colh/*p6mm* – Colr2/*c2mm* – Colr4/*c2mm* –Colr/*p2mg* and further increase of the lateral chain length leads to a novel types of layer structures –Lam (lamellar) – SmAb (biaxial Smectic A) –SmA (uniaxial Smectic A). The formation of such phases has been explained by the micro-segregation of the polar amphiphilic cores from the lipophilic lateral chains, leading to mesophases built up by two or three distinct sets of subspaces [29-33]. Since this dissertation is not concerned with lyotropic liquid crystals it will not be discussed here.

1.2.2 Thermotropic liquid crystals:

In thermotropic liquid crystals, mesomorphic behaviour is induced due to change in temperature. The vast majority of thermotropic liquid crystals are composed of rod-like molecules (one molecular axis is longer than the other two) [34]. A typical calamitic liquid crystal is shown in figure 1.3.

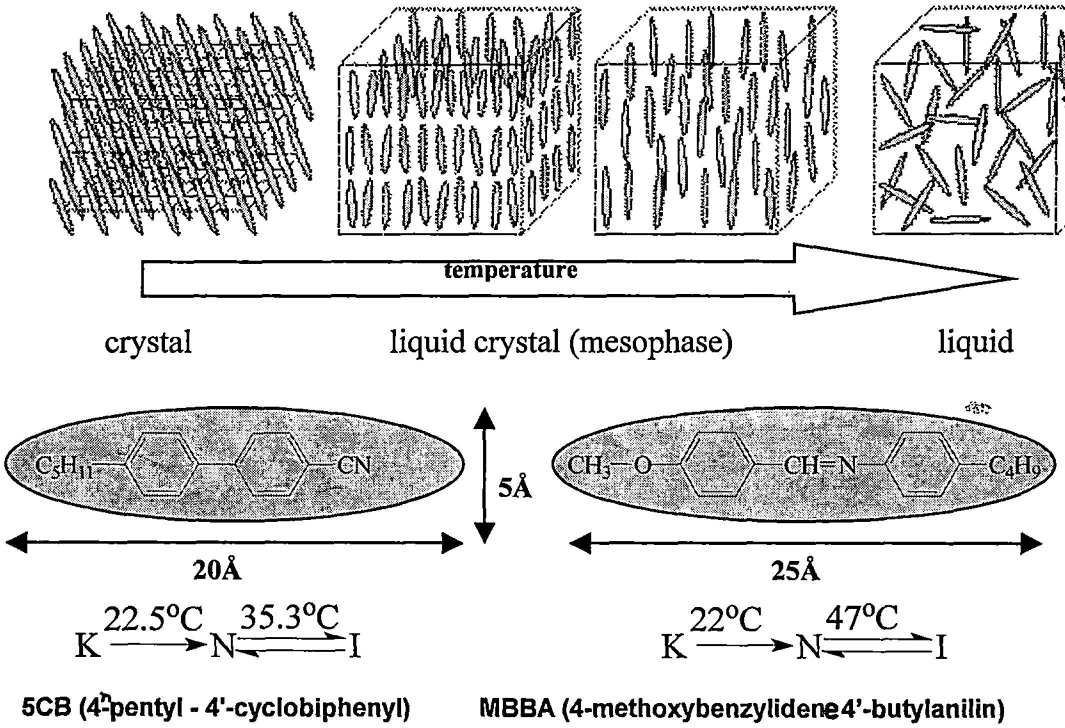


FIGURE 1.3: A typical calamitic liquid crystal with transition temperatures.

Thermotropic liquid crystals that exhibit reversibility of phase transition are called ‘enantiotropic’; and in certain cases mesomorphism is observed only during cooling of the compound and these transitions are called ‘monotropic’ transitions. Friedel [35] from his detailed optical and x-ray studies have classified thermotropics into three main types: nematic, cholesteric and smectic. Classifications of smectic liquid crystals are based mainly on the optical and miscibility studies of Demus and Richter [36]. A brief description of different thermotropic mesophases is given below.

1.2.3 Nematic liquid crystals:

In nematics, there is no correlation between the molecular centre of gravity, but the direction of molecular long axis do statistically have a preferred direction called director denoted by **n** (figure 1.4). Since there is no restriction regarding the positions of the centre of mass, the molecules in the phase have a high degree of mobility.

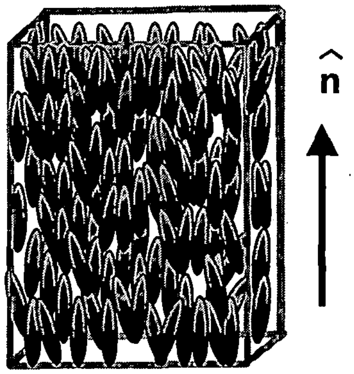


FIGURE 1.4: Schematic illustration of ordinary nematic liquid crystal.

Deformation in alignment of the nematic molecules can be induced by small external influences and this property is extremely useful in various display devices. The ordinary nematics shows an optically positive uniaxial behaviour, but a biaxial modification has also been discovered. Another characteristic property of this phase is that the mirror images are indistinguishable, i.e., achiral, indicating the system to be a racemic mixture of right- and left-handed molecules. X-ray studies indicate that fluctuation of smectic like order parameter manifest itself in certain nematic phases, called "cybotactic nematics", first observed and classified by Adrian de Vries [37].

1.2.4 Cholesteric or chiral nematic (N^*) phases:

The cholesteric (or chiral nematic) [38-40] liquid crystal phase is typically composed of nematic mesogenic molecules containing a chiral center, which produces intermolecular forces that favour alignment between molecules at a slight angle to one another. This leads to the formation of a structure that can be visualized as a stack of very thin two-dimensional nematic-like layers with the director in each layer twisted with respect to those above and below it. So the directors actually form a continuous helical [41] pattern about the layer normal as shown in figure 1.5.

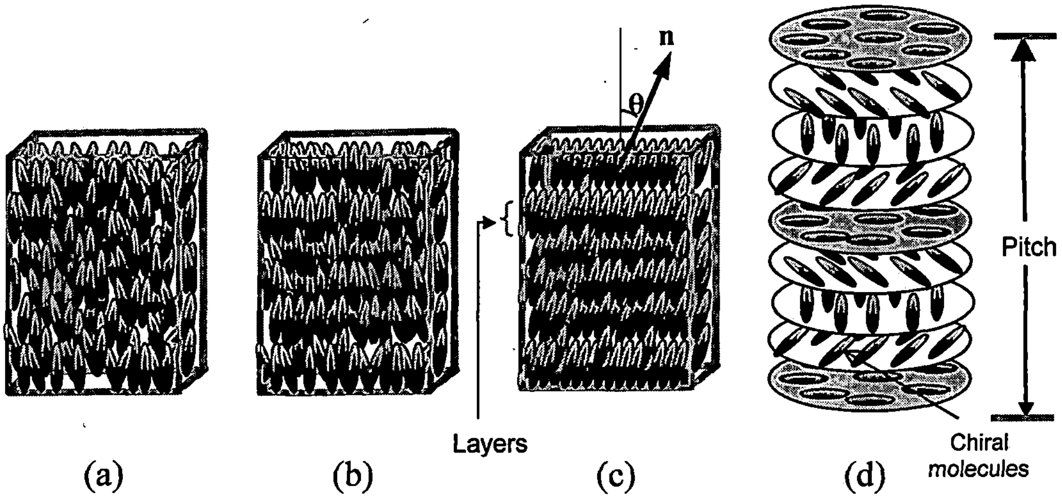


FIGURE 1.5: Schematic representation of **(a)** nematic phase **(b)** orthogonal smectic A phase and **(c)** tilted smectic C phase **(d)** helical structure of the cholesteric liquid crystals. The arrow indicates the director **n**.

The helix may be right handed or left handed depending on the molecular conformation. An important characteristic of the cholesteric mesophase is the temperature dependent pitch (p) which is defined as the distance it takes for the director to rotate one full turn in the helix. The helical structure of the chiral nematic phase enables it to selectively reflect light of wavelengths equal to the pitch length. This property is utilized in liquid crystal thermometers.

1.2.5 Smectic liquid crystals:

Smectic liquid crystals have layered structure. The centres of gravity of the elongated molecules lie in equidistant planes. The molecules are parallel to the preferred direction, which may be normal to the plane or may be tilted at a certain angle. The arrangement of the molecules within the plane may be random or regular. The smectic liquid crystals are generally more viscous than nematics. The interlayer attractions are smaller in comparison to the lateral forces between the molecules and the layers can slide over one another [42-52], thus showing fluid behaviour. A large number of smectic phases identified [8,52-55] by observed variants are as follows

SmA, SmC, SmB, SmD, SmE, SmF, SmG, SmH, ...

Since my work is concerned with nematic, smectic A and smectic B phases only, I will not go into details of other smectic phases here.

1.2.6 Smectic A phase (SmA):

In smectic A liquid crystals, the molecular orientation is perpendicular to the plane in which the centers of mass of the molecules are situated. There is a long-range positional order normal to the smectic layers, but within each layer the distribution of the molecular centers is random [42-44] or with only a short-range order typical of liquids. The smectic A molecules can rotate about the long axis sweeping out a volume which is cylindrical in shape. Due to this infinite fold rotational symmetry about an axis parallel to the direction normal to the layer, smectic A liquid crystals at thermal equilibrium are uniaxial systems [11,56]. In this phase usually the layer spacing (*d*) is approximately equal to the molecular length (*l*). However, other modifications are also possible. Smectic A phase can be subdivided into several distinct phases [45-52,53-60] such as monolayer smectic A

(SmA_1), bilayer smectic A (SmA_2), partially bilayer smectic A_d (SmA_d) and smectic antiphase Smectic Ã, as shown in figure 1.6 (a-d) respectively.

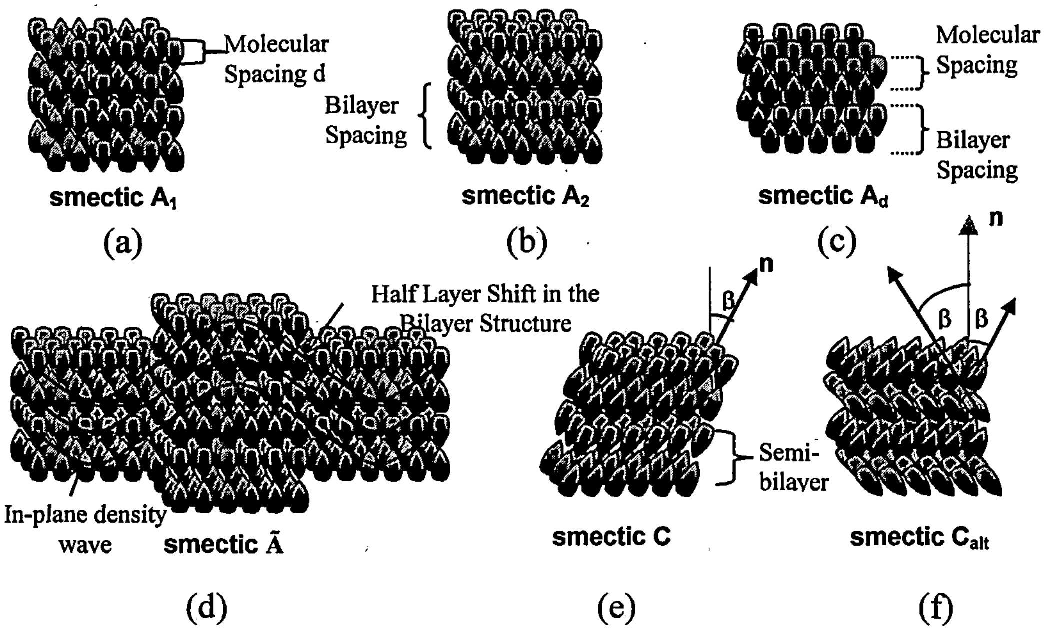


FIGURE 1.6: Bilayer and monolayer structures of the smectic phases.

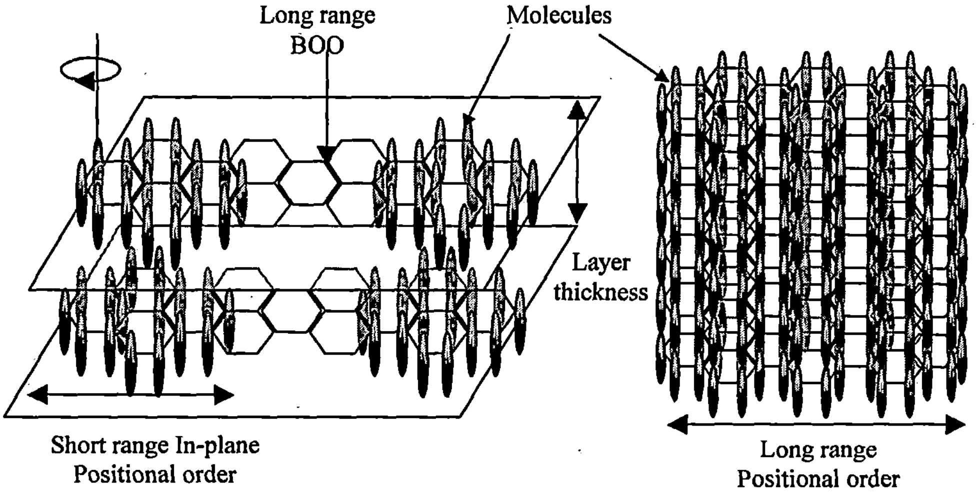
1.2.7 Smectic C phase (SmC):

In the smectic-C mesophase, molecules are arranged in layers as in the smectic-A mesophase, but the molecules are inclined with respect to the layer normal as shown in figure 1.6(e). The layer thickness $d = l\cos\beta$, (where l is the length of the molecule and β is the tilt angle) in the smectic C phase is less than that of the corresponding smectic A phase due to this tilt. The tilt angle β varies from compound to compound, and for a given compound it may or may not be temperature dependent. The smectic C phase is optically biaxial and more viscous than that of nematics. Levelut et al [53-55,60-63] has reclassified the SmC phase as alternating smectic C phase (SmC_{alt}), wherein the tilt angle of the molecules are rotated by 180° while passing from one layer to the other, in contrast to that of traditional SmC phase (figure 1.6(f)).

1.2.8 Smectic B phase (SmB):

The smectic-B liquid crystals also have layered structure with the molecular long axis perpendicular to the layer normal. However, within the layers the molecules are arranged into a network of hexagons. According to Birgeneau and Lister [64], the smectic B phase is a realization of the stacked hexagonal phases possessing bond orientational order (BOO) found in two dimensions. On the basis of x-ray [65] and electron diffraction [66] experiments done on bulk aligned samples as well as on thin films the traditional smectic B phase has been further reclassified into the Hexatic B (SmB_{hex}) [67] and Crystal B (Cry B) phase.

The SmB_{hex} phase has short range in-plane positional order and long-range bond orientational order as shown in figure 1.7(a). The crystal B phase however has long-range inter- and intra- layer translational order and long-range bond orientational order as well. The Crystal B phase is still considered liquid crystal because of weak coupling between the smectic layers. Hence they exhibit shear and flow properties under stress and the Mossbauer spectra of this phase is also inconsistent with that of solid.



(a) (b)

FIGURE 1.7: Structure of the **(a)** hexatic smectic B phase and **(b)** crystal B phase

1.3 Other liquid crystalline phases:

1.3.1 Blue phase:

Cholesterics liquid crystals of pitch less than about 0.5mm exhibit what are known as blue phases. These phases exist over a small temperature range (~1°C) between the liquid crystal phase and the isotropic liquid. These liquid crystalline materials display bluish-violet colour below its cholesteric-isotropic phase transition temperature [68-72], which may be due to the defects in a cubical array. Blue phases exhibit optical activity and selective reflection of circularly polarized light without possessing optical birefringence [73].

1.3.2 Twist grain boundary smectic A (TGBA) phase:

Goodby et al [74,75] have discovered a new liquid crystal phase in 1989, called Twist Grain Boundary Smectic A (TGBA) phase, wherein the molecules are arranged in layers with their long axis perpendicular to the layer plane. Due to the rotation of different blocks of the layers around the normal to the long axis of the molecules a helical structure is formed with the axis of the helix parallel to the layer plane. Renn and Lubensky [76,77] in their model specified that TGBA are responsible for rotating each blocks of the chiral A^* layers with respect to each other. Since then many new TGBA and TGBC phases have been identified.

1.3.3 Ferroelectric liquid crystals (FLC):

Ferroelectricity in liquid crystals has been known from the pioneering work of R. B. Meyer et al [78]. Chirality in a tilted Smectic C phase is introduced by chiral dopants or by chirality of the constituting molecules themselves results in a breaking of mirror symmetry and this chiral smectic phase is denoted by SmC^*. In such chiral tilted phases the symmetry group is reduced to C_2. Hence it permits the appearance of the spontaneous electric polarization P_s in each layer of the smectic C^* phase. However, in bulk the equilibrium structure will be twisted into a helix so that the polarization of the layers precesses around the layer normal and in macroscopic sample the spontaneous polarization averages to zero and a surface stabilization is required to obtain bi-stable ferroelectric switching. Anti-ferroelectric [79] and ferrielectric smectic phases were also discovered in liquid crystal materials [80-82]. A very successful concept for ferro and anti-ferroelectric smectic phases is based on achiral bent shape molecules – the so-called "banana" [83] phases. Because of the close packing of bent molecules and high rotational hindrance about the long molecular axis an in-layer polar order emerges despite the achiral nature of the molecules. To have material with high information content colour displays and of fast switching speed, study of both ferroelectric and antiferroelectric liquid crystals has become important today.

1.3.4 Discotic liquid crystals:

In 1977, Chandrasekhar, Sadashiv and Suresh discovered that [84] disc like molecules also form liquid crystalline phases in which the axis perpendicular to the plane of the molecule (the director) tends to be along a specific direction. In the nematic (N_D) state, the disc-like molecules appear to stack one on top of the other, rather like a pile of disordered plates. Apart from the N_D phase disc like molecules give rise to columnar phases [85] in which the molecules are in stacks that lie side by side to form a two dimensional lattice. The different columnar phases are classified into orthogonal or tilted phases (figure 1.8). The tilt refers to the angle between the director and columnar axis. Different type of lattice structures have been identified by Levelute [85] viz., hexagonal, rectangular and oblique. Significant research works have been performed during last ten years [86,87].

FIGURE 1.8: Schematic representation of columnar structures of discotic mesogens: (a) upright columns and (b) tilted columns.

1.3.5 Polymer liquid crystals:

Liquid crystal polymers (PLC's) exhibit both the characteristic properties of ordinary liquid crystals, as well as retain the versatile properties of polymers. For a polymer to display liquid crystal characteristics they must incorporate either rod-like (calamitic), discotic, amphiphilic or chiral molecules of low molecular weight, which are attached to the polymer backbone either in the main chain, or as side groups into their chains. Placement of these monomers plays an important role into the determination of the type of PLC's. Main chain polymer liquid crystals are formed when the mesogens are themselves becomes a part of the main chain of a polymer, whereas in the side chain polymer liquid crystals mesogens are connected as side chains to the polymer by a flexible 'bridge'. Factors that may affect the mesomorphic behavior of the polymer include the presence of long flexible spacers, a low molecular weight, and regular alternation of rigid and flexible units along the main chain. Polymer dispersed liquid crystals (PDLC's) are widely used in displays, switchable windows and other light shutter devices [88-90]

1.4 Liquid crystal mixtures:

In the past 20-30 years liquid crystalline materials have received significant attention due to their increased applicability in display devices. Although more than 100,000 liquid crystalline compounds have been synthesized so far [33], to meet the specific demands of the electro-optic display devices, mixtures of pure compounds are often used where the compositions of the individual components are adjusted so that better materials may be produced for display applications. Mixtures enable us not only to lower the melting point but also to adjust the mixture properties such as viscosity, birefringence, electric permittivity and elastic constants. In this way mixtures with optimal electro-optical characteristics for the best display performance can be obtained. The physical properties of such mixtures however, cannot always be interpolated from the properties of the pure components, notable examples being formation of an induced smectic phase in a mixture of pure nematogens [91-103], and exhibition of re-entrant phenomena in mixtures of liquid crystal chemicals [104-105], which do not show such phase in their pure form. Intermolecular attractive forces such as Vander Waals forces, hydrogen bonds, electron-donor interactions and intermolecular repulsion (steric forces) influence the situation of molecules in the mesophase. Each of those forces, separately or together, may be responsible for increasing or decreasing the stability of liquid crystalline phases or for creating new phases.

The presence of induced smectic phase in the operational temperature range of the display device must be avoided. However, its presence at a lower temperature is advantageous since it decreases the bend to splay elastic constant ratio [106] thus increasing the sharpness of the electro-optical display devices. Hence, measurement of physical properties of mixtures is very important from the point of view of selection of proper liquid crystal materials for display devices. A considerable volume of work has been reported in the literature on systems involving polar non-polar mixtures exhibiting the induced smectic phase behaviour [91-103,107-115]. The creation of new phases in binary mixtures of mesogenic compounds will be discussed here.

1.4.1 Formation of induced and enhanced smectic phases:

(1) Liquid crystalline phases (nematic or smectic) existing in pure compounds in bi-component or multi-component systems enhance their own thermal stability or new phases of higher order are injected. These enhanced or injected phases are commonly termed as induced phases or chemically induced phases [92,116-117]. Such behavior is usually observed in binary mixtures of a compound having a strongly polar terminal group and a compound having a non-polar terminal group [104, 118-119]. The induction of smectic phases is also possible in systems containing two polar nematics [111-112]. This phase can be induced in mixtures of non-polar nematics [89-90,92] as well.

(2) Smectic phases existing in pure compounds in the bi-component or multi-component systems decrease their smectic stability and new phases of lower order are created. These phases are termed as phases created by depressing smectic stability [116-117].

A quantitative theory of induced smectic phase is difficult since it would require the inclusion of position dependent attractive and repulsive interactions for both the components. Wagner [120] has tried with limited success to explain the phase diagram of mixtures showing induced smectic phase using McMillan's theory for smectics. He however, could not reproduce the nematic – isotropic phase boundary. Longa and de Jeu [121] using mean field approximation gave a theoretical model in which the influence of complex formation on the nematic–smecticA transition temperature was estimated. Their model confirms that the complication involved at S_A-N phase transition is a consequence of the interactions between complexes. Dispersion forces are mainly responsible for these interactions. Using an extension of Maier-Saupe theory [122], Palffy-Muhoray et al [123] have determined the nematic-isotropic co-existence region for the entire range of concentrations of induced smectic system and they have proposed a relation between the refractive index of the binary mixture and order parameters of its components in the nematic phase. Sharma and Schneider [95,96], Matsunaga and Araya [112-113], Iida [114] observed charge-transfer bands in the investigated mixtures and on that basis they attributed a great deal of importance to donor-acceptor interactions.

1.4.2 The Re-entrant phenomena:

One of the most interesting phenomena exhibited by liquid crystals is the formation of re-entrant phase. When a compound exhibits both smectic and nematic phases, then as a rule, the nematic phase occur at the higher temperature. An exception to this rule, Cladis [105] discovered the re-entrant phase, in certain strongly polar materials in 1975. This phase has been observed in mixtures [124-125] as well as in single component at high [126] and atmospheric [127-128] pressures. Evidence shows that the re-entrant phenomenon is not only possible in strong polar systems, but also in low polar systems containing calamitic [103] or discotic [129] molecules and in mixed systems containing compounds of high and low polarity [130-133]. Systems including chiral compounds [134-135] and low and high molecular weight [136] compounds are also described to exhibit this phase. Re-entrant smectic phases have also been reported in terminal polar compounds [137]. In binary mixtures of terminal non-polar compounds the phase sequence SmA-SmC-SmA has been detected [138-139]. A multiple re-entrant polymorphism has also been found in pure substances as well [8, 137].

Cladis [140-141] has explained the mechanism of formation of nematic phase at lower temperature. A more complete theoretical discussion by considering attractive forces and hard-core repulsions, Longa and de Jeu [142] showed that there could exist a low temperature nematic phase. From the molecular point of view, S. Chandrasekhar [143] has discussed the re-entrant phenomena qualitatively. By extending McMillan's treatment of SmA phase, Luckhurst and Timmi [144] have developed a molecular theory for re-entrant nematic and SmA mesophases.

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