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Abstract. A spinning-drop technique was used to study the thermal variation in the surface tension at a liquid crystal–isotropic liquid interface. A polymesomorphic liquid crystal with nematic and smectic A phases bounded by an isotropic liquid (glycerine) was used for the present study. The surface tension–temperature characteristics, unlike the monotonically decreasing dependence found in most isotropic liquids, showed regions with a positive slope for both the smectic A and the nematic phases. A sharp increase in slope of the surface tension–temperature characteristic was observed near the smectic A–nematic and nematic–isotropic transition temperatures, indicating that excess surface order is developing near these transitions. The observed results are in compliance with the available theoretical predictions.

1. Introduction

Liquid crystals are used in liquid crystal displays (LCDs) and their surface properties play an important role in the working process of the display cells. When a liquid crystal is placed in contact with another phase (solid, liquid or gas), a surface is created whose characteristics may have a profound difference from those of the bulk interior. Surface effects in liquid crystals have mainly been studied in nematics. The reason for this is the simplicity of their structure—the local order aligning the molecules parallel to each other can extend to a macroscopic scale. This is not the case in all mesophases; when a phase shows two different kinds of order, namely microscopic and macroscopic, the surface effects are much more complex.

As the name indicates, liquid crystals exhibit characteristics which are common to isotropic liquids and crystalline solids. This ambivalence is apparent even in the surface characteristics of these systems. This leads to a great diversity of phenomena which may be classified into the following three types (Jérôme 1991). The first concerns the perturbation of the liquid crystalline structure close to the surface. Beyond this transition region, the bulk liquid crystalline structure is recovered with an orientation which is fixed by the surface; this phenomenon of the orientation of liquid crystals by surfaces is the so-called *anchoring*. Finally, close to the bulk phase transitions, critical adsorption or wetting can occur at surfaces, as is seen in isotropic systems.

Since the pioneering work by Schenck (1898) and Jaeger (1917) there have been numerous reports of surface tension measurements on liquid crystals (Ferguson and Kennedy 1938, Naggiar 1943, Schwarz and Moseley 1947, Gorskii and Sakevitch 1968, Churchill and Bailey 1969, Langevin and Bouchiat 1972). This area has also attracted an enormous amount of theoretical work. Several theories, which nearly all consider a sufficiently strong coupling between orientational and translational degrees of freedom, predict an excess orientational order at the surface (Parsons 1976, Rosenblatt and Ronis 1981, Kimura and Nakano 1985, Hoylst and Poniewierski 1988, Tjipto-Margo and Sullivan 1988). However, experimental evidence for this is rather conflicting. By means of experimental surface tension measurements, excess orientational order was found near the nematic–isotropic (N–I) transition temperature T_{NI} at the free surface of p-azoxyanisole (PAA) (Neumann *et al* 1974, Krishnaswamy and Shashidhar 1976), p-cyanobenzylidene-p'-n-octyloxyaniline (CBOOA) (Krishnaswamy and Shashidhar 1977, Sohl *et al* 1980), 4-n-pentyl-4'-cyanobiphenyl (5CB) and 4-n-octyl-4'-cyanobiphenyl (8CB) (Gannon and Faber 1978). On the contrary, excess disorder was found at the free surface of anisaldazine (Langevin 1972, Krishnaswamy and Shashidhar 1976).

Most of the works reported on surface tension measurements are when the liquid crystal is in contact with a solid or gaseous surface. It appears that there are only few reports of surface tension measurements at the liquid crystal–isotropic liquid interface. Lavrentovich and Tarakhan (1986) reported the interfacial tension of a liquid crystal with smectic A, cholesteric and blue phases bounded by an isotropic liquid. Later, they (Lavrentovich and Tarakhan 1990) extended their studies to two liquid crystals: 4-n-pentyloxy-4'-cyanobiphenyl (5OCB) with the nematic phase and 4-n-octyloxy-4'-cyanobiphenyl (8OCB) with the nematic and smectic A phases. Similar studies were reported by Mohandas and George (1992) for two cyanobiphenyl nematic liquid crystals E_7 and E_8. In all cases, anomalies were reported near each of the phase transitions.

Despite the great progress which has been made in recent years in the study of liquid crystals, the surface properties of these materials appear to be relatively less understood. In view of this we report here the surface tension measurements of a polymesomorphic liquid crystal K_{24} (BDH Chemicals, UK) with the nematic and smectic A phases bounded by an isotropic liquid (glycerine). The N–I transition temperature T_{NI} and the smectic A–nematic (S_A–N) transition temperature T_{AN} found by thermal microscopy were 40.5 °C and 33.5 °C, respectively.

2. Experimental details

The spinning-drop technique described by Cayias *et al* (1975) was used for the present investigation. This method involves evaluating the interfacial tension by measuring the shape of a drop of liquid (liquid crystal) in a more dense liquid contained in a rotating horizontal tube. A hysteresis synchronous motor whose speed can be controlled by varying the frequency from a frequency generator was used to rotate 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. The stability of the liquid crystal drop contained in the horizontal tube determines the rotational speed. Generally the best accuracy is obtained when the speed is so adjusted that the drop is 0.5–1 cm in length depending on the width. A Gaertner

travelling microscope with filar eyepiece was used to measure the length and width of the drop. This enables the measurement to be done to an accuracy of 1 in 10^5. The tube housing and the assembly were designed to accept a precision-ground Pyrex glass tube rounded on one end and sealed against a rubber septum on the other. A glass cell enclosed the apparatus to permit temperature studies. Thermostatting of the system to $\pm 0.1\,°C$ was obtained. Measurements were repeated at least three times at each temperature to ensure reproducibility.

Details of the measurement and the subsequent calculation of the surface tension from the drop profile have been discussed in an earlier communication (Mohandas and George 1992). The density data which were needed for the calculation were available from earlier work (George 1991). To test the accuracy, the interfacial tension of the benzene–water system was measured at 20 °C and the results when compared with the values in the literature (Adamson 1967) show that an accuracy within the limit of 0.15% was obtained.

3. Results

The thermal variation in the surface tension at the liquid crystal–isotropic liquid interface is given in figure 1. The surface tension values reported here are those taken while cooling. However, readings were rechecked randomly at every point, on either heating or cooling, and in all cases very little variation was observed. Nevertheless, the nature of the curve reported here shows the general characteristics of the liquid crystal.
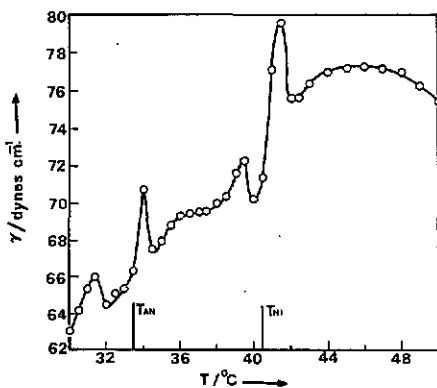

Figure 1. Temperature dependence of surface tension γ at the K_{24}–glycerine interface. T_{AN} and T_{NI} are the S_A–N and the N–I transition temperatures respectively.

Sharp increases in the surface tension are observed near T_{NI} and T_{AN}, in both cases slightly above the transition temperatures. However, the increase near T_{AN} is smaller than that observed at T_{NI}. In all other regions in the mesomorphic phase the surface tension increases with increasing temperature except slightly below T_{AN} and T_{NI} where it drops after reaching a peak value. In the isotropic phase, slightly above the transition temperature, the surface tension shows a tendency to increase with increasing temperature. However, far above T_{NI}, as in most isotropic liquids, the surface tension decreases with increasing temperature.

4. Discussion

Before going into the details of the anomalous surface tension–temperature $\gamma(T)$ characteristics it may be worth examining the possibility of realignment of molecules near the surface as the temperature changes. The orientation of molecules arises mainly from the changes in density and order in the interface. There are a few reports on the surface studies on different types of liquid crystal. Bouchiat and Langevin (1971) studied the alignment of molecules at the free surface of two nematic liquid crystals, PAA and p-methoxybenzylidene-p'-n-butylaniline (MBBA). In PAA the molecules are found to be parallel to the surface and the alignment is independent of temperature. In MBBA the molecules are inclined at an angle of about $75°$ to the surface and the tilt angle varies only slightly with temperature. Lavrentovich and Tarakhan (1986) observed that the cholesteryl pelargonate molecules are aligned parallel to the interface regardless of temperature in the cholesteric and smectic A phases. The present authors in a previous communication (Mohandas and George 1992) found no specific changes in the surface alignment of molecules with temperature in two liquid crystals which they have studied. In view of the above, we assume that the anomalous $\gamma(T)$ characteristics cannot be attributed to the alignment effects at the interface.

The thermodynamics of the two phase transitions S_A–N and N–I are well understood for the liquid crystal K_{24}. From the ultrasonic velocity and specific volume studies, George (1991) has concluded that the N–I transition is first order while the S_A–N transition is second order. It is seen that $T_{AN}/T_{NI} = 0.83$ for K_{24}, which is below the value of $T_{AN}/T_{NI} = 0.88$ predicted to be necessary for a first-order phase transition (McMillan 1973, Meyer and McMillan 1974). This further substantiates the fact that the S_A–N transition in K_{24} is second order.

It is reasonable to assume that in going from an ordered state to a less ordered state (from smectic A to nematic or from nematic to isotropic) the surface energy increases, reflecting an increase in disorder. These changes may be shown as an increase in surface tension as the transition temperature is approached. In our case the surface tension increases near to both T_{AN} and T_{NI}. The behaviour near T_{NI} was similar to that observed by Krishnaswamy and Shashidhar (1976, 1977) as well as previous work by the present authors (Mohandas and George 1992). The $\gamma(T)$ characteristic at the S_A–N transition is relatively less understood and the results that are available are conflicting. Gannon and Faber (1978) have reported a discontinuity in γ at T_{AN} but do not claim any reproducibility for their results. Sohl et al (1980) have reported that the surface tension increases as T_{AN} is reached. Lavrentovich and Tarakhan (1990) have reported a peak in γ at the S_A–N transition temperature. Our results, as expected, show an increase in γ near T_{AN}. However, it may be noted that the increase in γ near T_{AN} is smaller than that observed near T_{NI}, and this may depict the different nature of the phase transitions involved. Further the peaks in γ are observed at a temperature slightly above both T_{AN} and T_{NI}. This discrepancy may be attributed to the presence of minute impurities. Further, although the two liquids are immiscible, the possibility of very slow chemical degradation of the sample cannot be ruled out. Similar difficulties in which the discontinuities were observed slightly below or above the transition temperatures were experienced by previous workers carrying out surface tension measurements (Gannon and Faber 1978, Krishnaswamy and Shashidhar 1976, 1977). Nevertheless, we believe that the discontinuities observed here, although slightly above T_{AN} and T_{NI}, are associated with the phase transitions.

Croxton and Chandrasekhar (1975) by extending the theory of simple liquids have discussed the statistical thermodynamics of the nematic surface. According to them the slope of the $\gamma(T)$ characteristic is related to the excess entropy per unit area as

$$d\gamma/dT = -(S_1 - S_0) \tag{1}$$

where the subscripts 1 and 0 refer to the surface and bulk states, respectively. It is evident from the above equation that, should a situation where $S_1 < S_0$ arise corresponding to a relatively ordered surface state, the $\gamma(T)$ characteristics may show a positive slope. However, thermal delocalization of the liquid surface with increasing temperature will inevitably result in progressive disordering, and the usual monotonic decreasing form of $\gamma(T)$ may be regained corresponding to $S_0 < S_1$. Liquid crystals are likely to show such positive regions over limited thermal ranges (Croxton and Chandrasekhar 1975).

One way to check whether the liquid crystal surface is more ordered or disordered than the bulk is to observe the sign of the jump in the surface tension observed at the phase transition. Another way is to check the sign of $d\gamma/dT$, the slope of the $\gamma-T$ curve. If $d\gamma/dT$ shows a positive slope around the transition temperature, then excess order is found at the surface whereas a negative $d\gamma/dT$ corresponds to excess disorder (Jérôme 1991). With this in mind we have taken the slope of the $\gamma-T$ curve at different temperatures. In figure 2, $d\gamma/dT$ is plotted against temperature in the vicinity of T_{AN}. In figure 3 the same values are plotted in the vicinity of T_{NI}. Careful consideration of figures 2 and 3 reveals that there are two regions showing a positive slope in both the smectic A and the nematic phases. Near the transitions at both T_{AN} and T_{NI}, the slope is positive and reaches a maximum slightly above both transition temperatures. This indicates that excess surface order is observed near the transition temperatures.
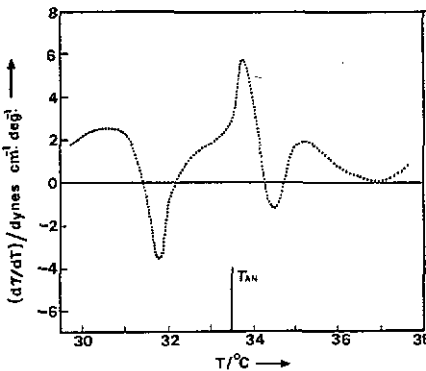

Figure 2. $d\gamma/dT$ against temperature in the vicinity of T_{AN}.

The approximation employed in equation (1) leads to the expression (Horn *et al* 1981)

$$\frac{d\gamma}{dT} \simeq \int_{-\infty}^{+\infty} [\rho(z)\sigma^2(z) - \rho_0\sigma_0^2 + \rho(z)\eta^2(z) - \rho_0\eta_0^2] \, dz \tag{2}$$

where the constants ρ_0, σ_0 and η_0, respectively, are the density of the liquid crystal and the orientational and translational order parameters far from the interface; $\rho(z)$,
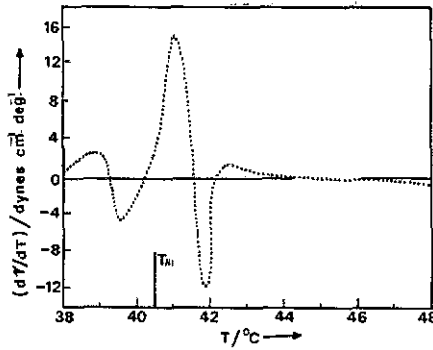
Figure 3. $d\gamma/dT$ against temperature in the vicinity of T_{NI}.

$\sigma(z)$ and $\eta(z)$ are the corresponding values near the interface and depend on the distance z from it. In this expression,

$$\rho(-\infty) = \rho_0 \qquad \sigma(-\infty) = \sigma_0 \qquad \eta(-\infty) = \eta_0.$$

Equations (1) and (2) show that, if the order parameters σ and η near the interface exceed their bulk values σ_0 and η_0, the 'classical' monotonic decrease will be suppressed and $\gamma(T)$ will increase with increasing temperature and should show a positive slope. This is evident from figures 2 and 3.

Several types of ordering are possible at the liquid crystal–glycerine interface. In the smectic A phase with tangential boundary conditions, we expect an additional translational ordering perpendicular to the smectic A layers. The translational order parameter η' will thus vanish in the interior but be non-zero near the surface. The existence of smectic order at the nematic–solid or nematic–air interface has been shown in different experiments: surface tension measurements (Gannon and Faber 1978), structural force measurements (Horn *et al* 1981) and the Freedericksz transition behaviour (Rosenblatt and Ronis 1981). Thus, in the nematic phase, a smectic ordering may persist near the surface ($\eta'' \neq 0$) but vanish in the interior ($\eta_0'' = 0$). In addition to this, a higher degree of surface alignment ($\sigma''(z) \geqslant \sigma_0''$) may also be present.

It may be noted that, at a temperature $T > T_{NI}$ in the isotropic phase, the surface tension initially increases with increasing temperature. Here we are referring to the region above which the discontinuity was observed, which in our case is slightly above T_{NI}. At higher temperatures, $\gamma(T)$ exhibits a normal behaviour associated with a negative $d\gamma/dT$. It was shown for an isotropic–vapour interface that the initial positive gradient $d\gamma_{IV}/dT$ at $T \geqslant T_{NI}$ is a necessary consequence of the approach to complete wetting at T_{NI} (Tjipto-Margo *et al* 1989). Here the subscripts IV refer to the isotropic–vapour interface. This follows from Landau treatment similar to those used in other discussions of wetting (Aukrust and Hauge 1987, Sullivan and Lipowsky 1988) based on analysing the free energy $\gamma_{IV}(l)$ as a function of the order parameter l (equal to the wetting-layer thickness). For large l and temperature close to T_{NI}, $\gamma_{IV}(l)$ should have the asymptotic form (Tjipto-Margo *et al* 1989)

$$\gamma_{IV}(l) \simeq \gamma_{IV}(\infty) + W/l^2 + \Lambda tl \qquad (3)$$

where $t \equiv (T - T_{NI})/T_{NI}$, $\gamma_{IV}(\infty) = \gamma_{NV} + \gamma_{NI}$ evaluated at $T = T_{NI}$, W is the Hamaker constant related to the microscopic van der Waals forces and Λ is essentially

the bulk latent heat of the N–I transition at T_{NI}. Minimization of equation (3) with respect to l gives

$$l_{eq} \simeq (2W/\Lambda)^{1/3} t^{-1/3} \tag{4}$$

and

$$\gamma_{IV}(l_{eq}) \simeq \gamma_{IV}(\infty) + 3W^{1/3}(\Lambda/2)^{2/3} t^{2/3} \tag{5}$$

where $\gamma_{IV}(l_{eq})$ is identified with the equilibrium isotropic–vapour surface tension at $T \geqslant T_{NI}$. Equation (5) shows that γ_{IV} should increase initially with increasing temperature, but the gradient $d\gamma_{IV}/dT$ exhibits a singularity at about $(T - T_{NI})^{-1/3}$. Our results are in compliance with what is expected on the basis of the above equation. However, it may be noted that there are other possible contributions to the free energy of the nematic wetting layers which may lead to different values of the exponent of t in equations (4) and (5) (Sullivan and Lipowsky 1988).

Acknowledgments

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