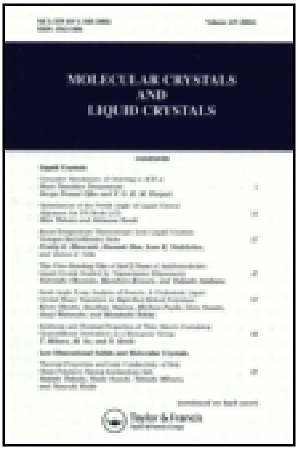

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 28 Mar 2007.

To cite this article: S. Krishnaswamy & R. Shashidhar (1976): Experimental Studies of the Surface Tension of Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals, 35:3-4, 253-259

To link to this article: http://dx.doi.org/10.1080/15421407608083675

Mol. Cryst. Liq. Cryst., 1976, Vol. 35, pp. 253–259
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Printed in Holland

Experimental Studies of the Surface Tension of Nematic Liquid Crystals

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(*Received November 18, 1975; in final form March 2, 1976*)

Equilibrium measurements of surface tension have been carried out on nematic compounds using the pendant drop method. A drop of the liquid crystal is suspended at the tip of a capillary tube inside a completely enclosed thermostatic chamber filled with an inert gas and is maintained in equilibrium with its saturated vapour throughout the experiment. The surface tension-temperature characteristic for all the compounds studied show anomalous behaviour. The slope in the nematic phase is initially negative but changes sign near the nematic-isotropic transition for *p*-azoxyanisole, *p*-anisaldazine and *p*-methoxy benzylidene-*p*′-*n*-butylaniline, whereas for *p*-azoxyphenetole the change of slope occurs in the isotropic phase. The original monotonically decreasing trend is regained in all the cases at higher temperatures in the isotropic phase. The data on *p*-azoxyanisole, *p*-azoxyphenetole and *p*-anisaldazine confirm the earlier measurements of Ferguson and Kennedy[1] on the same compounds. The observed features are in qualitative agreement with the theoretical predictions of Croxton and Chandrasekhar.[6]

1 INTRODUCTION

The surface tension of nematic liquid crystals has been the subject of a number of experimental studies. However, the results obtained by the different authors are rather conflicting. Ferguson and Kennedy[1] found that for all the three compounds they studied, viz., *p*-azoxyanisole, *p*-azoxyphenetole and *p*-anisaldazine, the slope of the surface tension-temperature (γ-T) characteristic was initially negative but changed sign as the nematic–isotropic transition temperature (T_c) was approached. All subsequent measurements on *p*-azoxyanisole[2–4] gave a monotonically decreasing trend for γ in the entire nematic range and doubts have been expressed about the accuracy of Ferguson and Kennedy's data.[5]

Croxton and Chandrasekhar[6] have recently discussed the statistical thermodynamics of the nematic free surface. Considering the orientational contributions to the surface excess quantities for a nematic, they find that $\partial\gamma/\partial T$, the gradient of the surface tension, is determined as a competition between the orientational order and the spatial disorder which develops at the liquid surface. They also find that if the orientational states are highly ordered, then the γ-T characteristic can show a *positive* slope, though at higher temperatures the usual monotonic decreasing trend is regained owing to the spatial delocalization of the surface. Associated with the discontinuous variation of the bulk order parameter with temperature at the nematic–isotropic transition, the slope as well as the absolute value of γ may show a discontinuous behaviour in the neighbourhood of T_c. Another possibility that they have considered is that the weak surface field may establish a residuum of orientational order at the isotropic liquid surface over a short thermal range above T_c resulting in the γ-T characteristic showing a positive slope even in the isotropic phase. These authors have also stressed the fact that to observe these features described above it is crucial that a truly equilibrium measurement of γ should be made, i.e., the liquid crystal should be maintained in equilibrium with its saturated vapour so that there is no net flux of atoms across the liquid–vapour interface.[7] We have therefore undertaken a systematic experimental study of the surface tension of liquid crystals under equilibrium conditions.

The surface tension of a nematic liquid crystal is expected to be strongly dependent on the alignment of the molecules at the free surface.[8] Since the molecular orientation is highly sensitive to the wall effects, it was necessary to choose a method wherein the orienting influence of the solid surface does not affect the surface tension measurements. After considering various experimental techniques it was decided to use the pendant drop method which is known to be suitable for viscous liquids.[9] This method has several advantages:

a) The area of the drop which is in direct contact with the solid surface is very small compared to the total area of the drop.

b) The values obtained are independent of the angle of contact.

c) It is a static method so that the viscous drag of the liquid does not play any part.

By completely enclosing the drop in an airtight chamber it could be maintained in equilibrium with its own vapour. In this paper we describe the determination of surface tension of 4 nematic compounds by this method. The results for *p*-azoxyanisole and *p*-anisaldazine have been reported previously,[10] but for the sake of comparison we also present the data for these two compounds.

2 EXPERIMENTAL

A drop of the liquid crystal was formed at the end of a thin uniform capillary tube whose tip was cut and ground so that it was perpendicular to the axis of the capillary and free from any irregularities. The upper end of the capillary was connected through a rubber tube to a hypodermic syringe. The drop size was controlled by the fine movements of a screw attached to the piston of the syringe. The lower portion of the capillary was enclosed in an airtight copper chamber (provided with two optically flat glass windows) which could be electrically heated. In order to avoid a horizontal thermal gradient across the windows which sometimes resulted in condensation taking place on the glass, two additional side heaters were provided so that the outside temperature near the windows could be maintained the same as that inside the chamber. Further, the upper portion of the capillary outside the chamber was maintained at the same temperature as the chamber itself by a separate heater. This was most important as any vertical thermal gradient in the capillary tube made the drop grow or contract and prevented it from attaining equilibrium.

The capillary filled with the liquid crystal was inserted into the chamber which was then evacuated and filled with dry nitrogen in order to prevent the decomposition of the compounds by oxygen and moisture. The process of evacuation and filling was repeated several times to ensure that the chamber was completely free from any traces of air. The chamber was then sealed and the drop of the liquid crystal formed at the tip of the capillary tube by careful adjustments of the control screw. A parallel beam of monochromatic light was made to fall on the drop and the image was focussed onto the focal plane of a camera by a suitable lens system. It was checked beforehand that the photographic system did not introduce any distortions. The experiment was carried out by taking photographs of a single drop at different temperatures, ensuring that the drop was in perfect equilibrium at each temperature. At a given temperature it was necessary to wait for about 30 minutes before steady state could be attained, and before taking the photograph it was ascertained visually that the drop was stationary for at least 15 minutes and also that the temperature itself was constant during this period. A complete experiment on a single drop wherein photographs were taken for about 20 temperatures took nearly 15 hours.

Before starting measurements on liquid crystals, the experimental set up was checked by determining the surface tension of pure water at different temperatures. The values obtained were within 1.5% of the standard values and therefore the accuracy of the measurement is also reckoned to be within this limit.

3 CALCULATION OF THE SURFACE TENSION FROM THE PENDANT DROP PROFILE

The pendant drop is held in equilibrium by the action of gravitational and surface energy forces, and its shape can be described exactly by a differential equation which has been discussed in detail in standard reviews on the subject.[11,12] Andreas, Hauser and Tucker[13] have shown that surface tension (γ) can be calculated from the pendant drop profile by the relation

$$\gamma = g\rho\, d_{\max}^2/H$$

where g is the acceleration due to gravity, ρ the density, $d_{\max}$ the maximum equatorial 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 $S = d_s/d_{\max}$ where d_s is the diameter of the drop measured on the horizontal plane at a height equal to $d_{\max}$ from the vertex. Andreas *et al.* obtained a table giving H^{-1} vs. S from measurements of the surface tension of 'conductivity' water whose surface tension at different temperatures is accurately known. Later more accurate tables have been compiled[14,15] by numerical solutions of the fundamental differential equation. Ryong-Joon Roe, Bacchetta and Wong[16] made a further improvement wherein it is possible to verify that the drop has attained equilibrium. They defined a series of diameters d_n ($n = 8, 9, \ldots, 12$) which are respectively measured at heights of $(n/10)d_{\max}$ from the vertex of the drop. The corresponding characteristic ratios are now given by $S_n = d_n/d_{\max}$. A series of tables giving H^{-1} vs. each S_n have been computed. By ascertaining the constancy of H^{-1} obtained for the different ratios, the attainment of equilibrium is confirmed and the accuracy of the results improved. We have followed this method of Ryong-Joon Roe *et al.*

4 RESULTS AND DISCUSSION

The surface tension (γ)-temperature (T) characteristic has been studied for 4-nematic compounds: *p*-anisaldazine, *p*-methoxy benzylidene-*p*′-*n*-butyl aniline (MBBA), *p*-azoxyanisole (PAA) and *p*-azoxyphenetole (PAP) whose nematic-isotropic transition temperatures are 182.1, 43.2, 135.2 and 166.6°C respectively. In each case, the γ-T characteristic has been obtained by photographing a single drop at different temperatures. All the compounds except MBBA were purified by several recrystallizations from a suitable organic solvent. MBBA, a room temperature nematic which gets easily contaminated by oxygen and moisture, was vacuum distilled and the experiment was carried out immediately after purification. It should however be mentioned that preliminary experiments revealed that purity of the sample did not critically affect the shape of the γ-T curve.

The γ-T curves for the four compounds are shown in Figures 1–4. In all cases γ decreases initially with increase of temperature, changes slope around T_c and finally at high temperatures the monotonically decreasing trend is regained. In *p*-anisaldazine and MBBA the reversal of slope takes place a little below T_c and γ reaches a maximum at T_c. In *p*-anisaldazine, there is a discontinuous drop in the value of γ at T_c, whereas in MBBA the discontinuity is not so marked. However, in both cases γ starts decreasing again in the isotropic phase. In PAA also the first reversal of slope takes place

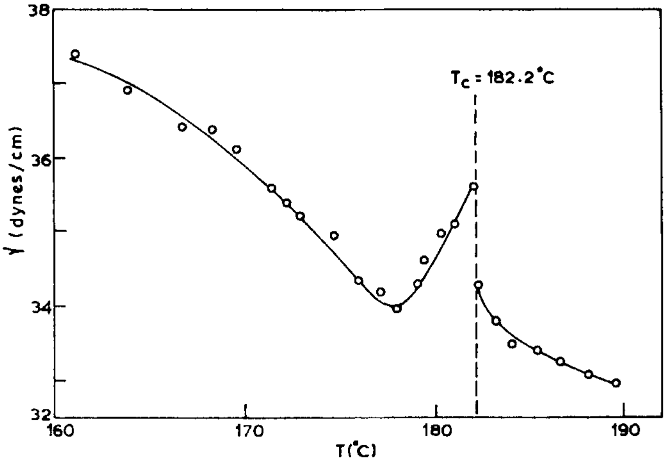

FIGURE 1 Surface tension of *p*-anisaldazine in the nematic and isotropic phases.

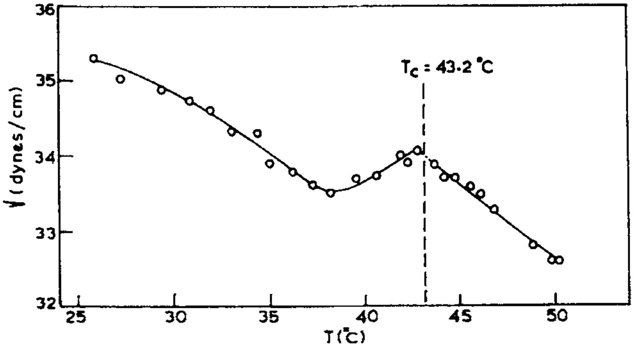

FIGURE 2 Surface tension of *p*-methoxy benzylidene-*p*′-*n*-butylaniline in the nematic and isotropic phases.

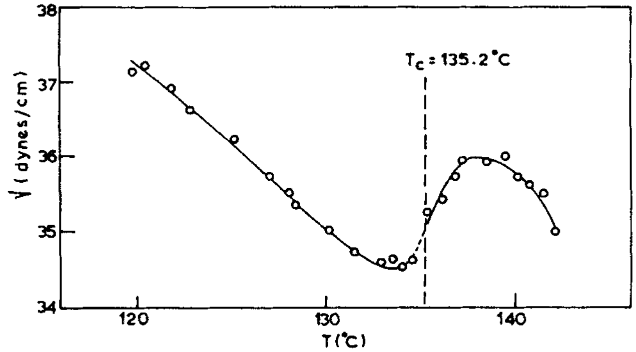

FIGURE 3 Surface tension of *p*-azoxyanisole in the nematic and isotropic phases.

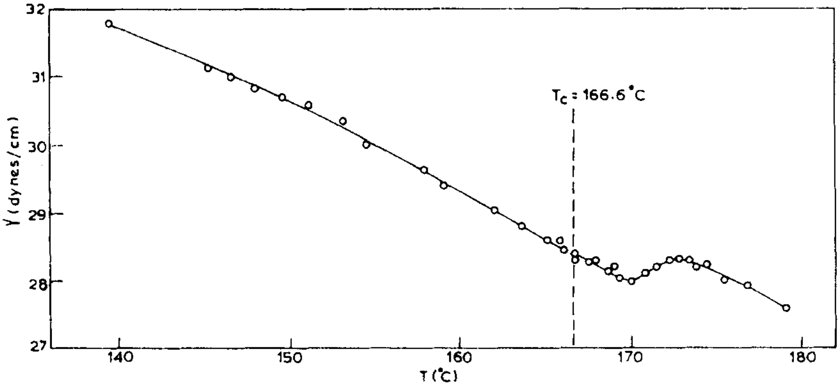

FIGURE 4 Surface tension of *p*-azoxyphenetole in the nematic and isotropic phases.

below T_c but the positive trend continues for a few degrees in the isotropic phase before changing sign again. In PAP, the behaviour is slightly different; the usual decreasing trend continues even in the isotropic phase before the anomaly sets in. The results for PAA, PAP and *p*-anisaldazine are in close agreement with the early measurements of Ferguson and Kennedy.[1]

The question arises whether the anomaly in the γ-T characteristic is due to a reorientation of the molecules at the surface in the neighbourhood of T_c. The alignment of the molecules at the free surface has been studied for PAA and MBBA using light scattering techniques.[17] It is found that in PAA the molecules lie parallel to the surface and the orientation is independent of temperature. In MBBA the molecules are inclined at ~75° to the surface, the tilt angle being only slightly dependent on temperature. It would appear therefore that the shape of the γ-T curve is not due to any molecular rearrangement at the surface. The observed trends are in qualitative agreement with the theoretical predictions of Croxton and Chandrasekhar.[6]

To investigate further the dependence of surface tension on the direction of alignment at the surface, experiments are underway to study the effects of external magnetic field on the shape of the drop.

Acknowledgements

These experimental studies were initiated by Professor S. Chandrasekhar. The authors are highly indebted to him for his keen interest and also for many useful discussions.

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