

CHAPTER I

INTRODUCTION

Nature of Liquid Crystals

Many organic compounds are **known** to exhibit intermediate phases between the crystalline solid and the isotropic liquid. These intermediate phases are called **liquid crystalline** phases or mesomorphic phases. Liquid crystalline **phases** may be thermotropic or lyotropic. The former are those in which the mesomorphism is brought about by purely thermal processes, **i.e.**, by heating the solid or cooling the isotropic liquid, and are observed in pure compounds (or their mixtures). The latter are those in which mesomorphism is induced by suitable solvents. We shall be concerned here only with thermotropic liquid crystals,

Friedel¹ classified thermotropic liquid crystals into three types based upon the molecular arrangements in them. They are (1) nematic, (2) **cholesteric**, and (3) **smectic**.

Nematic liquid crystals

Nematic liquid crystals have a long **range** orientational order but do not have a long range positional or translational order (see fig. 1.1). **The** molecules tend to orient themselves along a mean direction $\hat{n}$, called the director, but they can easily slide **past** one another. **Thus** the nematic **is** a **fluid** phase. The **degree** of orientation is **given** by an order parameter ' η ' which is defined as

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

where θ is the angle between the **long** molecular axis and the director. **The** angular brackets denote a statistical average. **The value** of η is unity for

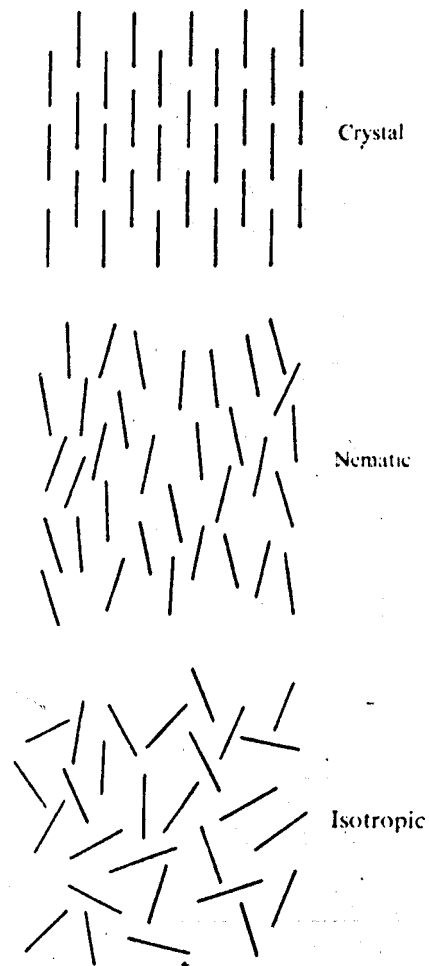


Fig.1.1: Schematic representation of molecular order in the **crystalline**, nematic **and** isotropic phases.

a perfectly ordered sample and it is zero for a completely random orientation, which describes the isotropic phase. In the nematic phase the value of η lies between zero and unity, and it is strongly temperature dependent. X-ray studies by de Vries² and Chistyakov³ have indicated that some nematics are composed of groups of molecules, the molecular centres being arranged in layers in each group. Such groups are called cybotactic groups.

A nematic liquid crystal is optically uniaxial, positive and strongly birefringent. When a thin film of unaligned nematic sample is examined through a polarising microscope, complex optical patterns can be seen. This is due to the collection of disclinations in the sample. In an unaligned sample the director changes from point to point. A monodomain sample can be obtained by applying a magnetic field or by treating the boundary surface in a suitable manner. If the long axes of

the molecules are parallel to the boundary surface, the sample is said to be homogeneously aligned. If they are perpendicular to the surface, the sample is said to be homeotropically aligned.

Cholesteric liquid crystals

Cholesteric liquid crystals have a **nematic**-like structure except that they are composed of optically active molecules. As a **consequence**, the structure is helical with the screw axis **normal** to the director (**Fig.1.2**). Because of the helical structure, the **cholesteric** phase **has** some characteristic properties like selective reflection of circularly polarised light, very high optical rotatory power, etc. Thermodynamically the **cholesteric** phase is not very different from the nematic phase.

Smectic liquid **crystals**

Smectic liquid crystals have a **lamellar**

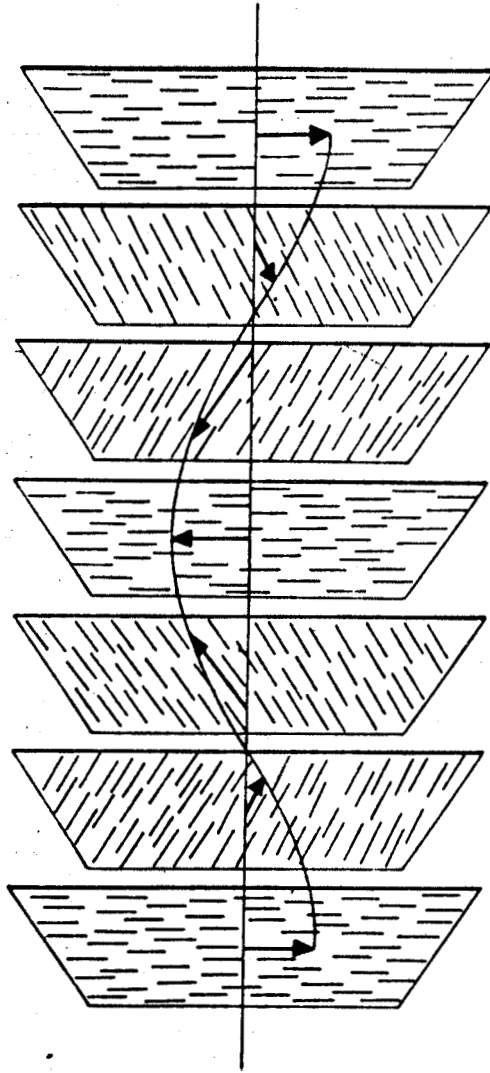


Figure 1.2: Schematic representation of the helical **structure** in a cholesteric liquid crystal.

structure **with** a well defined layer spacing.

Based on the arrangement of molecules in each layer, smectics are classified into different kinds - smectic A, smectic B, smectic C, etc.

In our studies here, **we** are concerned only with the smectic A phase.

In smectic A the long axes of the molecules are **normal** to the layers with the molecular centres randomly distributed in each layer (see fig. 1.3). **The** binding between the layers is very weak and hence they can slide easily giving rise to fluidity. However, the viscosity is higher in the smectic A phase than in the nematic phase.

Generally the sequence of phases that occur in a thermotropic compound is as shown below.

Crystal $\longleftrightarrow$ smectic $\longleftrightarrow$ nematic $\longleftrightarrow$ isotropic

On cooling a sample **it** goes over from a less ordered state to a more ordered state. But recently

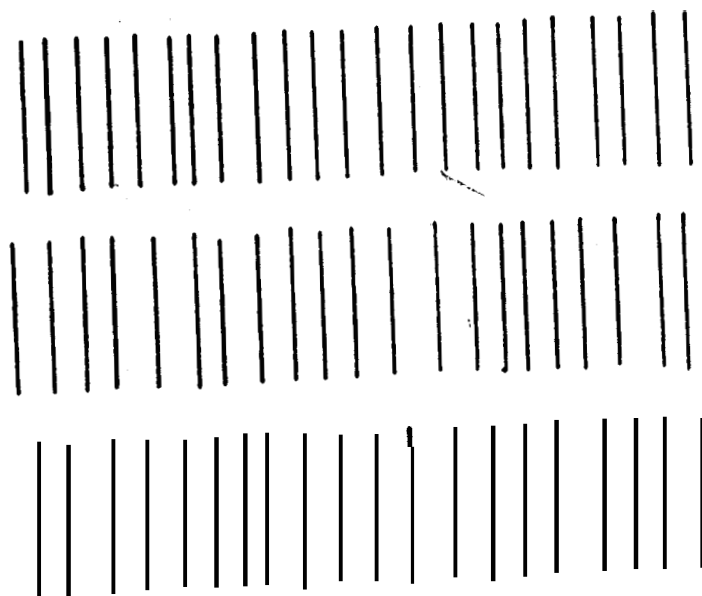


FIGURE 1.3

Structure of smectic A phase

it has been found ~~out~~⁴⁻⁶ that some compounds exhibit a second lower temperature nematic phase which has been referred ~~to as~~ the reentrant nematic phase.

The characteristic feature of a **mesogenic** compound is that it is composed of geometrically anisotropic molecules. For a long time it was generally believed that only compounds with long rod shaped molecules exhibit mesomorphism. Very recently **Chandrasekhar et al**⁷ discovered that flat disc-like molecules also show liquid **crystalline** phases. These mesophases have a **columnar** structure; the flat molecules are stacked one upon another in **columns**, the different **columns** forming a two-dimensional lattice like array (fig. 1.4).

The study of liquid crystals **is** very interesting **as** some of their properties are quite different from those of ordinary liquids. Surface tension is

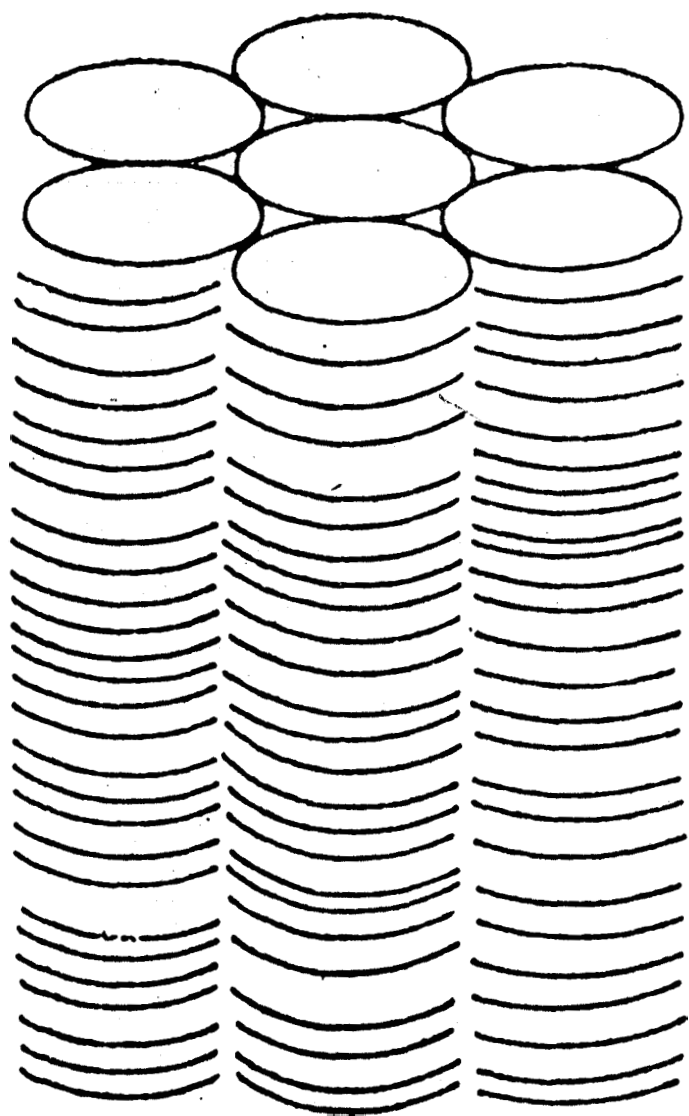


Figure 1.4: Schematic representation of columnar phase of disc-like molecules.

one such property which may be expected to reflect the anisotropic nature of liquid crystals. The present thesis deals with the experimental studies conducted by the author on the surface properties of nematic and smectic A liquid crystals.

Earlier experimental studies on the surface tension of liquid crystals

The surface tension (γ) of liquid crystals has been the **subject** of a number of experimental investigations. However the results obtained by the different workers are quite conflicting. One of the earliest studies were those of Jaeger.⁸ He used the ~~maximum~~ bubble pressure method in an atmosphere of nitrogen and measured the surface tension of five liquid crystalline compounds **as** a function of temperature. The **compounds** were - p-azoxyanisole, p-azoxyphenetole, **anisaldazine** and ethyl p-ethoxybenzalamino- α -methyl **cinnamate**, which are nematic, and ethyl p-azoxybenzoate, which is

smectic. He found that in every case the value of γ initially decreased with the increase of temperature in the **mesophase** and suddenly rose to a maximum at the transition point (Fig. 1.5, 1.6 and 1.7). In the case of ethyl-p-aeoxybenzoate, he found that the value of γ decreased rapidly after the smectic A - isotropic transition (T_{AI}) to a steady value and about 50°C above T_{AI} , again showed an increasing trend (Fig.1.7).

In 1938 Ferguson and Kennedy⁹ measured the surface tension of p-azoxyanisole, p-azoxyphenetole and **anisaldazine** as a function of temperature by a different method. They carried out their experiment both in the nematic **and** isotropic phases. Briefly, **the** method adopted by them consists in forcing a thread of the liquid crystal along a horizontal capillary tube **and** adjusting the pressure at one end of the liquid column until the surface of the liquid at the open end of the tube is **plane**. **The**

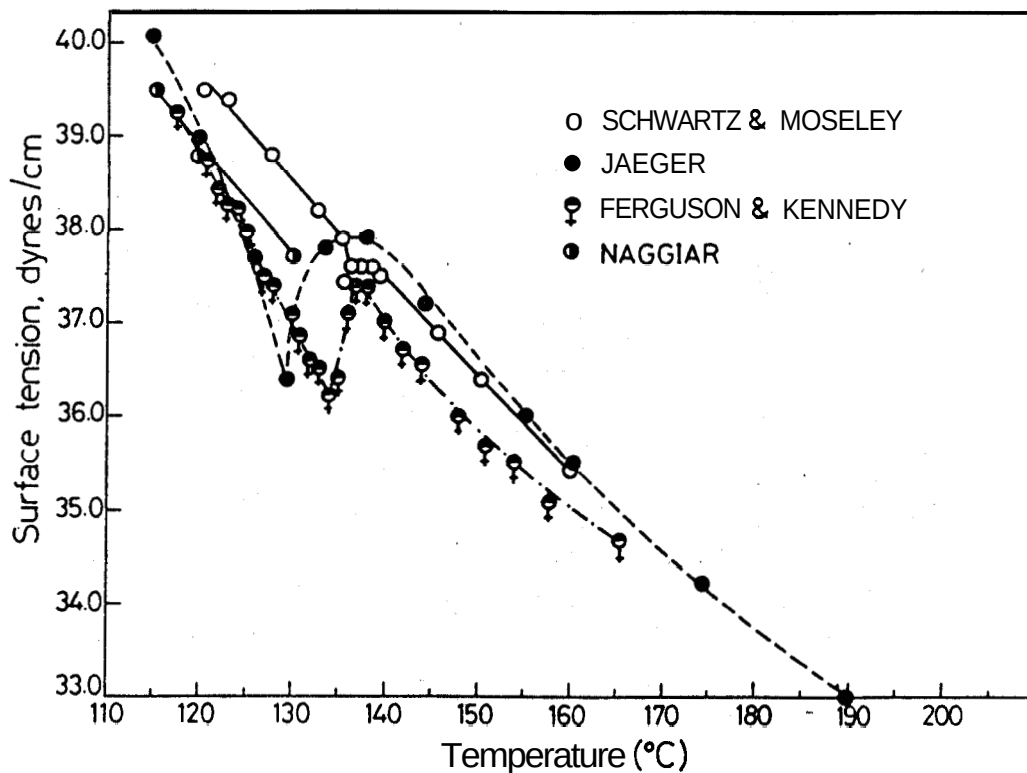


Figure 1.5: Surface tension - temperature characteristics of PAA obtained by earlier **workers** (After references 8 to 11).

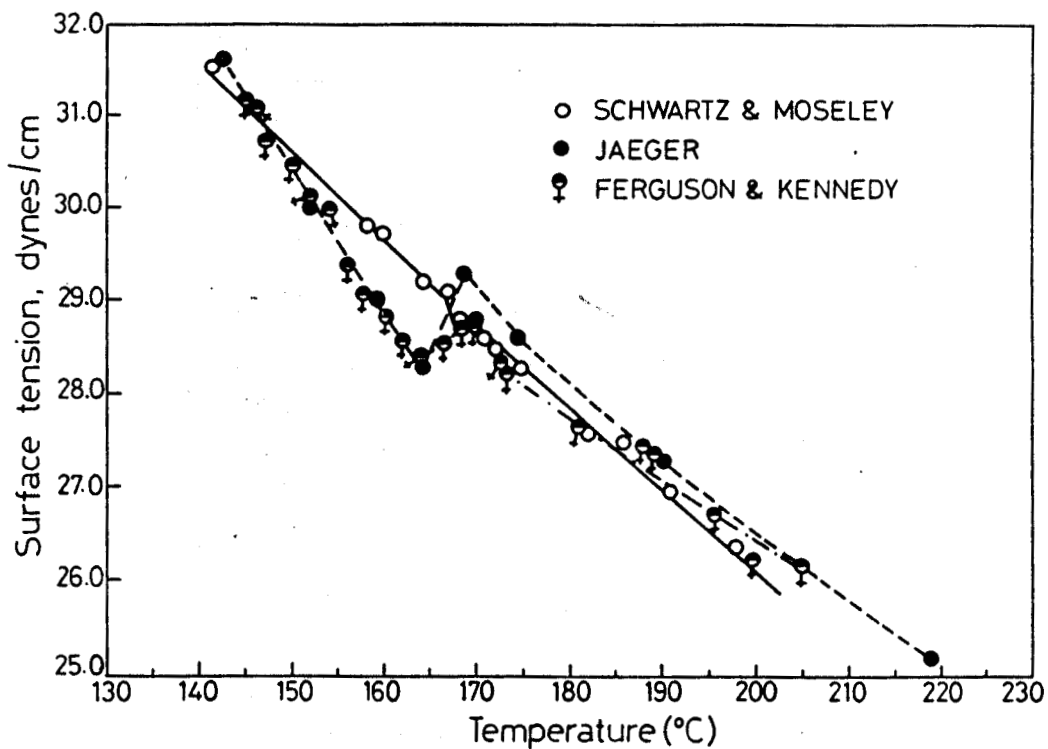


Figure 1.6: **Surface** tension-temperature characteristics of
PAP obtained by earlier workers (After reference 8,9 & 11).

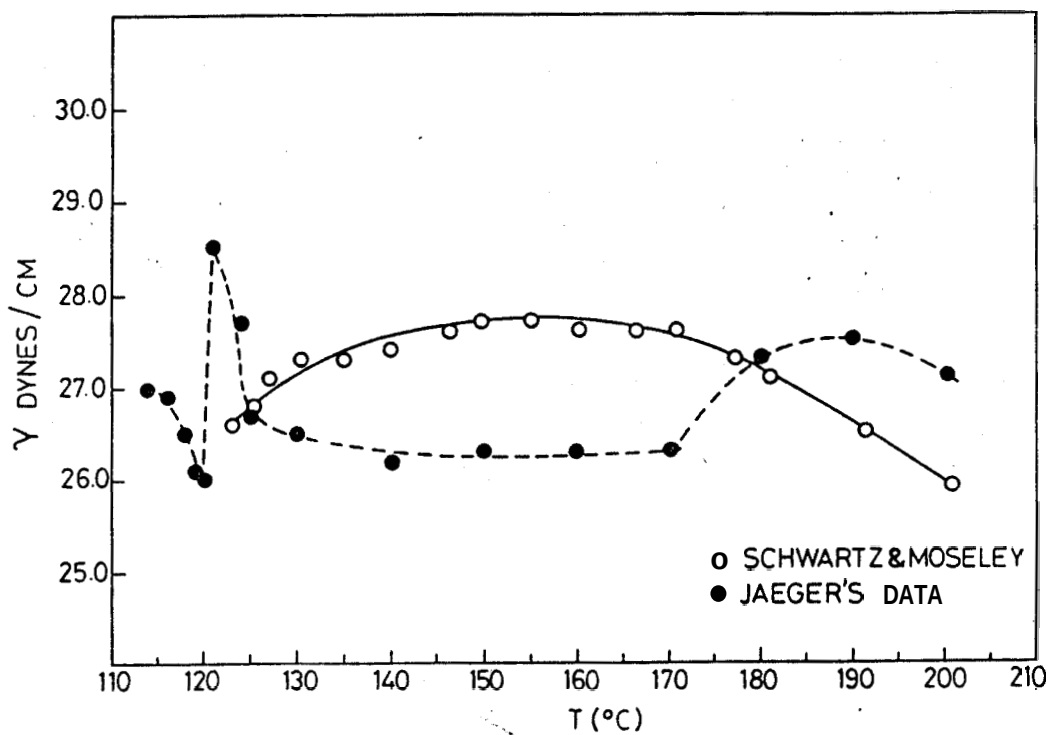


Figure 1.7: Surface tension-temperature characteristics of ethyl-p-azoxybenzoate obtained by Schwartz and Moseley (open circles) and Jaeger (black circles).

planarity of the meniscus is tested by illuminating it by a **lamp** and watching it with a lens. By measuring the pressure required to make the meniscus plane at the free end, the surface tension could be estimated. In the case of anisaldazine (**Fig.1.8**) they found that the surface tension decreases with temperature initially but starts increasing as the nematic–isotropic transition is approached giving rise to a positive slope for the surface tension (**y**) temperature (**T**) characteristic. In the isotropic phase it regains the monotonically decreasing trend. In the case of PAA, the behaviour is similar to that of anisaldazine in the nematic phase, but in the isotropic phase, the surface tension continues to increase for a short range of temperature **and** later assumes the decreasing trend. As a result, the slope of the γ -**T characteristic** curve becomes positive **as** the **N-I** transition is approached and continues to be so in the isotropic phase for a short

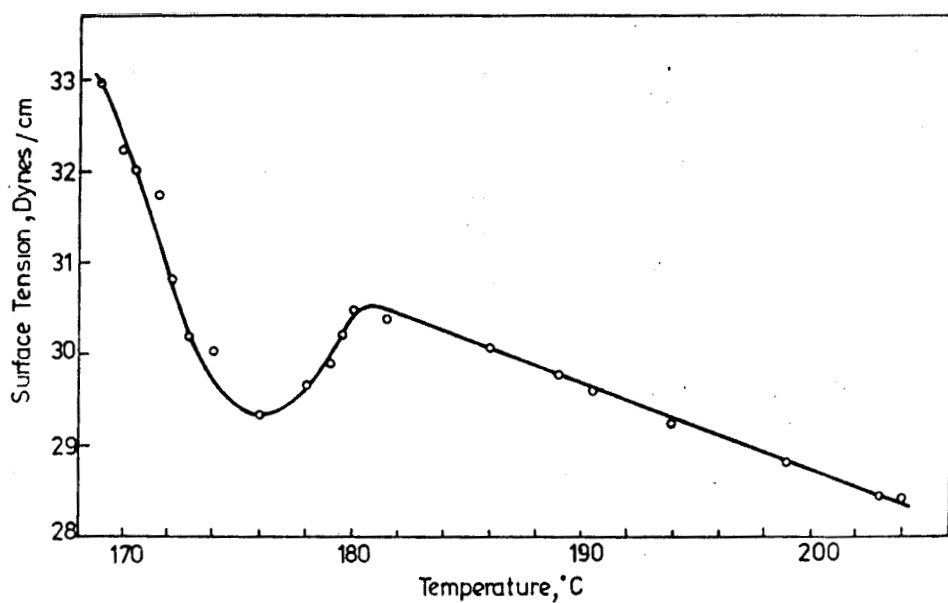


Figure 1.8

Surface tension-temperature **characteristic** curve for **anisaldazine** (After **Ferguson** and Kennedy⁹)

range of temperature (Fig. 1.5). These results are unusual when **compared** with the **behaviour** of isotropic **liquids** for which surface tension decreases **continuously** with increasing temperature.

Later **Naggiar**¹⁰ measured the surface tension of PAA in the nematic phase. He used a thin film of the liquid crystal stretched over a hole drilled in a supporting surface* ~~The~~ surfaces of the suspended film became curved under the influence of the gravity. By using a microscope, the **curvature** of the upper **and** lower surfaces of the film and its thickness were measured. ~~He~~ calculated the surface tension using the expression

$$2\gamma\left(\frac{1}{R_1} - \frac{1}{R_2}\right) = \rho g t$$

where R_1 **and** R_2 **are** the radii of the curved surfaces at the centre of each of the surfaces, ρ is the density of the **liquid** crystal forming the film, g is the gravitational acceleration **and** t is the **thickness** of the

film at its centre. By enclosing the film in an electrically heated compartment Naggiar was able to carry out his experiment at a number of temperatures. The γ -T characteristic obtained by him is a straight line which is not in agreement with the results of Ferguson and Kennedy (Fig.1.5). Naggiar did not make any measurement in the isotropic phase.

Naggiar's result on PAA was confirmed by Schwartz and Moseley¹¹ in 1947. They measured the surface tension of PAA, PAP and ethyl p-azoxybenzoate using a ring type du Nouy tensiometer. They carried out their experiments both in the mesomorphic and isotropic phases. The γ -T characteristics obtained by them for PAA and PAP were straight lines which again contradict the results of Jaeger^L and also of Ferguson and Kennedy (Fig.1.5 and 1.6). Another experimental data on PAA is by Gorski¹¹ and Sakevitch¹². They used the maximum bubble pressure method and measured the

surface tension of PAA, only in the nematic phase up to 125°C. They have found a monotonic decreasing trend in the γ -T characteristic. They have not made any measurement in the vicinity of the transition temperature which is the most interesting region.

In the case of ethyl p-azoxybenzoate, 'Schwartz and Moseley'¹¹ have stated that it was not possible to carry out the measurements in the smectic phase, because of its high viscosity. However, in the isotropic phase, they found that the surface tension increased with the temperature up to about 30°C above the transition temperature, after which they found a monotonically decreasing trend. This result is quite contrary to Jaeger's results as can be seen from the comparison of the two curves in Fig. 1.7.

Thus, as already pointed out, the different determinations gave conflicting results. In particular the measurements of Naggiar, and Schwartz and

Moseley are at variance with the earlier data of Ferguson and Kennedy, so much so that doubts have been cast on the validity of the measurements of Ferguson and Kennedy. For example, Gray¹³ has remarked that the anomalous **behaviour** observed by Ferguson and Kennedy may be due to the drawback of the method used by them in dealing with liquid crystals as they are composed of **anisotropic** molecules.

The reason for the lack of unanimity in the results may be partly due to the limitations of the methods, particularly when they are applied for the study of liquid crystals as Gray has pointed out, and partly due to the **lack** of precautionary measures that need to be taken in setting up the experiment. Liquid crystals are **composed** of geometrically anisotropic molecules. Hence the surface tension may depend upon the orientation of the molecules at the free surface.¹⁴ So the method used to study the

surface tension should be such that the orientation of molecules in the free surface is not affected by the solid which is in contact with the liquid crystal. Secondly, **as** has been pointed out by Croxton and Chandrasekhar,¹⁵ the thermodynamic equilibrium of the liquid surface with its vapour is very essential to observe the true behaviour of surface tension. White⁶ has demonstrated this aspect experimentally. Some liquid metals (e.g., zinc and copper) show a positive slope in the γ -I characteristics when the experiment is done under equilibrium condition. By deliberately allowing continuous vapourisation, White could reverse the sign of the slope in the γ -T characteristic of zinc. It is not clear whether the earlier workers investigating the surface tension of liquid crystals had taken sufficient care about these points.

Theoretical background

In 1973, Croxton and Chandrasekhar¹⁵ pointed

out for the first time that the γ -T characteristic of a nematic liquid crystal can be expected to develop a positive slope in the vicinity of the N-I transition point. The possibility of a discontinuity in the γ -T characteristic at the transition point is also anticipated by them. **Later** Parsons¹⁷ has also predicted the possibility of discontinuity at the N-I transition point with γ having a higher value in the isotropic phase.

From thermodynamic considerations it can be shown^{1*} that the gradient of the γ -T curve is related to the excess entropy per unit area developed at the surface. Let us consider the Helmholtz; free energy of a classical single component system,

$$F = F(T, V, A)$$

having a free plane surface of area A. The infinitesimal change in Helmholtz free energy dF arising from small changes in temperature, volume and area

is given by the total differential

$$dF = \left(\frac{\partial F}{\partial T} \right)_{V,A} dT + \left(\frac{\partial F}{\partial V} \right)_{T,A} dV + \left(\frac{\partial F}{\partial A} \right)_{T,V} dA \quad (1)$$

Since

$$\left(\frac{\partial F}{\partial T} \right)_{V,A} = -S, \quad \left(\frac{\partial F}{\partial V} \right)_{T,A} = -P, \quad \left(\frac{\partial F}{\partial A} \right)_{T,V} = \gamma$$

where S is the entropy, P is the pressure and γ is the surface tension, we have from (1)

$$dF = -SdT - PdV + \gamma dA \quad (2)$$

Since we are concerned here primarily with the thermodynamics of the surface region of the system, we may assume that the bulk properties remain essentially unmodified by extensions of the surface area. Then equation (2) can be expressed in terms of the surface excess quantities:

$$dF_s = -S_s dT + \gamma dA \quad (3)$$

At constant temperature (3) gives

$$F_s = \gamma A \quad (4)$$

Equation (4) has the total differential

$$dF_s = \gamma dA + A d\gamma \quad (5)$$

From (3) and (5) we get

$$-S_s dT = A d\gamma$$

or

$$\frac{d\gamma}{dT} = -\frac{S_s}{A} = -s_e \quad (6)$$

where s_e is the excess entropy per unit area of **surface** region. It represents the **additional** entropy per unit area possessed by a system with surfaces over and **above** the amount that the **same** quantity of the fluid would possess under the same conditions of temperature and pressure in the body of a larger quantity of the fluid. If s_σ and s_β are the entropies of the surface ^{the} and ~~bulk~~ bulk, respectively, equation (6) can be written as

$$\frac{d\gamma}{dT} = -s_e = -(s_\sigma - s_\beta) \quad (7)$$

Croxton and Chandrasekhar emphasized that the possibility exists of the liquid crystals developing an excess **orientational** order at the free surface and in consequence, s_σ may be less than s^β . In these circumstances $d\gamma/dT$ can have a positive sign. These authors argued that in nematics **such** a situation can arise in the vicinity of the **nematic-isotropic** transition on either side. More recently Croxton¹⁹ **has extended** the theory to **smectic** liquid crystals, and has predicted a positive sign for $d\gamma/dT$ in the case of **smectics** also. **This** theoretical background and the conflicting experimental results obtained by earlier workers prompted the author to take **up** a systematic experimental study of the surface tension of liquid crystals, which forms the subject matter of this thesis.

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