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Measurement of the Surface Tension of CBOOA

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In continuation of our previously reported experimental studies on the surface tension of liquid crystals, measurements have been carried out on *p*-cyanobenzylidene *p*'-*n*-octyloxyaniline (CBOOA) in its smectic A, nematic and isotropic phases. The surface tension-temperature (γ-T) characteristic shows a positive slope throughout the smectic phase, changes sign at the smectic A–nematic transition, remains negative over the entire nematic range and again reverses sign immediately after the nematic–isotropic transition, the positive slope now continuing for a few degrees in the isotropic phase. These trends are compared with the theoretical predictions of Croxton and Chandrasekhar.

INTRODUCTION

Croxton and Chandrasekhar[1] have recently discussed the statistical thermodynamics of the nematic free surface. Considering the orientational contribution to the surface excess quantities of a nematic, they have shown that the gradient of surface tension is determined as a competition between the orientational order and the spatial disorder which develops at the liquid crystal surface. Should the situation corresponding to highly ordered orientational states occur, then the γ-T characteristic will show a positive slope, although with increasing temperature, the usual monotonic decreasing trend will be regained owing to the spatial delocalization of the surface. Associated with the discontinuous variation of the order parameter at the nematic–isotropic transition temperature (T_{NI}) the slope as well as the absolute value of γ may show a discontinuity in the vicinity of T_{NI}. If the weak surface field establishes a residuum of orientational order at the isotropic liquid surface over a short thermal range above T_{NI}, then the positive slope may be seen even in the isotropic phase. These authors have emphasized the fact that to observe these features a truly equilibrium experiment has to be conducted, i.e., the liquid crystal has to be maintained in equilibrium with its saturated vapour so that there is no net flux of atoms across the liquid crystal-vapour interface.

Very recently Parsons[2] has developed a molecular theory of surface tension in nematic liquid crystals by applying the Fowler–Kirkwood–Buff approximation to the interface. His conclusions, which are essentially similar to those of Croxton and Chandrasekhar, are that there should be a discontinuity in surface tension at T_{NI} and that the surface tension in the nematic phase is less than the value in the isotropic phase.

Although the early measurements of Ferguson and Kennedy[3] on some nematic compounds did show positive slope for the γ-T curve in the neighbourhood of T_{NI}, all subsequent measurements[4–6] gave only a monotonically decreasing trend and doubts were expressed on the validity of the earlier data (see, e.g., Gray[7]). Recently, we have carried out equilibrium measurements of γ[8,9] on 4 nematic compounds using the pendant drop method.[10] The γ-T characteristic of all the compounds studied show anomalous behaviour near T_{NI}, as envisaged by Croxton and Chandrasekhar. In this paper, we present our data on the surface tension of CBOOA in its smectic A, nematic and isotropic phases.

EXPERIMENTAL

CBOOA obtained from Vari-Light Corporation, USA, was recrystallized from *n*-heptane several times and then dried in vacuum. The transition temperatures were: solid–smectic A 75°C, smectic A–nematic 83.2°C and nematic–isotropic 107°C. A drop of the liquid crystal was formed at the tip of a capillary and was enclosed in a thermostatic chamber filled with an inert atmosphere. The drop was maintained at all times in equilibrium with its saturated vapour. By taking the photographs of a single, steady drop at different temperatures, the surface tension was evaluated at each temperature from the profile of the pendant drop. The details of the experimental set up as well as the method of calculation used have already been described.[9]

RESULTS AND DISCUSSION

The γ-T characteristic of CBOOA in its smectic A, nematic and isotropic phases is given in Figure 1. It is seen that the slope is positive throughout the smectic phase and changes sign at the smectic A–nematic transition temperature. A monotonic decreasing trend is shown in the entire nematic region. The curve again reverses sign just after the nematic–isotropic transition. The positive slope now continues for a few degrees till at 109.7°C it once again becomes negative. These trends are again in qualitative agreement with the theoretical predictions of Croxton and Chandrasekhar.

It is known that the surface tension of nematic liquid crystals is dependent on the molecular alignment at the free surface.[11] The question may therefore be asked whether the anomaly in the γ-T characteristic, which has been observed for all the liquid crystals studied, is due to a reorientation of the molecules at the surface in the neighbourhood of T_{NI}. The orientation of molecules at the free surface has been studied as a function of temperature for 2 nematic compounds, viz., *p*-azoxyanisole (PAA) and *n*-*p*-methoxybenzylidene *p*′-*n*-butylaniline (MBBA), using light scattering techniques.[12]

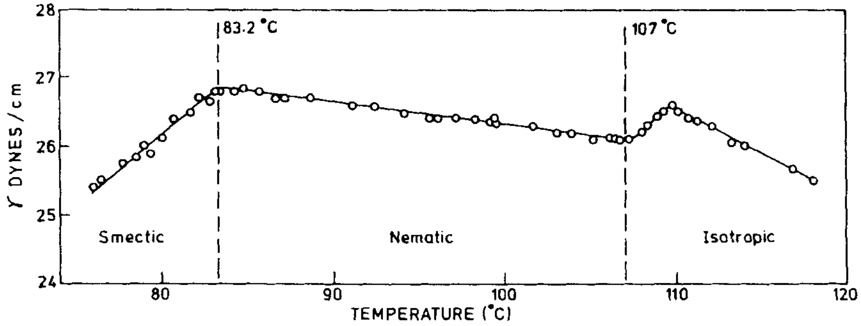

FIGURE 1 Surface tension of *p*-cyanobenzylidene *p*′-*n*-octyloxyaniline in the smectic, nematic and isotropic phases.

It is found that in PAA the molecules lie parallel to the free surface and that this orientation is independent of temperature. In the case of MBBA, the molecules are found to lie at approximately 75° to the surface, the angle being only slightly dependent on temperature. It appears therefore that the shape of the γ-T curve is not due to any molecular rearrangement at the surface.

For a further understanding of the problem of the dependence of γ on the surface alignment of molecules, it will be interesting to study the effect of an external magnetic field on the shape of the drop. Such experiments are underway.

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