

STUDIES ON
THE SURFACE PROPERTIES OF **LIQUID** CRYSTALS

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By

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DECLARATION

I hereby declare that the thesis was composed by me independently and that it has not formed the basis for the award of any Degree, Diploma, Associateship, Fellowship or other similar title.


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CERTIFICATE

I certify that this thesis **has** been composed by Mr. **S.Krishna Swamy** based on investigations carried out by him at the Liquid Crystals Laboratory, **Raman** Research Institute, under my supervision. The subject matter of this thesis has not previously formed the basis of the award of any degree, diploma, associateship, fellowship or other similar title.



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P R E F A C E

This thesis describes the results of experimental studies conducted by the author on the surface properties of liquid crystals. The surface properties studied are: (i) the surface tension (γ) of nematic and smectic A liquid crystals as a function of temperature, and (ii) the surface ordering at the free surface of the isotropic phase of nematogens. These are some of the properties which reflect the anisotropic nature of liquid crystals.

In chapter I, a short description is given of the different types of thermotropic liquid crystals. This is followed by a discussion of the earlier experimental work on the surface tension of liquid crystals. A brief theoretical background which is partly responsible for the author's undertaking the present investigations is also given here.

The **results** obtained by the earlier workers¹⁻⁴ were not unanimous. Jaeger, and **Ferguson** and Kennedy observed positive slopes in the surface tension (γ) - temperature (T) characteristics of some nematic compounds, while **Naggiar** as well **as** Schwartz and Moseley did not observe such a behaviour for the same compounds. Similar contradictions were found in the results of Jaeger, and Schwartz and Moseley for ethyl p-azoxybenzoate which shows smectic A and isotropic phases.

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The reason for the lack of unanimity ~~may~~ be partly due to the limitations of the methods used by the earlier workers, particularly when applied to liquid crystals (as ~~has~~ indeed been emphasized by Gray⁵), and partly due to the lack of precautionary measures that **have** to be **taken** in conducting the experiment.

Liquid crystals are composed of anisotropic

molecules and the surface tension **may** depend on the orientation of the molecules⁶ at the free surface. So the method chosen for the study of surface tension of liquid crystal should be such that the orientation of the molecules at the free surface is not influenced by the solid in contact with the liquid crystal. In fact the solid surface in contact with the liquid crystal has a great influence on the orientation of the molecules at the interface, the study of which is of prime importance in the display technology. Kobayashi and his coworkers⁷ have studied properties like anchoring and alignment of liquid crystals on treated substrates, and also the modification of the order parameter in the vicinity of a treated surface. Here we are interested in the properties of the free surface of liquid crystals and hence we wish to avoid the influence of the solid surface.

Secondly the method should be suitable for even

highly viscous liquids, as liquid crystals are generally viscous, and in particular, smectics are highly viscous. Because of the high viscosity **Schwartz** and **Moseley**⁴ and later Churchill and Bailey⁸ and also **Gannon** and **Faber**³ found that they could not obtain reproducible measurements in the smectic phase.

Croxtan and Chandrasekhar¹⁰ have pointed out that the thermodynamic equilibrium of the liquid surface with its own vapour is most essential to observe the true nature of the γ - T characteristic curve. Indeed White¹ has demonstrated this experimentally. Some liquid metals (e.g., zinc and copper) show a positive slope in the γ - T characteristic 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 took this precaution in their experiments

on liquid crystals.

It can be shown^{1*} on thermodynamic grounds that the gradient ($d\gamma/dT$) of the γ - T characteristic is related to the excess entropy (s_e) per unit area at the surface of a liquid as

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

where σ and β refer to the surface and the bulk states respectively. If there is an excess surface order we have a situation where $s_\sigma < s_\beta$ and the slope $d\gamma/dT$ becomes positive. In 1973 Croxton and Chandrasekhar¹⁰ emphasized that such a situation can arise in the case of nematic liquid crystals in the vicinity of nematic-isotropic **transition** temperature (T_{NI}) because of excess orientational order developing at the surface. **This** theoretical background, together with the conflicting results of the earlier workers prompted the author to take up a systematic

equilibrium study of the surface tension of liquid crystals.

In chapter **II** a brief summary of the theories of liquid crystals is given. Croxton and Chandrasekhar¹⁰ have discussed the qualitative forms of the γ - T characteristics of nematic liquid crystals on the basis of an expression for $d\gamma/dT$ which they have obtained by statistical methods. They predict the possibility of a positive slope in the vicinity of N-I transition and a discontinuity in the value of γ at T_{NI} . Parsons¹³ has also discussed the statistical mechanical theory of surface tension of nematic liquid crystals and has predicted a discontinuity in the value of γ at T_{NI} . Later Croxton¹⁴ extended the theory to **smectics** and predicted a positive slope throughout the smectic phase. Our experimental results are found to be in qualitative agreement with these theoretical predictions.

In chapter **III**, we describe the experimental

technique used for the measurement of γ in our experiments. After a brief discussion of the different methods which are in common use, we describe the Pendant drop method which appears to be probably the ideal one for liquid crystals. After a careful consideration of its merits and suitability for liquid crystals, it was decided to use this method.

In this method, 'a drop of the liquid is suspended from the tip of a glass capillary tube. A photograph of the drop is taken when it is in static equilibrium. Since the equation governing the drop shape involves (i) the surface tension (γ), (ii) the diameters of the drop at some selected planes, (iii) the density (ρ) of the liquid forming the drop and (iv) the gravitational acceleration, γ can be calculated by taking a few measurements on the photograph of the drop, provided the other parameters are known. Some of the main advantages of this method are -

- 1 The results are independent of the angle of contact and hence there is no influence of the solid in contact with the liquid crystal.
- 2 The results are not influenced by the viscous drag as it is a static method.
- 3 Measurements can be made without disturbing the surface physically.

The apparatus was designed and constructed with great care taking into account the various factors that have to be borne in mind in order to observe the true behaviour of the γ - T characteristics of liquid crystals. Capillary tubes with perfectly circular cross sections were selected for the drop formation. The drop **was** formed inside a massive air-tight copper chamber which was filled with pure and dry nitrogen. As the chamber was air-tight the thermodynamic equilibrium of the liquid crystal drop with its vapour was ensured. The experiment was carried out by taking

photographs of a single drop at different steady temperatures after ensuring that the drop was in perfect static equilibrium. It was necessary to wait for about 30 minutes to attain a steady temperature. Before taking the photograph, it was ascertained visually that the drop was stationary for at least 15 minutes and also that the temperature was constant during this interval. A complete experiment on a single drop, wherein photographs were taken at about 25 different temperatures took about 20-24 hours. In some cases, where the measurements were done over a wide range of temperature, the duration of the experiment was about 48 hours.

The experimental set up was earlier checked thoroughly for getting reliable results by measuring the surface tension of water and benzene. The results obtained were within 1% of the standard reported values. Hence the accuracy of the present measurements is reckoned to be within this limit.

The values of γ were calculated from We photographs using the method adapted by Andreas et al.¹⁵ and improved by Ryong Joon Roe et al.¹⁶ By considering the excess of pressure inside the pendant drop, Bashforth and Adams¹⁷ have derived the fundamental equation which defines the shape of the drop. Based on this equation, Andreas et al found out a method for the calculation of γ . They have shown that γ can be calculated using the equation

$$\gamma = \frac{\rho g d_e^2}{H}$$

where ρ is the density of the liquid forming the drop, d_e is the maximum or equatorial diameter of the drop., g is the gravitational acceleration and H is a factor which depends on the drop shape. The drop shape is defined by a ratio $S = d_s/d_e$, where d_s is the diameter at a height equal to d_e from the vertex of the drop. A table of S vs. $1/H$ can be prepared by numerical integration of the fundamental equation which defines the drop shape.

Ryong Joon Roe et al improved the method of calculation by constructing five tables of S vs. $1/H$ by defining five ratios $S_n = d_n/d_e$ ($n = 8, 9, \dots, 12$) which characterise the drop shape. Here, d_n are the diameters of the drop at heights $z_n = \frac{n}{10} d_e$ from the vertex of the drop. For a particular drop, the different values of S_n should give same value of $1/H$ provided the drop is in static equilibrium at the time of taking the photograph. Hence while calculating γ from the photographs, only those photographs were considered, for which the difference in $1/H$ values was within 1%. Others were discarded. Actually very few photographs had to be discarded like this. The diameters on the photographs were measured carefully using a comparator with which an accuracy of 0.001 mm could be achieved.

In this way γ - T characteristics of five nematic and two smectic A compounds were studied.

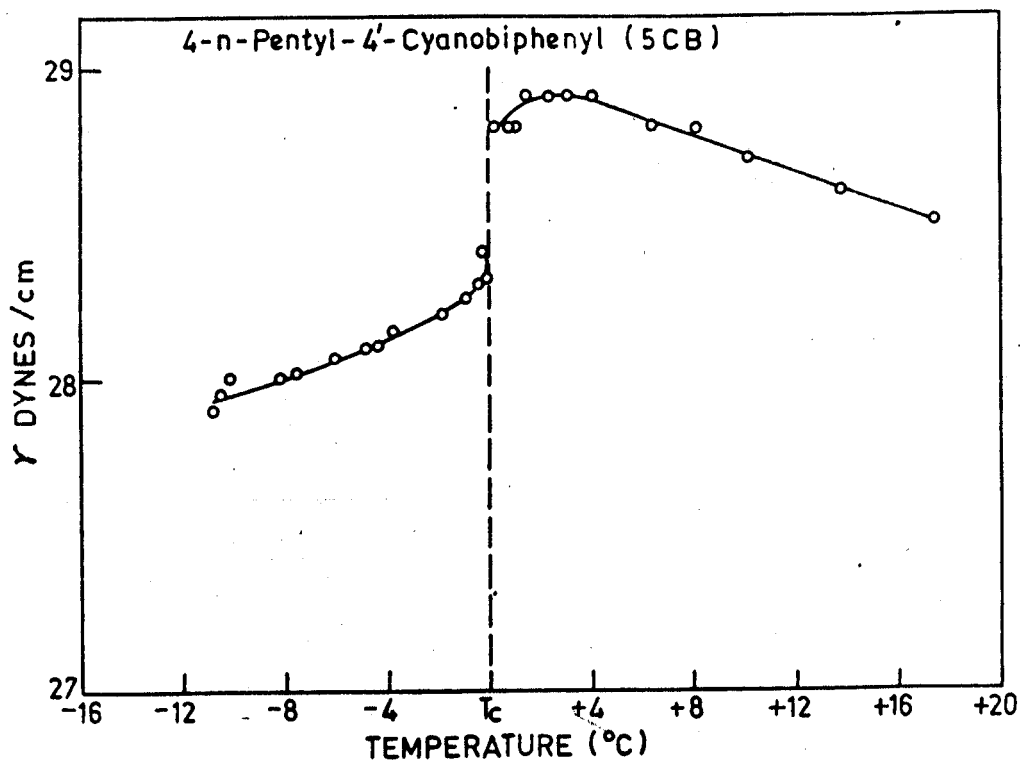
In chapter IV we report the results obtained on five nematic liquid crystals - (i) p-azoxyanisole (PAA), (ii) p-azoxyphenetole (PAP), (iii) anisaldazine, (iv) 4-methoxybenzylidene-4'-butylaniline (MBBA) and (v) 4'-n-pentyl-4-cyanobiphenyl (5CB). In all the five cases experiments were repeated and reproducible results were obtained.

In the first four cases we observe a positive slope in the γ -T characteristics in the vicinity of the N-I transition. In the case of 5CB, we observe a positive slope throughout our range of measurements (about 12° prior to T_{NI}) in the nematic phase. The positive slope persists for a certain range of temperature in the isotropic phase also. We find that the γ -T curves obtained by Ferguson and Kennedy² for PAA, PAP and anisaldazine are similar to the curves obtained in the present investigations. A recent investigation of the γ -T curve for PAA by Brown and Mann¹⁸ who used the light scattering technique also agrees well with our

results. Similarly a recent γ -T curve obtained for 5CB by Gannon and Faber⁹ using the Wilhelmy plate method is very closely similar to the one obtained by us for this compound (Figure 1 & 2).

Our results are in qualitative agreement with the theoretical predictions of Croxton and Chandrasekhar and also of Parsons. As our experiments were conducted under thermodynamic equilibrium and as the results are free from the influence of viscosity and angle of contact, the results unambiguously indicate the development of excess orientational order at the free surface of nematogens. In some cases it develops near the N-I transition point and in some other cases it develops much earlier in the nematic phase. In most of the cases it persists in the isotropic phase also for a certain range of temperature.

In chapter V we report the results obtained for two smectic liquid crystals: (i) n-p-cyanobenzylidene-p-n-octyloxyaniline (CBOOA) and (ii) ethyl-p-azoxybenzoate.



In both the cases experiments were repeated and reproducible results were obtained. After the early efforts of Jaeger,¹ there was no other successful measurements of γ in the smectic phase. Schwarte and Moseley⁴, later Churchill and Bailey⁸ as also Gannon and Faber⁹ found that they could not get reproducible results in the smectic phase. Hence our success clearly indicates the superiority of the pendant drop method in dealing with highly viscous liquids.

In the γ -T characteristics of both the compounds we observe a positive slope throughout the smectic phase and also for a certain range of temperature in the isotropic phase also. These results are in very good agreement with the theoretical expectations.¹⁴

In the last chapter we describe the experimental studies made on the optical reflectivity of the free surface of two nematogens - (i) 4'-n-pentyl-4-cyano-biphenyl (5CB) and (ii) 4'-n-heptyl-4-cyanobiphenyl (7CB)

in the isotropic phase, which provides a direct evidence of the existence of a surface orientational order.

The principle of the method is illustrated by a simple model consisting of a layer of homeotropically aligned molecules of thickness τ on the isotropic bulk liquid. It can be shown that the optical reflectivity (R_0) of such a layer increases as the thickness of the surface layer (τ) decreases and assumes the maximum value at $\tau = 0$. The experimental results for both the compounds show that the reflectivity (R) increases as the temperature increases above T_{NI} and assumes a steady value at about 1°C above T_{NI} before it starts decreasing slightly probably due to (f) the increased thermal fluctuations of the surface and (ii) the decreasing value of the refractive index.

A qualitative comparison of the experimental and the theoretical results clearly indicates the existence of an ordered layer at the free surface in

the isotropic phase whose thickness decreases as the temperature increases. A quantitative comparison of the results is not **significant** here as the model assumed is oversimplified, We hope to improve the technique of the experiment as well as to develop a more realistic model before we try to draw quantitative conclusions.

The results reported in chapters IV and V have been published in the following papers.

- 1 Experimental determination of the surface tension of nematic liquid crystals (S. Krishnaswamy and R. Shashidhar). **Int. Liquid Crystals Conf.**, Bangalore, December 9 1973, **Pramana Suppl. No.1**, p.247.
- 2 Experimental studies of the surface tension of nematic liquid crystals. (S.Krishnaswamy and R.Shashidhar) - **Mol.Cryst.Liq.Cryst.** 35, 253 (1976).
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