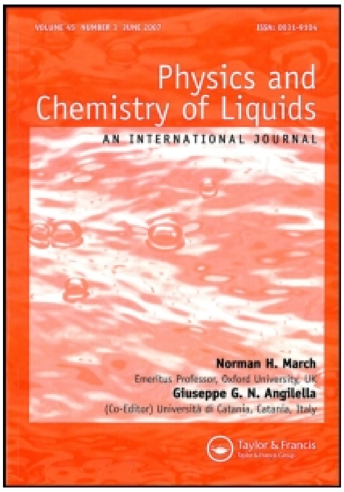

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Pre-Transitional Surface Ordering and Disordering at Liquid Crystal-Isotropic Liquid Interface

A. K. George[a]; K. P. Mohandas[b]
[a] Department of Physics, College of Science, Sultan Qaboos University, Muscat, Sultanate of Oman [b] Chemical Engineering Department, College of Engineering, Kerala, India

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PRE-TRANSITIONAL SURFACE ORDERING AND DISORDERING AT LIQUID CRYSTAL-ISOTROPIC LIQUID INTERFACE

A. K. GEORGE

Department of Physics, College of Science, Sultan Qaboos University,
P.O. Box 36, Al Khodh Postal Code 123, Muscat, Sultanate of Oman

K. P. MOHANDAS

Chemical Engineering Department, College of Engineering,
Trichur 9, Kerala, India

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The existence of pre-transitional surface ordering and disordering at the liquid crystal-isotropic liquid interface has been established from the surface tension measurements. A spinning-drop technique has been used for this study. Measurements were carried out in the smectic $A(S_A)$, nematic (N) and isotropic (I) phases of the liquid crystals and reproducible results were obtained. The results suggest that the equilibrium value of γ changes discontinuously in the N and S_A phases. The slope $d\gamma/dT$ is positive for both the isotropic phase just above T_{NI} as well as for the nematic phase just below it. Similar positive slope has been obtained in the vicinity of T_{AN}. A positive value of $d\gamma/dt$ implies excess surface order than that of the bulk interior. From the density measurements it has been observed that there is a correlation between the anomalies in the temperature dependence of surface tension and density in the isotropic phase.

KEY WORDS: Liquid crystals, surface order, interfacial tension.

1. INTRODUCTION

The orientation of one anisotropic phase by another has been known for several years and when the two phases are solid crystals this phenomenon is known as *epitaxy*. Since the solid crystals are characterised by the long range positional order, which are difficult to propagate, monocrystalline solid phases can be obtained by epitaxial growth only under restricted conditions. Liquid crystals on the other hand, combine liquid-like properties due to the absence of three-dimensional positional order and crystal-like properties due to orientational order. This order is easy to propagate and as a result, surface orientational effects are easy to obtain in liquid crystals. Understanding the orientational ordering induced in a liquid crystal film by various substrate treatment is of crucial importance for technological applications. Of special importance with regard to applications in displays is the surface order induced by a solid substrate which can be varied by suitable physico-chemical treatments.

Near the surface, liquid crystals often exhibit specific structures. In the isotropic phase of a liquid crystal, theory predicts the formation of a boundary layer with nematic order, which increases in thickness on approaching the transition temperature T_c[1]. Temperature dependent studies performed in the isotropic phase of liquid crystals using birefringence measurements[2] and evanescent-wave as well as reflection ellipsometric techniques[3-5] confirm a strong increase in order on approaching T_c. Further the growth of nematic or smectic phase at the free surface of liquids which are isotropic in the bulk phase also has been demonstrated by earlier investigators[6-8].

The liquid crystal surface has been the subject of several theoretical and experimental investigations, but as yet there is no consensus about the nature of the order close to the surface. Molecular theories of liquid crystals are not refined enough to make predictions on the surface order in specific cases: there are models which allow for more as well as less order[1,9-15]. Experiment also suggests that sometimes there is excess[6,10,17-19] and sometimes deminished[17,20] surface order.

Though there has been numerous reports of surface tension measurements when the liquid crystal is in contact with a solid or gaseous surface, there appears to have been only few studies to measure the interfacial tension at liquid crystal-isotropic liquid interface. Remarkable anomalies were reported in surface tension near the transition temperature of polymesomorphic liquid crystals by Lavrentovich and Tarakhan[21] when the liquid crystal is in contact with an isotropic liquid. Similar results were reported by the present authors[22,23] from their study of nematic and polymesomorphic liquid crystals. The problem of interfacial properties of liquid crystals at the interface with another isotropic liquid is a rich one, with much experimental work yet to be done. Recently it was reported that there exists a correlation between anomalies in the temperature dependences of surface tension and the density for the isotropic phase of liquid crystals[24]. In the light of this we are reporting here the density as well as the interfacial tension of two liquid crystals.

Chemical stability of compounds is of great importance when surface tension measurements are in view, since the impurities that are surface active can greatly affect this parameter. Cyanobiphenyl liquid crystals are known to be more stable than most other liquid crystals and as a result they are less likely to undergo chemical changes during use and accumulate impurities. In view of this we have chosen two cyanobiphenl liquid crystals, M_{21} with nematic phase and M_{24} with nematic and smectic A phases. Both liquid crystals were supplied by M/s BDH Chemicals (UK) and were used without further purification.

2. EXPERIMENTAL DETAILS

Details of the experiment and the subsequent calculation of surface tension using a spinning-drop technique was described in an earlier communication[22]. However, we are describing here very briefly the experimental set-up. A spinning-drop technique described by Cayias *et al.*[25], in which the surface tension is evaluated by measuring the shape of a drop of liquid (liquid crystal in our case) in a more dense liquid contained in a rotating horizontal tube, is used for the present investigation. A hysteresis synchronous motor whose speed can be controlled by varying the frequency from a frequency generator was used for rotating the horizontal tube containing the liquid crystal sample. The rotational stability was one part in 10^5 as determined by a period averaging counter stable to one part in 10^8. A Gaertner travelling microscope with filar eyepiece was used to measure the length and width of the drop. This enables measurement to be done to an accuracy of 1 in 10^3. The tube housing and the assembly was designed to accept a precision ground glass tube rounded at one end and sealed against a rubber septum on the other. A glass cell enclosed the apparatus to permit temperature studies. Temperature was controlled to $\pm 0.1°C$ during measurement. Careful loading of the sample was essential to avoid formation of air bubbles inside the tube. This was particularly essential in the present case since the two liquid crystals studied here are in solid form at room temperature. In view of this, the tube was first filled with glycerine and was heated to a temperature near to T_{NI}. The liquid crystal in its nematic form was then injected into the tube using a pre-heated syringe.

Measurements reported in the paper were those taken while cooling. However, readings were rechecked randomly at every point, either on heating or cooling, and in all cases very little variation was observed. An accuracy within the limit of 0.15% was obtained when the measured value of interfacial tension at benzene-water interface using the above technique was compared with the literature values[26].

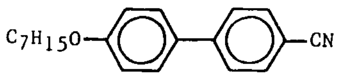
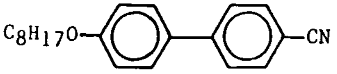
The density measurements were made using a pycnometer which was made from one piece of precision bore capillary that had a sample chamber fromed on it by blowing a bubble at one end of the tube. Once the sample chamber was formed, the piece was bent into a U-tube and a fiducial mark was scratched on the capillary about 1cm above the sample chamber. The pycnometer used had a volume of about 2.5 ml. Temperature studies were carried out by immercing the pycnometer in a bath whose temperature was controlled to $\pm 0.1°C$ using a HAKE D8 thermostat. The liquid height in the pycnometer was measured using a cathetometer, the precision of the total height measurements was generally 0.001 cm. The pycnometer was calibrated using freshly boiled, deionized water. The precision in measuring the density is reckoned to be $\pm 10^{-4}\,\mathrm{g\,cm^{-3}}$.

3. RESULTS

The structure of the two liquid crystals and their transition temperatures obtained by thermal microscopy are given in Table 1.

Thermal variation of surface tension at the liquid crystal-isotropic liquid interface are given in Figures 1–3. In Figure 1 we have plotted γ against temperature (T) for M_{21}. For better clarity γ–T characteristics of M_{24} are presented as two figures. Figure 2 shows the γ-T characteristics of M_{24} in the vicinity of T_{NI} while in Figure 3 the same parameters are shown in the vicinity of T_{AN}. In all cases discontinuities were observed near T_{AN} and T_{NI} along with considerable pre-transitional anomalies.

Table 1 Structure and transition temperature of liquid crystals, M_{21} and M_{24}.

Liquid Crystal	*Chemical Formula*	*Melting Point* T_M/°C	S_A–*N Transition Temperature* T_{AN}/°C	*N–I Transition Temperature* T_{NI}/°C
M_{21}		54.0	-	74.0
M_{24}		54.5	67.0	80.0

A maximum in surface tension was observed near T_{NI} for M_{21} and M_{24}, but in both cases slightly above T_{NI}. In the nematic phase surface tension decreases with decreasing temperature except in the vicinity of T_{NI} where it drops after showing a maximum (Figs. 1 and 2). It may also be noted that in the isotropic phase far form T_{NI}, the liquid crystal behaves like a normal liquid. However, slightly above the point where γ drops after reaching a peak value near T_{NI}, it shows a tendency to increase again. In the case of M_{24}, the variation of the surface tension with temperature in the vicinity of T_{AN} is analogous to that observed at T_{NI}, with a peak slightly above T_{AN} (Fig. 3). However, it may be noted that the increase in surface tension near T_{AN} is slightly lower than that observed near T_{NI}.

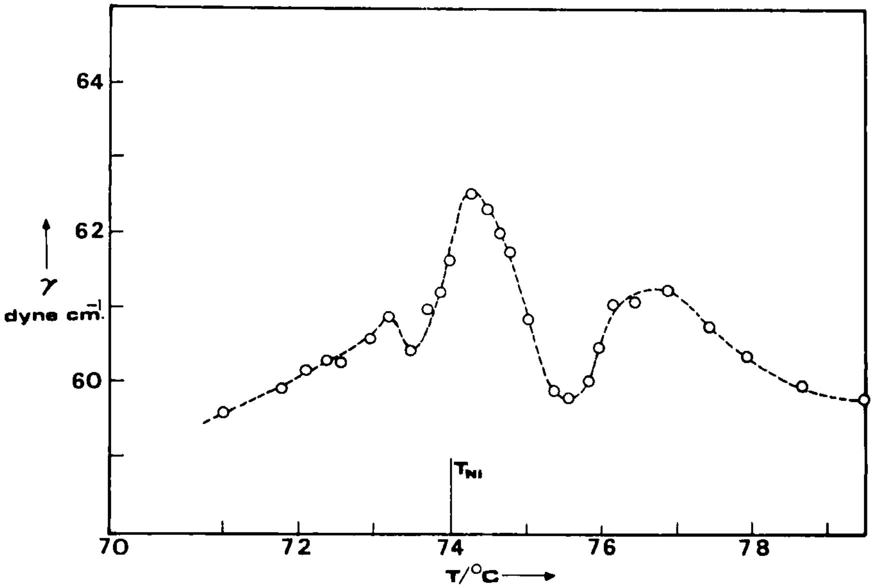


Figure 1 Temperature dependence of surface tension (γ) at M_{21}-glycerine interface. T_{NI} is the nematic-isotropic transition temperature.

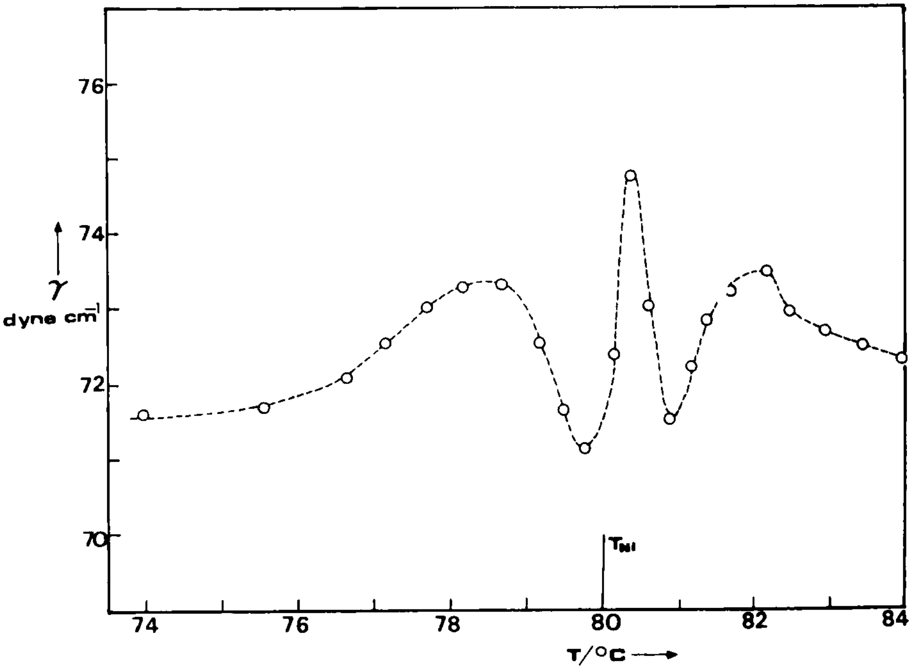


Figure 2 Temperature dependence of surface tension (γ) at M_{24}-glycerine interface in the vicinity of nematic-isotropic transition temperate, T_{NI}.

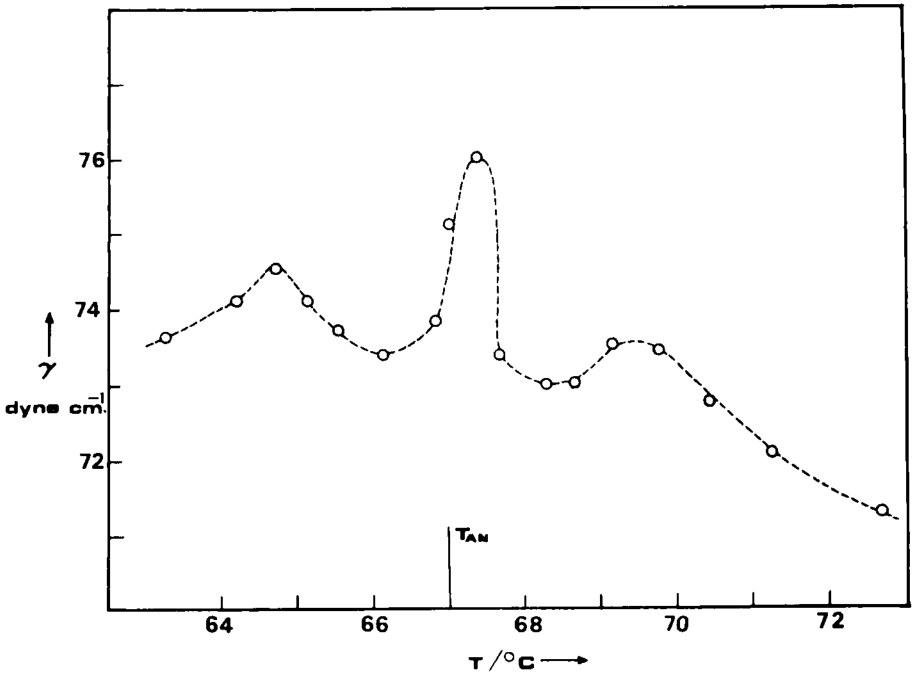


Figure 3 Temperature dependence of surface tension (γ) at M_{24}-glycerine interface in the vicinity of smectic A-nematic transition temperature, T_{AN}.

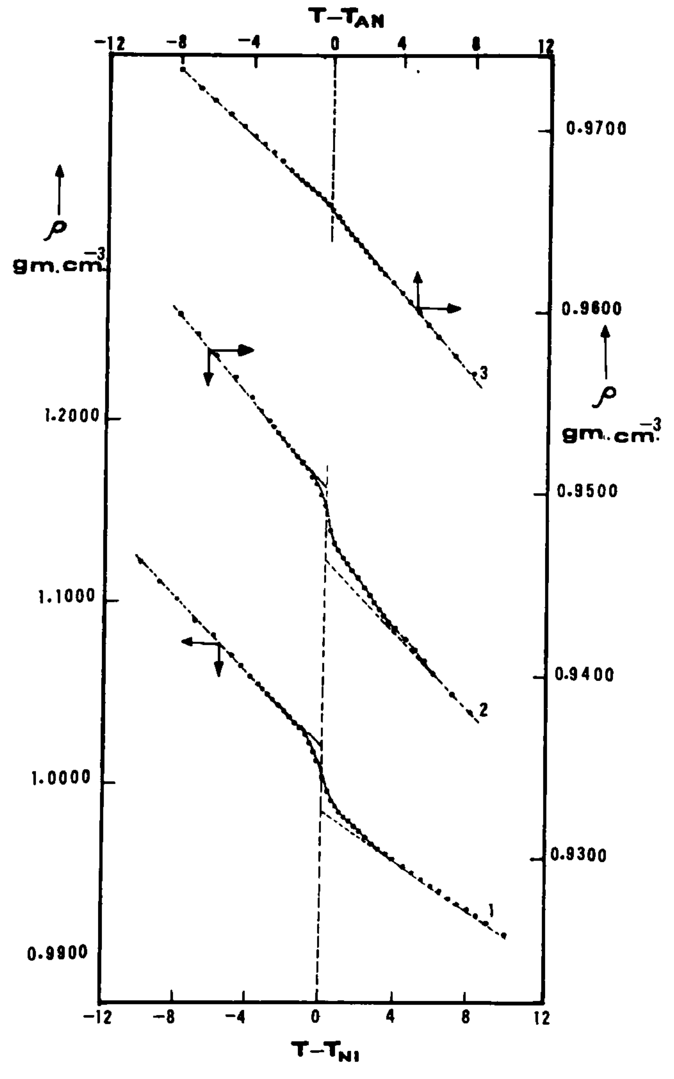


Figure 4 Temperature dependence of density. Curves 1 and 2 are for M_{21} and M_{24}, respectively, near the nematic-isotropic transition, while curve 3 is for M_{24} near smetic A-nematic transition.

Overall results for the density versus temperature for the two liquid crystals are presented in Figure 4. With increase in temperature the density shows a slow decrease in the nematic phase and drops abruptly at the *N-I* transition (Fig. 4, curves 1 and 2). The density data shows considerable pre-transitional effects. No sudden change was observed at S_A-N transition, but the density data in the two phases are characterised by a change in slope (Fig. 4, curve 3).

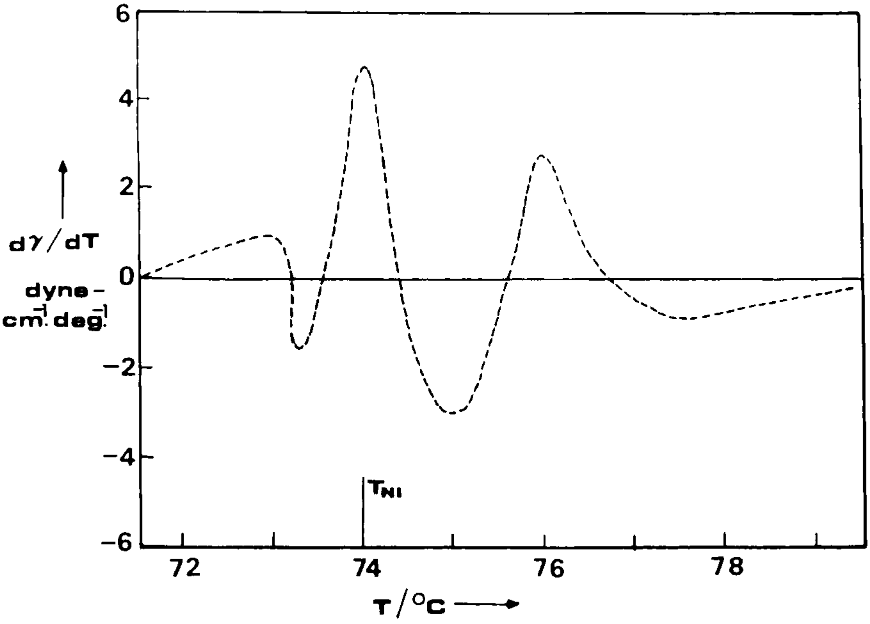


Figure 5 $d\gamma/dT$ in the vicinity of T_{NI} for M_{21}.

4 DISCUSSION

A close look into the nature of the two phase transitions involved, *viz.*, N–I and S_A–N may be useful at this stage. The N–I transition involves the growth of the long-range orientational order of the nematic phase from disordered isotropic phase and this is established as a first-order transition with no controversy about the nature of the transition. The S_A–N transition involves the growth of one dimensional translational ordering in addition to the long-range orientational ordering present in the nematic phase. In the molecular model of McMillan[27] an important parameter which decides the order of the transition is the ratio $r = T_{AN}/T_{NI}$. The transition is second-order for $r > 0.87$; first-order for $r > 0.87$; $r = 0.87$ corresponds to the tricritical point. In the present case, $r = 0.84$ for M_{24} which suggests that the S_A–N transition is second-order.

The well known Maxwell relation

$$\frac{d\gamma}{dT} = -\left(\frac{\partial S}{\partial A}\right)_T = -\sigma \qquad (1)$$

where S is the entropy, γ is the surface tension and A is the surface area, shows that when $d\gamma/dT$ is positive, the surface entropy per unit area, σ, is negative in which case the liquid crystal must be in some way more ordered near the surface than the interior. In view of this we have taken the slope of the γ–T curve at different

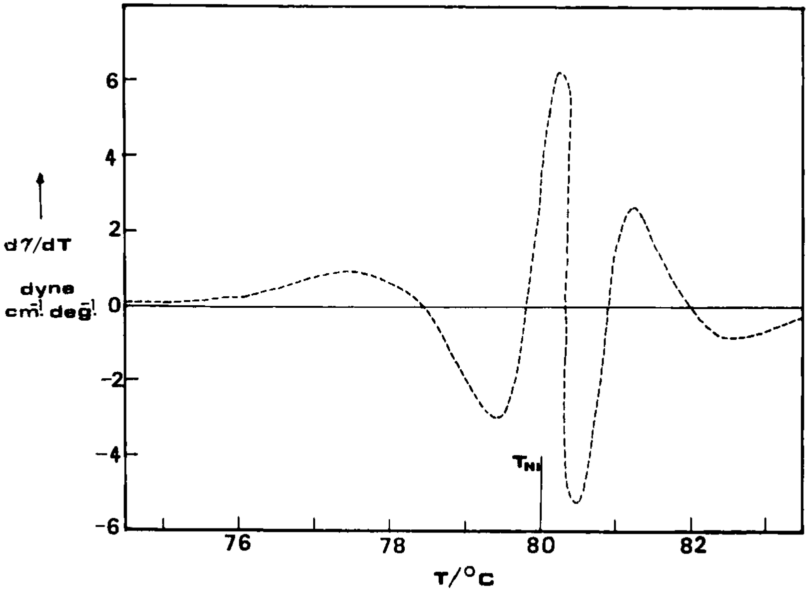


Figure 6 $d\gamma/dT$ in the vicinity of T_{NI} for M_{24}.

temperatures. In Figures 5 and 6, $d\gamma/dT$ is plotted against temperature near T_{NI} for M_{21} and M_{24}, respectively. In Figure 7, the same parameters are plotted in the vicinity of T_{AN} for M_{24}. Careful consideration of these figures reveal that $d\gamma/dT$ is positive in the vicinity of both T_{AN} and T_{NI} which indicates that the surface region is

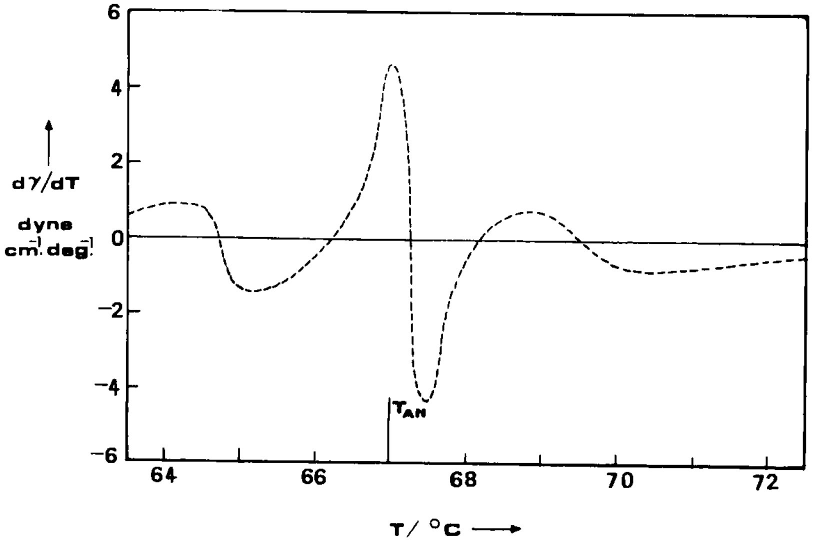


Figure 7 $d\gamma/dT$ in the vicinity of T_{AN} for M_{24}.

more ordered than the bulk interior as the transition is approached. It may be argued, as speculated by Gannon and Faber[6] that the increased order might be due to the orientational order parameter

$$Q = \langle P_2(\cos\theta)\rangle \tag{2}$$

taking some value Q_1 at the surface which is greater than its value Q_o in the interior.

A cyanobiphenyl liquid crystal molecule is composed of a hydrophilic polar (cyano) head group and a hydrophobic alkyl tail group. Such liquid crystal molecules in the bulk form pairs with polar groups pointing antiparallel to each other[28]. However, the introduction of a surface limiting the nematic phase creates a perturbation of the structure near the interface due to the symmetry breaking induced by the surface. The nematic phase which is characterised by the translational invariance is broken by the presence of the surface and as a result the centre of mass of the molecules near to the surface may have a tendancy to be located in a plane parallel to the surface. Due to the intermolecular interactions the existence of this layer favours the formation of many layers similar to this. The presence of a surface is thus likely to induce a positional order of the molecules at the interface between a nematic liquid crystal and another phase and also the interface between a nematogen in the isotropic phase and another phase. When the molecules are perpendicular or tilted with respect to the layer plane the order existing at the interface is that found in the smectic phase. This order is characterised by the superposition of nematic-like orientational order and a positional order in which the molecules form successive layers. Experimental techniques which are sensitive to the position of the molecules are essential to study the surface induced positional order. X-ray reflectivity measurements which is the most suitable method for this study gave an ambiguous proof for the existence of smectic order at the free surface of 8OCB liquid crystal, both in the nematic and isotropic phases[29].

In the region of the transition temperature T_{NI}, $d\gamma/dT > 0$ (Figs. 4 and 5) for both the liquid crystals M_{21} and M_{24}. Although γ values drops after reaching a peak value slightly above the transition, the anomalous behaviour with positive slope is preserved in the isotropic phase above T_{NI} to some temperature T_f. The width of this interval for both the liquid crystals investigated is around 3–4 K. Similar behavior was predicted by Tjipto–Margo *et al.*,[1] in the isotropic phase of nematic liquid crystals. These results compare favourably with that of Lavrentovich and Tarakhan[21] where they measure the interfacial tension of 5OCB and 8OCB liquid crystals at glycerine interface.

Density data also reveals a striking correlation: in the $\rho(T)$ curve the pretransitional anomalies in the isotropic phase persists roughly to the same temperature T_f (Fig. 4, curves 1 and 2). Thereafter the density decreases linearly with increasing temperature. Such a correlation between anomalies in the temperature dependence of surface tension and density for the isotropic phase has been reported by Yu. Ivlev *et al*[24]. They explained the anomalous behaviour of density by considering the fluctuations of the order parameter in the isotropic phase. This lead to a relative increase in the density and with rise of temperature a more rapid decline. When $T = T_f$ the correlation radius becomes comparable with the dimensions of the molecules, and therefore at higher temperatures this mechanism does not operate.

Finally, our results do not consider the role of elastic effect in the secondary instabilities in the liquid crystal-isotropic interface. It has been shown that some instabilities are always present, whatever the liquid crystal chosen and the sample thickness[30]. The extend to which these may affect our results is not known since there is no availbale data for the liquid crystal under study for comparison, particularly with the technique under consideration . However, the data available in the literature[21,24] for other liquid crystals using other techniques compare favourably with that of ours, which may indicate that these instabilites do not contribute significantly to the final result.

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