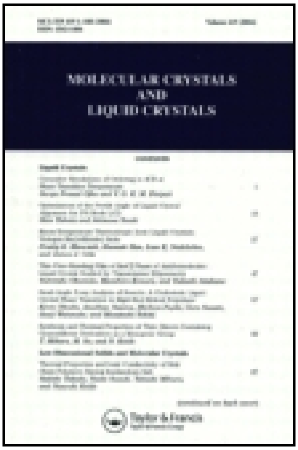

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

The Behaviour of the Interfacial Surface Tension of Liquid-Crystal Materials in the Vicinity of the Nematic-Isotropic Phase Transition

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Version of record first published: 05 Apr 2011

Mol. Cryst. Liq. Cryst., Vol. 494, pp. 114–126, 2008

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802430182

The Behaviour of the Interfacial Surface Tension of Liquid-Crystal Materials in the Vicinity of the Nematic-Isotropic Phase Transition

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The behaviour of the interfacial surface tension of nematics near the nematic-isotropic phase transition has been investigated by several researchers. However, the observations reported by the various authors appear to be inconsistent. The present work is an attempt to identify the causes of such inconsistencies. A detailed study of the behaviour of the interfacial surface tension of 5CB by two different techniques (pendant drop and sessile drop) as well as optical observations of the surface of the drop near the nematic-isotropic transitions is presented. Our observations would indicate that close to the transition the phase at the surface may not be uniform; some areas on the surface appear to be fluctuating between the isotropic and the nematic phase. These fluctuations occur at temperatures corresponding to the range between the spinodal points.

Keywords: 5CB; nematic-air interface; pendant drop; sessile drop; surface tension

INTRODUCTION

The behaviour of the surface tension of a nematic material in the vicinity of the nematic-isotropic phase transition is still an open question. There are in the literature several reports of theoretical [1–4] as well experimental studies in various nematic materials [4–10]. However, published experimental data appears to be inconsistent. The present

This work was financially supported by Sultan Qaboos University research grant IG/SCI/PHY/04/03.

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work is an attempt to understand the reasons for such inconsistencies in the observed behaviour of the surface tension. The behaviour of the interfacial surface tension is directly related to the order in the surface relative to that of the bulk. The slope of the surface tension–temperature graph is the excess entropy of the surface

$$\frac{\partial \gamma}{\partial T} = -(s_s - s_b) \quad (1)$$

where s_s is the entropy of the surface layer and s_b the entropy of the bulk. Therefore the sign of this slope and of any possible discontinuity at the transition depends on whether a film of nematic wets the isotropic bulk or vice versa. All the techniques to measure the interfacial surface tension involve a finite area of the interface, for example the surface area of a drop. In writing Eq. (1) to interpret experimental data it is implicitly assumed that s_s is uniform over the whole area involved in the measurement. The work reported here would suggest that this is not necessarily the case near the nematic-isotropic transition.

When investigating the behaviour of the surface tension of a nematic near the transition temperature one would like to address the following questions: Is the surface tension a monotonic function of the temperature? Is there a discontinuity at the transition? What is the sign of the discontinuity if there is one? Does the surface tension in the nematic phase depend on orientation of the director at the surface? How does the Frank elastic energy affect the surface tension on a curved interface? Another important point concerns the relation between the surface *tension* (a force-based quantity) with the surface *free energy*. These quantities are the same in an isotropic (and only in an isotropic) fluid, and indeed the ambiguity extends to this paper. However, in other systems, this identity may no longer hold.

The present paper does not attempt to bring a direct answer to these questions. The questions addressed here are simpler and more empirically-based. Does the behaviour of the surface tension depend on the measuring technique? Are the standard methods for measuring the surface tension appropriate for a liquid close to the nematic-isotropic phase transition? Are there any fluctuations on the surface that prevent a reliable measurement of the surface tension? The experimental data presented is a summary of a large number of measurements carried out with different techniques and different experimental conditions over a period of three years. However, a detailed understanding of the differences which we encounter between different kinds of surface tension measurements may in the end contribute to a more detailed understanding of the liquid-vapour interface in the region of the nematic phase.

THE EXPERIMENTAL METHODS

All the data to be reported in this paper is from measurements on 5CB. The material was purchased from Kingston Chemicals (Hull, UK) and used without any further purification. The density of 5CB at various temperatures in the isotropic phase and in the nematic phase was calculated using a cubic fits to density measurements obtained in each phase using an Anton-Paar densitometer. The two main techniques used to measure the surface tension are the pendant drop and the sessile drop techniques. The data was taken using the OCA200 instrument from *Dataphysics*. We discuss first the data obtained from the pendant drop technique. Although this technique presents more challenges in the procedures, it has yielded more consistent results than the sessile drop technique.

The Pendant Drop Technique

The principle of the instrument is illustrated in Figure 1. The drop under investigation is formed inside a thermal chamber using an electronic dosing syringe. The temperature inside the chamber is controlled to better than 0.1°C by two heating plates, one plate at the top and one at the bottom to minimize temperature gradients. The temperature of the air inside the chamber is monitored by a thermometer placed close to the drop. The drop is illuminated by a diffused light source and the image of the drop captured by a high-speed video camera. The contour of the drop is fitted by the controlling computer to the Young-Laplace equation. The software returns the surface tension, the drop volume and an estimate of the discrepancy between the

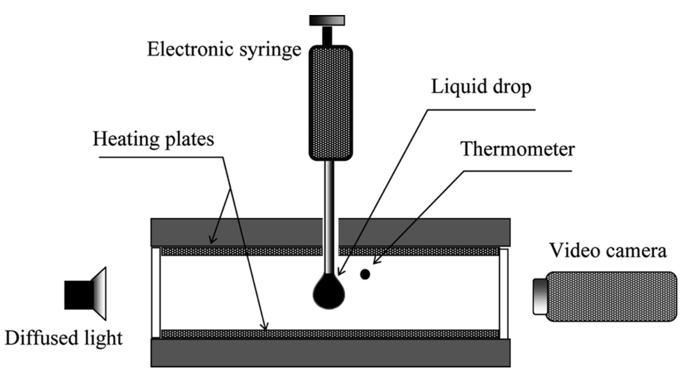

FIGURE 1 Schematic of the experimental setup for the pendant drop technique.

measured contour and the one computed from the fit to the Young-Laplace equation. The instrument is calibrated using the diameter of the needle of the syringe.

The exact transition temperature could be determined by observing changes in the light spot in the image of the drop. Figure 2 shows the image of the drop at temperatures just below and just above the transition. The changes at the transition are quite clear. Note that at the temperature 35.3°C there are in the light spot well defined areas with different contrasts. These areas observed only in a 0.3°C temperature range above the transition temperature are seen to move randomly on the drop. A possible interpretation of the area will be discussed in the next paragraph.

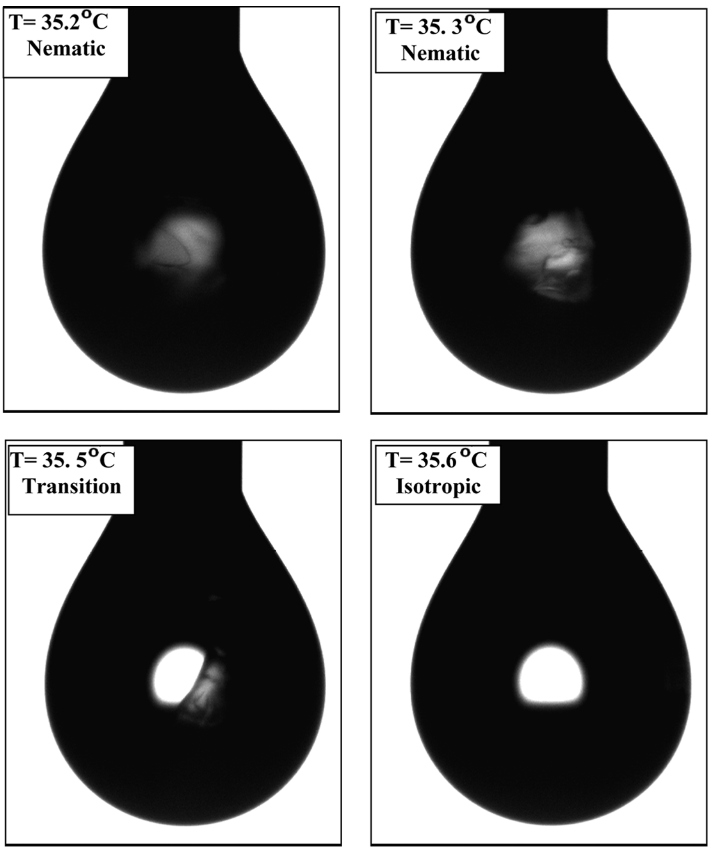

FIGURE 2 A pendant drop of 5CB observed with unpolarised diffused light at temperatures just below and just above the nematic-isotropic transition.

Several difficulties that had to be overcome were encountered in the experimental procedures with the pendant drop:

The first problem is due to the fact that the 5CB material wets the needle; the material creeps first up the needle during the drop injection and then, when the material falls to form a drop, there is significant length of the needle that remains inside the drop. The portion of the drop for the contour analysis was therefore limited to the lower 60% part of the drop.

The second experimental difficulty is the fact that, as the temperature is increased, the drop slides down the needle thus changing the volume of the portion of the drop that is taken into account for the contour analysis. In principle, a change of volume should not affect the calculation of the surface tension. However, like previous authors [5,11] we have observed that a small variation of volume causes significant changes in the calculated surface tension. These changes are small, but of the same order of the singularities that are being investigated. It has been shown [12,13] that, if the drop is large enough, the changes in volume do not affect the calculated surface tension. With the present set-up the drop falls off the needle before it has reached the minimum required size which in the present case is the order of 7–8 μl. It was therefore essential to ensure that the volume in the portion of the drop selected for the contour analysis was kept constant for all the measurements. This was better achieved by first measuring the variation of the calculated surface tension as a function of volume at fixed temperatures and then extracting by interpolation a value for the surface tension an arbitrarily fixed volume.

The third problem occurs during the data acquisition. Any small vibration of the instrument or variation in the atmospheric pressure causes the drop to oscillate with a very low period of the order of several minutes. These oscillations bring the drop away from equilibrium during the data collection and therefore the contour of the drop deviates from the one expected from the Young-Laplace equation. This problem was overcome by collecting the data late in the night when there was no one else moving in the building.

The last experimental difficulty is due to the fact that even small vibrations of the drop during the contour acquisition by the software results in an error of the order of 0.1 dyne/cm in the calculated surface tension. Again such error is not a problem for most applications; however, in the present work this error is unacceptable because it is of the same order as the magnitude of the singularities investigated. Since this error is a random error the surface tension at each temperature was taken as the average over 800 to 1000 measurements. The uncertainty on the measurement was thus reduced to 0.01 dyne/cm.

The data acquisition is very time consuming; including the wait for thermal equilibrium each point requires 20 to 30 minutes.

A large number of runs to measure the temperature dependence of the surface tension have been done. Drops of different sizes have been used; some data was taken on fresh drops, some on drops two or three days old; some data was taken with increasing temperature, some with decreasing temperature and some alternating one point in the isotropic phase and one in the nematic phase within a four degrees temperature range around the transition temperature. Almost all the runs displayed the same behaviour as the one shown in Figure 3. The data presented in the figure is a compilation of representative data from only a few of the runs. The trend observed is in agreement with the one observed by Gannon and Faber [7] using the Wilhelmy plate technique.

Away from the transition temperature in the nematic phase, the surface tension decreases with a slope of approximately -0.33 dyne/cm per degree. The negative sign implies that, as it is usually the case, the bulk is more ordered than the surface. At about 3 degrees below the transition temperature T_C the slope begins to increase and a turning point is observed at $(T_C - 1.5)$ degrees. Between $(T_C - 1.5)$ degrees

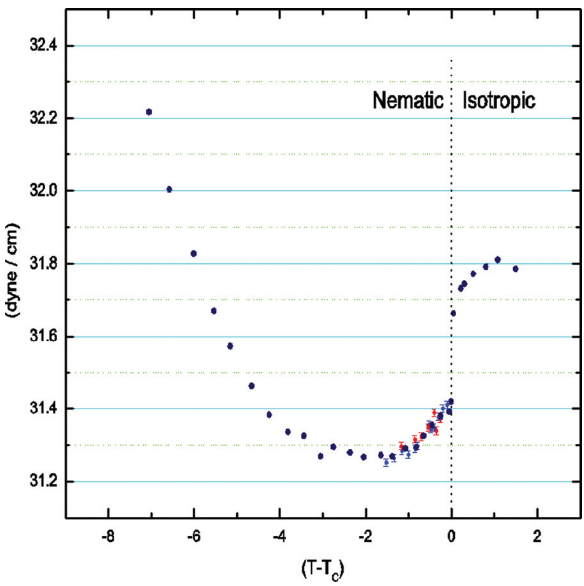

FIGURE 3 The behaviour of the interfacial surface tension of a pendant drop of 5CB as a function of temperature.

and T_C the surface tension increases with temperature which implies that in that temperature range the surface is more ordered than the bulk. At the transition temperature of the bulk from nematic to isotropic, there is a discontinuity with an increase of about 0.23 dyne/cm in the surface tension and the surface tension continues to increase with temperature for about one degree in the isotropic phase. This observation would indicate that in the isotropic phase just above the nematic-isotropic transition the surface of the drop is more ordered than the bulk. At temperatures higher than $(T_C + 1)$ degrees the surface tension decreases as expected in an isotropic fluid.

Before concluding this section we mention that variations up to 5% in the returned value of the measured surface tension have been observed between different runs therefore, only the trend and not the value of the surface tension should be considered in Figure 3. Gannon and Faber [7] also reported such variations in their measurements and scaled all their data to an arbitrarily fixed point. Finally, we mention that in some runs we have observed erratic deviations from the trend shown in the Figure 3. These accidental deviations will be discussed later.

The Sessile Drop Technique

The sessile drop technique appeared to be a simpler technique than the pendant drop because the drop is resting on a substrate and therefore the measurements are less affected by vibrations and changes in the atmospheric pressure due to activity in the building. In practice several problems have arise. Firstly, it has been difficult to obtain drops with a circular base. Large drops tend to present an irregular base; smaller drops have a more regular shape; however, the uncertainty in the fitting procedure to the contour of a very small drop can be prohibitively large. Suitable drops for the measurements were selected by trial and error. The quality of the substrate was suspected to be responsible for the irregular shape of the drops; different types of substrates such as standard cover slips, floated glass, silicon wafers have been used but made little difference. In order to avoid temperature gradients across the drop the substrate and the drop were lifted away from the heating plate as shown in Figure 4. As with the pendant drop the transition temperature could be observed as a change of contrast in the light spot in the drop. At temperatures sufficiently different from the transition the data acquisition was straightforward; in most cases an average over 100 measurements was sufficient to achieve the desired statistical uncertainty of less than 0.01 dyne/cm. However, in a temperatures range of about 3 to 4 degrees below the

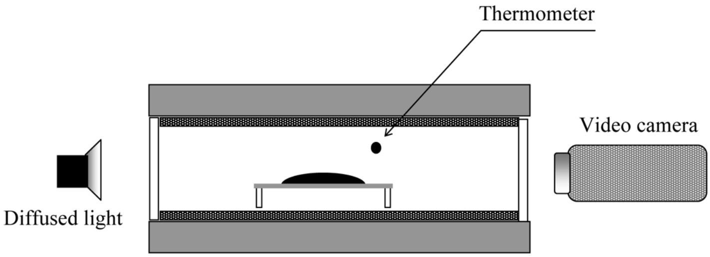

FIGURE 4 Schematic of the experimental setup for the sessile drop technique.

nematic-isotropic transition the random error on a single measurement increases significantly (see Fig. 7). This should be interpreted as a deviation of the contour of the drop from the one predicted by Young-Laplace equation due to random fluctuations in the contour of the drop or to irregularities on the surface. An average over more than a thousand runs was necessary to achieve the statistical uncertainty of less than 0.01 dyne/cm. Furthermore, in that temperature range we have observed an inconsistent behaviour in the variation of the surface tension as a function of temperature. However, out of a very large number of runs with drops of different large sizes (3–4 mm diameter at the base) and on different types of substrates we would tend to conclude that the behaviour of the surface tension observed with this technique is the one shown in Figure 5.

The values for the surface tension in Figure 5 are about 3% lower than the ones in Figure 3 however, this variation is well within the 5% observed between different runs with the pendant drop and therefore the discrepancy should not be considered significant.

Apart from the obvious fact that the discontinuity at the transition has the opposite sign to the one observed with the pendant drop technique there are some other differences between the trends of the graphs in Figure 5 and in Figure 3.

The slope in the nematic phase away from the transition temperature is -0.43 dyne/cm, significantly smaller than the one obtained with the pendant drop. This would imply that the difference in order between the bulk and the surface is less in a sessile drop than in a pendant drop. The gradual change in the slope begins at about 5 to 6 degrees below the transition. The discontinuity at the nematic-isotropic transition is about -0.6 dynes/cm with the opposite sign and more than twice the magnitude of the one observed with the pendant drop. In the data shown in Figure 5, the slope near the transition in the nematic phase is almost zero; however, this has not been a sufficiently

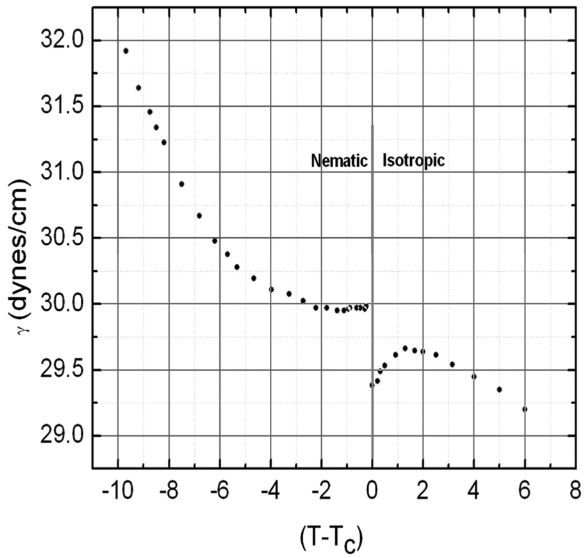

FIGURE 5 The behaviour of the interfacial surface tension of a sessile drop of 5CB as a function of temperature.

consistent observation to enable one to draw a definite conclusion. Some runs have shown a positive slope and some other a negative slope. In the isotropic phase the behaviour is identical to the one observed on the pendant drop with a decreasing positive slope up to a temperature of 1.5°C above the transition.

The data presented in Figure 5 comes from one particularly favourable incident-free run and is given to illustrate what we believe to be the most likely behaviour in a sessile drop. Our judgment is based on the fact that this is the behaviour which has been observed in a more consistent manner with the sessile drop. In many of the runs the observed behaviour was more erratic. An illustration of the kind of data obtained in some of the less favourable runs is presented in Figure 6.

The values of the surface tension presented in Figure 6 have not been corrected for the calibration factor and are therefore in arbitrary units. The figure on the left shows some apparent oscillations in the nematic phase. The figure on the right is the superposition of the data from several runs on the same drop. It appears that on the nematic side there are two paths one with a positive slope at the transition and one with a negative slope. The various repeated measurements followed either one path or the other and sometimes switched from one path to the other during the run. Space does not allow to present

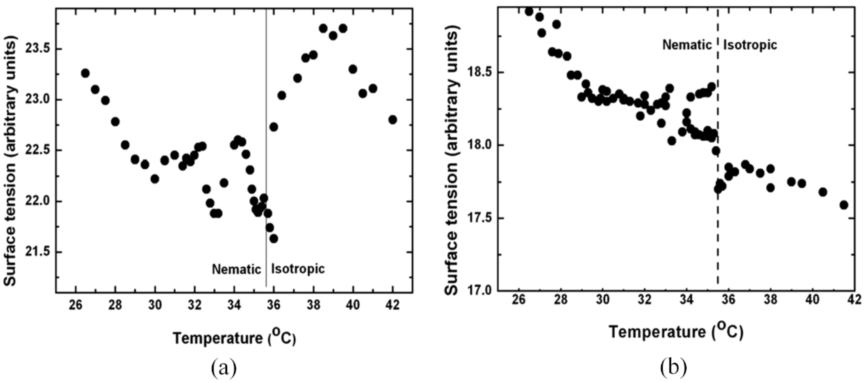

FIGURE 6 Some of the observed erratic behaviour of the interfacial surface tension of a sessile drop of 5CB as a function of temperature.

here more of the inconsistencies that have been observed with this technique. In the next section we discuss three possible causes for the observed inconsistencies. The first is the fact that the data is an average of a large number of measurements taken over a long period of time and may include some time variations. The second is the fact that both techniques used are based on a fit of the contour of a large portion of the drop to the Young-Laplace equation. The third is related to possible fluctuations on the surface.

DISCUSSION OF THE EXPERIMENTAL INCONSISTENCIES

In order to investigate the possible presence of drifts in the value returned for surface tension the raw data taken over several hours on sessile drops at constant temperature was analysed. It was found that significant slow drifts in the average returned value can occur. A tentative cause for those drifts will be given in the next section. Figure 7 shows the data from one of such runs, there is a significant drop in the returned value of γ. The gradual drop starts about two hours after the beginning of the run and occurs over a period of 100 minutes. One can see that if several averaged measurements had been taken at different temperatures during that time an erroneous trend as a function of temperature could have been obtained. Since increases as well as drops in the returned value of the surface tension have been observed, one may record apparent oscillations as a function of temperature that are in fact caused by these slow time variations of the data. No drifts were observed during the run presented in Figure 5.

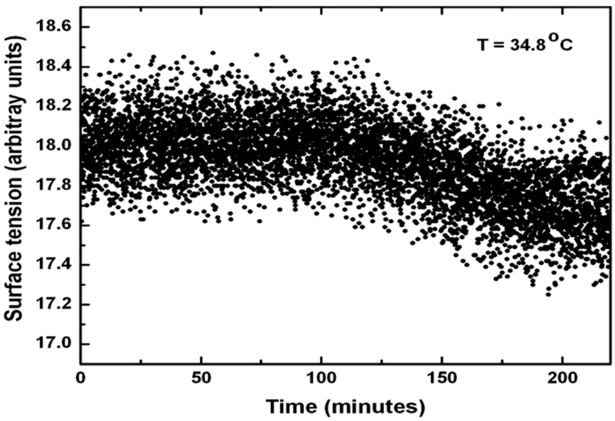

FIGURE 7 Observed drift in time of the value of the surface tension obtained from the fit of the contour of a sessile drop of 5CB in the nematic phase near the nematic-isotropic transition. Each dot is the result from a single fit.

The second possible pitfall in the measurement is the possibility of the coexistence of nematic and isotropic phases on the surface. The drop has been observed with polarised light at temperatures near the transition. Several observations have been made that may affect the recorded surface tension. We observe that the material in contact with the substrate becomes nematic at a slightly lower temperature than the material at the top of the drop. This cannot be attributed to temperature gradients across the drop since it is observed either on cooling or on heating. The Maltese cross is always observed on cooling and a sudden texture change is observed when the entire drop becomes nematic; this latter texture remains when the drop is

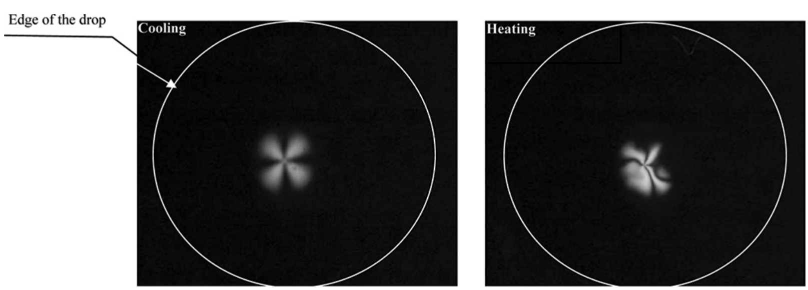

FIGURE 8 The sessile drop observed by reflection between crossed polarisers. The two photos were taken at the same temperature of 35.6°C. The left hand one on cooling from the isotropic phase and the right hand one on heating from the nematic.

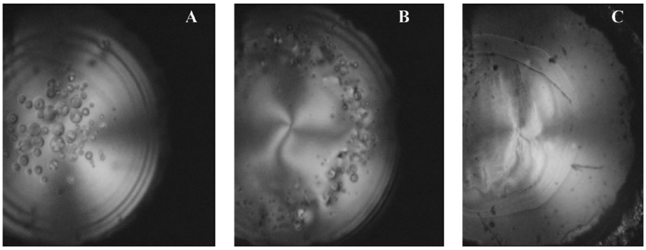

FIGURE 9 Fluctuating domains on the surface of a sessile drop of 5CB in the nematic phase close to the nematic-isotropic transition, A: T = 35.4°C, B: T = 35.4°C after e few minutes, C: T = 35.3°C.

heated as seen on the right-hand side photo in Figure 8. In a temperature range of about 0.8°C there are two phases and a nematic-isotropic interface line present on the surface of the drop. A single value of the surface tension derived from a fit of the entire drop contour to the Young-Laplace equation has therefore little real meaning.

The third problem is observed on the surface of the drop in the nematic phase. At a temperature of about 35.4°C circular domains with a well defined boundary appear near the top of the drop (Fig. 9A). These domains move randomly across the drop and they accumulate on a ring that expands and is gradually expelled at the bottom of the drop (Fig. 9B). The time evolution of these domains is probably responsible for the observed drift in the value of the surface tension. The domains seen here are probably similar to the ones observed moving on the pendant drop. In Figure 9C, the whole drop appears to be nematic and the circular domains have disappeared; however, there is an obvious boundary on the surface indicated by the arrow on the photo. It appears that there is a film of isotropic material on the surface of the bottom part of the drop. A tentative interpretation of the sequence observed in Figure 9 is that the domains are areas or isotropic material in a surface that is otherwise nematic; the circular domains coalesce at the bottom to form the isotropic film in Figure 9B. We note that the irregularities observed on the surface appear in the same temperature range where the erratic behaviour in the surface tension was observed; that temperature range corresponds also approximately to the range between the two spinodal points of the bulk nematic.

CONCLUSIONS

The present work shows that the behaviour of the air-nematic interface of a drop of 5CB in the vicinity of the nematic-isotropic transition is not simple. The surface of the nematic near the transition to isotropic can display a rich variety of behaviours depending on the geometry of the observation conditions. The measured surface tension on a drop using conventional techniques gives an average and depends therefore on the experimental technique.

The large contact of a sessile drop with the substrate has a significant influence on nature of the surface of the drop. The surface of the drop does not appear to be single phase and, at temperatures between the spinodal points, there appear to be fluctuations between the nematic and isotropic phase at the surface.

Techniques based on the fit of the contour of a drop are therefore not appropriate to investigate the behaviour of the surface tension near the nematic-isotropic transition. Such techniques yield an averaged surface tension that can vary in an unpredictable way according to the extent of the portion of the surface that is nematic compared to the one that isotropic.

A technique based of the force on a narrow rod as described by Rey [2] is currently being developed by the authors. This technique will probe a restricted area of the surface of the material; however, the area probed will be affected by the contact with the rod. Other methods with minimal disruption of the surface are also being investigated.

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