

Experimental determination of the surface tension of nematic liquid crystals

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Abstract. Equilibrium measurements of surface tension have been carried out on *p*-anisaldazine and *p*-azoxyanisole in the nematic and isotropic phases using the pendant drop method. The drop was completely enclosed in a chamber filled with inert atmosphere and maintained at all times in equilibrium with its saturated vapour. The surface tension-temperature characteristic shows a marked anomaly for both compounds; the slope in the nematic phase is initially negative and then reverses sign as the temperature approaches the nematic-isotropic transition point. For *p*-anisaldazine the slope again becomes negative immediately after the transition whereas for *p*-azoxyanisole the positive slope extends for a few degrees in the isotropic phase before changing sign at higher temperatures. The observed features are in qualitative agreement with the theoretical predictions of Croxton and Chandrasekhar.

Introduction

The experimental data available on the surface tension of nematic liquid crystals are meagre and rather conflicting. Ferguson and Kennedy¹ found for all the three nematic compounds they studied, *viz.*, *p*-azoxyanisole (PAA), *p*-azoxyphenetole and *p*-anisaldazine, that the slope of the surface tension-temperature ($\gamma - T$) characteristic was initially negative but reversed sign as the temperature approached the nematic-isotropic transition point (T_c). Naggiar² obtained for PAA a monotonically decreasing function throughout the nematic range. The values of Schwartz and Moseley³ as well as those of Gorskii and Sakevich⁴ for PAA also showed a decreasing trend except that the γ values obtained by the former had a tendency to be constant very near T_c .

However, none of these measurements were carried out under equilibrium conditions. Recent studies on the surface tension of liquid metals⁵ have demonstrated the importance of having the liquid in equilibrium with its saturated vapour so that there is no net flux of atoms across the liquid-vapour interface. The $\gamma - T$ characteristic determined under these conditions showed an inversion which was completely missed in all previous non-equilibrium measurements. Therefore, it was evident that an equilibrium experiment is essential for obtaining the true form of the $\gamma - T$ characteristic of the liquid crystal.

The surface tension of a nematic liquid crystal is expected to be strongly dependent on the alignment of the molecules at the free surface⁶. Since the molecular orientation is highly influenced by wall effects care had to be taken that measurements are not effected by the orienting influence of the solid surface in contact with the liquid crystal. This was a major factor to be considered in the choice of the experimental technique. After examining various possibilities, it was decided to use the pendant drop method which is known to be suitable for viscous liquids⁷. This method has several advantages:

- (i) Only a very small fraction of the total surface area of drop is in direct contact with the solid surface and the results are *independent* on the angle of contact.
- (ii) It is a static method so that the viscous drag of liquid does not play any part.
- (iii) The approach to hydrodynamic equilibrium is rapid, which is an important point to be borne in mind for viscous liquids.

Andreas *et al.*⁸ have shown that the surface tension γ can be calculated from the pendant drop profile by $\gamma = g \rho d_{\max}^2/H$ where g is the acceleration due to gravity, ρ the density, d_{\max} is the maximum diameter of the drop and H is a correction factor which depends on the shape of the drop. The shape can be characterized by a ratio $S = d_s/d_{\max}$, d_s being the diameter of the drop measured at a height equal to d_{\max} from the vertex. Andreas *et al.* obtained a table of $1/H$ vs. S from measurements on various pendant drops of conductivity water whose surface tension is accurately known. Later more accurate tables have been compiled by numerical solutions of the fundamental differential equation which exactly governs the shape of the pendant drop acted upon by gravitational and surface energy forces. Ryong-Joon Roe *et al.*⁹ made a further improvement whereby the attainment of hydrodynamic equilibrium can be verified. This is done by measuring the diameters of the pendant drop at several heights instead of only two. Tables required for the determination of $1/H$ from the different characteristic ratios of the drop diameters have also been computed by these authors. By ascertaining the constancy of $1/H$ values obtained from the different ratios, the attainment of equilibrium is confirmed and the accuracy of the results improved. We have used for our calculations of γ , this method by Ryong-Joon Roe *et al.*

Experimental

A drop of the liquid crystal was formed at the tip of a thin uniform capillary tube. The tip was ground so that it was free from any irregularities. The upper end of the tube was connected through a rubber tube to a hypodermic syringe. The drop size could be controlled by a fine

adjusting screw attached to the piston of the syringe. The lower portion of the capillary was completely enclosed in an air-tight thermostatic chamber. The top portion of the tube was enclosed in another heater with independent temperature controlling facility. The main chamber had two optically flat glass windows to allow the drop to be photographed. In order to prevent the vapour from condensing on glass, two additional side heaters were provided which could bring the windows to the same temperature as that at the centre of the chamber.

During the experiment the drop was in an atmosphere of nitrogen and was maintained at all times in equilibrium with its saturated vapour. To have a steady drop the entire system had to be at the same temperature, for even a gradient of less than 0.25°C between the top and bottom portions of the capillary tube was enough to push the drop completely into or out of the tube. Before taking the photograph at any temperature, it was visually checked that the drop was stationary for at least 15 min. A parallel beam of light from a mercury lamp was made to fall on the drop and focussed by a suitable lens system onto the focal plane of the camera. It was checked beforehand that the photographic system did not introduce any distortion. A green filter was used to avoid chromatic aberration effects. The temperature of the drop was measured using chromel-alumel thermocouple, the junction being kept close to the drop. As a preliminary check of the experimental set up, measurements were made on pure water and the values obtained at different temperatures agreed to within 1.5% with the reported values.

Results and discussion

p-anisaldazine: Experiments were first done on anisaldazine. The nematic-isotropic transition temperature of the sample was 182.2°C which appears to be the highest reported for this compound. Measurements were repeated using capillary tubes of different sizes and the values were found to be quite consistent. The $\gamma-T$ characteristic obtained from the photographs of a single drop at different temperatures is shown in figure 1. We see that initially γ decreases with increase of temperature. But as T_0 is approached, the slope changes and γ reaches a maximum at 182.1°C , which was the temperature closest to T_0 at which measurements could be made. Above T_0 , γ starts decreasing again, rapidly at first and then more gradually at higher temperatures.

p-azoxyanisole (PAA): Measurements were also made on PAA ($T_0 = 135.2^{\circ}\text{C}$). The $\gamma-T$ curve is shown in figure 2. Here again γ shows a decreasing trend at lower temperatures, but starts increasing near T_0 . A special feature here is that γ continues to increase in the isotropic phase reaching a maximum at 139.3°C after which it decreases again.

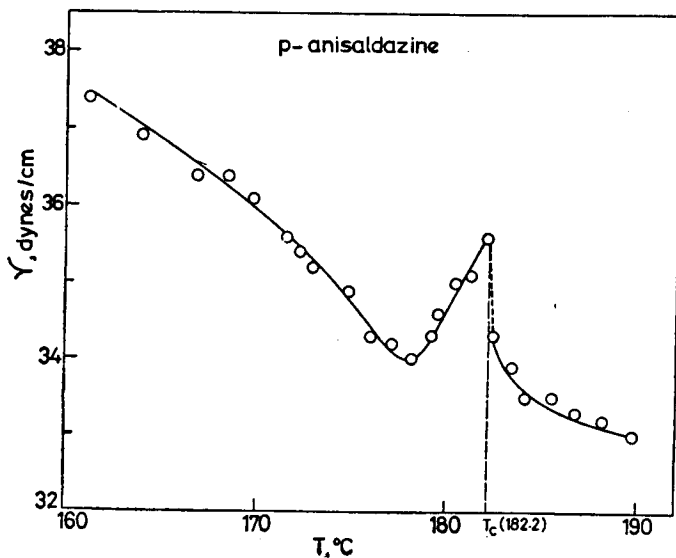


Figure 1 Surface tension of *p*-anisaldazine in the nematic and isotropic phases.

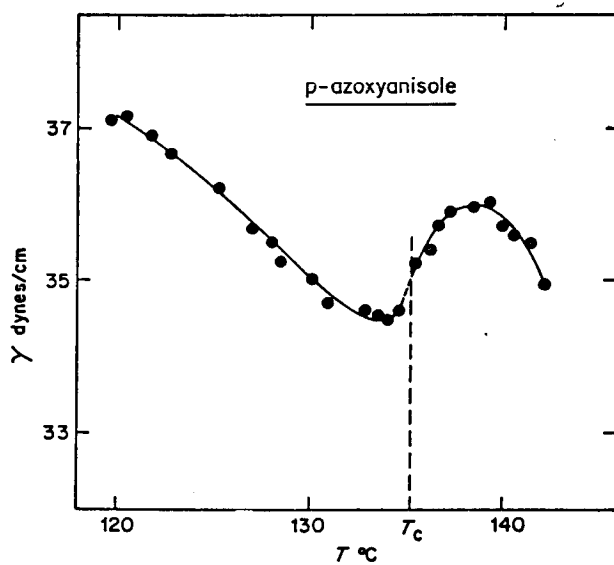


Figure 2 Surface tension of *p*-azoxyanisole in the nematic and isotropic phase.

The observed features of the γ - T characteristic of both compounds are in qualitative agreement with the theory of Croxton and Chandrasekhar¹⁰. There is evidence that in PAA the molecules are almost parallel to the

free surface¹¹ and that the orientation is practically independent of temperature in the nematic range. The surface orientation in anisaldazine is not known. In order to investigate the dependence of γ on molecular alignment at the free surface experiments are underway subjecting the drop to external fields.

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DISCUSSION

Billard: What method are you using to control the chemical purity of your samples?

Shashidhar: The compounds were purified by several recrystallisations and the purity checked by measuring the nematic-isotropic transition temperature. However, it appears that the purity of sample does not critically affect the shape of the γ - T curve. For instance, with anisaldazine the measurements were first made on a sample having $T_e = 181.5^\circ\text{C}$ and subsequently on a purer sample having $T_e = 182.2^\circ\text{C}$ (which appears to be the highest reported for this compound), but the γ - T characteristic had essentially the same features in both cases.

Kaul: The error involved in using a flat capillary should be taken into account because the contact surface area varies with the drop size, in the case of a flat capillary. Would not it be better to use a capillary with the outer walls tapered?

Shashidhar: It may be better to use a capillary tube with a sharp edge as suggested by you, though I feel it is unlikely to make much difference as far as the surface tension-temperature characteristic is concerned.

Leslie: Do you know the orientation of the anisotropic axis at the surface of the drop? Presumably the surface tension varies with this orientation, and one possible explanation of the shape of the curve near the isotropic transition is that the orientation changes near the transition.

Shashidhar: There is experimental evidence that in PAA the molecules are nearly parallel to the free surface and that their orientation is independent of temperature*. It would appear therefore that the suggestion that the shape of the curve is due to the change in orientation is not right. The surface orientation is not known in the case of anisaldazine.

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