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Renato Norio Shimizu; Nicole Raymonde Demarquette

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Study of the surface and interfacial tensions in systems containing a low molar mass liquid crystal

RENATO NORIO SHIMIZU and NICOLE RAYMONDE DEMARQUETTE*
Departamento de Engenharia Metalúrgica e de Materiais,
Escola Politécnica da Universidade de São Paulo, Av. Prof. Mello Moraes 2463,
Cidade Universitária, CEP 05508-900, São Paulo-SP, Brazil

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The surface tension of a low molar mass liquid crystal (LMMLC), 4-cyano-4′-*n*-heptyloxybiphenyl (70CB), was measured as a function of temperature using the pendant drop method, forming drops of different volumes ranging from 5 to 11 mm^3. Contact angles formed by drops of 70CB in the nematic and isotropic phases on plates of polystyrene (PS) and of a liquid crystal polymer (LCP), VECTRA A910, were also measured. Only large drops could be used for surface tension analysis. It was shown that in the nematic phase the surface tension of 70CB decreases with increasing temperature, and that in the isotropic phase the surface tension increases with increasing temperature. Using the values of contact angle and of surface tension of 7OCB it was possible to evaluate the interfacial energy between 7OCB and PS and between 7OCB and VECTRA. The interfacial energy between 7OCB and PS, and between 7OCB and VECTRA, decreased with increasing temperature for ranges of temperatures corresponding to both phases of 70CB.

1. Introduction

Recently, there has been an increasing interest in the study of composite systems involving liquid crystals and thermoplastics. For example, micro-droplets of a low molar mass liquid crystal (LMMLC) can be dispersed in a polymer matrix to form polymer dispersed liquid crystals (PDLCs). These PDLCs are largely used in electro-optical devices due to the presence of dispersed LMMLC; films of PDLCs can switch from a transparent state to a light scattering state when submitted to a low voltage [1]. When polymerized, liquid crystals, then called liquid crystal polymers (LCPs), can be blended with thermoplastics. The resulting blends are expected to produce self-reinforced materials, because of the fibrillar morphology of the LCP phase obtained during processing [2].

The properties of heterogeneous materials are greatly influenced by the interfacial interaction between their components. For example, interfacial tension between the components forming a blend is one of the key parameters that influences the quality of its morphology, which, in turn, controls its properties. It has been shown that the interfacial energy between the liquid crystal and the matrix, forming a PDLC, controls the response of the electro-optical device and the orientation of the liquid crystal through the matrix [1]. For each value of electric field applied, the LMMLC molecules within each droplet assume an equilibrium configuration which results from a balance between the electric force and the interfacial energy between the droplet and the polymer.

In the case of nematics, in both PDLCs and polymer blends involving LCPs it is expected that the order of the liquid crystalline molecules affects the interfacial interaction between the liquid crystalline and non-liquid crystalline materials. The study of surface tension of LMMLC and interfacial energy between LMMLC and thermoplastics can therefore be of great interest, because it will help in understanding the influence of the ordering of the liquid crystal on the interfacial energy between liquid crystals and thermoplastics.

Various methods can be used for the measurement of surface tension of liquids, among them the capillary rise technique, Wilhelmy plaque, Du Nouy ring, pendant drop methods, etc [3]. It has been reported that the pendant drop method may be the most appropriate to measure the surface tension of a liquid crystal [4], because the surface of the drop in contact with a solid wall is very small compared with its total surface. In the case of nematics, the surface tension is expected to depend strongly on the alignment of the molecules in the surface; this is extremely sensitive to wall effects.

The pendant drop method involves the determination of the profile of a drop of liquid suspended in air at mechanical equilibrium [5]. The profile of the drop is determined by the balance between gravity and surface

*Author for correspondence; e-mail: nick@usp.br

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forces. The equation of Bashforth and Adams [6] which is based on Laplace's equation, relates the drop profile to the surface tension through a non-linear differential equation:

$$\frac{1}{R_1/a} + \frac{\sin \Phi}{x/a} = -B\frac{z}{a} + 2. \tag{1}$$

The shape factor B is given by

$$B = \frac{a^2 g\rho}{\gamma} \tag{2}$$

where ρ is the density of the liquid, g is the gravitational constant, γ is the surface tension, a is the radius of curvature at the apex of the drop, x, z, Φ are the coordinates defined as in figure 1, and R_1 is the radius of curvature at the point with coordinates (x, z).

Much work has been done during the last 30 years to develop algorithms to infer the surface tension from pendant drop profile and to improve the method by coupling it with the ongoing progress of data acquisition and image analysis systems [7–9]. However, there are still issues open to discussion on how to use the pendant drop method to measure surface tension of liquids. For example, syringe radius should be optimized for each kind of liquid to avoid capillary and necking effects [8, 10]. Also, although according to Bashforth and Adams, surface tension measurements from the study of a drop profile should be independent of drop size, recent studies have shown that the value of surface tension obtained from the analysis of pendant drops may depend on the volume of the drop [11, 12], and that drops as large as possible should be formed in order to obtain accurate values. Recently, we showed that the dependence of surface tension on pendant drop volume may relate to the method used to infer the surface tension from the drop profile [13]. When the surface tension of glycerin was obtained from pendant drop profiles using the empirical formula of Huh and Reed [14] that relates the shape parameter to two diameters of the drops, it was shown to depend on drop volume. When the surface tension of glycerin was calculated using an algorithm based on a robust shape comparison between the experimental and the theoretical profiles developed by Anastasiadis *et al.* [9] the obtained values did not depend on drop volume, but the dispersion of the results was found to decrease with increasing volume. Therefore, in spite of the constant development and widespread use of the pendant drop method, the method can still be improved and should be tested carefully in its use to evaluate the surface tension of low molar mass liquid crystals.

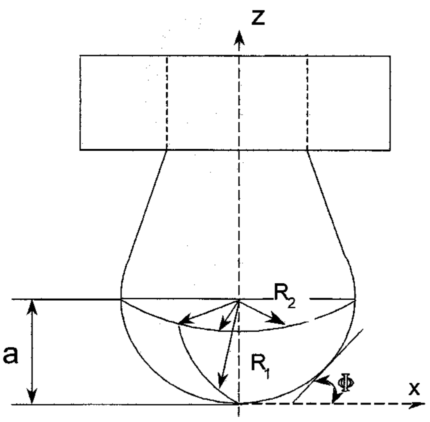


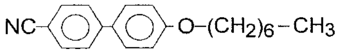
Figure 1. Geometry of a pendant drop.

The goal of the present work was to evaluate the influence of orientational ordering on the interfacial energy between a liquid crystal and a solid thermoplastic. Therefore the surface tension of a LMMLC, 4-cyano-4′-*n*-heptyloxybiphenyl (7OCB), was measured as a function of temperature, for temperatures ranging from 56.0°C to 89.0°C, using the pendant drop method, which was thereby evaluated as a tool to measure the surface tension of a liquid crystal. Contact angles, formed by droplets of 7OCB on surfaces of polystyrene or of a liquid crystal polymer (copolymer of 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid), were also measured and the experimental values used to evaluate the interfacial energy between 7OCB and the two different polymers.

2. Experimental

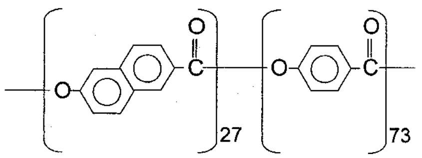
2.1. *Materials*

The low molar mass liquid crystal used in this work was 4-cyano-4′-*n*-heptyloxybiphenyl (7OCB). 7OCB presents a nematic phase melting at 55.0°C and a transition to the isotropic phase at 75.0°C. Its chemical structure is shown below:



It was obtained from Aldrich Chemicals and used without further purification. To our knowledge no surface tension data for 7OCB have previously been published. Only data for the interfacial tension between 7OCB and glycerine have been reported in the literature [15].

Commercially available polystyrene (PS) (Lustrex HH-101 from Estireno do Brasil) and a liquid crystal polymer were also used in this work. The liquid crystal polymer was a random copolymer of 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid, VECTRA A-910 from Ticona Polymers. Its chemical structure is shown below:



2.2. *Methods*

2.2.1. *Surface tension measurements*

The apparatus used in this work is very similar to the one used by Demarquette and Kamal [10]. It consisted of three parts: an experimental cell where the pendant drop was formed, an optical system to monitor the evolution of the drop, and a data acquisition system to infer the surface tension from the geometrical profile of the drop. The drop profile analysis was done using algorithms based on those developed by Anastasiadis *et al.* [9], which are based on a robust shape comparison between the experimental and theoretical profiles generated by solving the Bashforth and Adams equation. A subroutine was developed to measure the volume of the drop and to correct for optical distortion. The algorithms and apparatus used in the present study have been described in detail by Arashiro and Demarquette [16].

Pendant drops of 7OCB were formed in the sample chamber and the temperature was decreased from 89°C to 56°C. The drops were formed in an argon atmosphere. Images of the drop were taken at different temperatures. The surface tension of 7OCB was then evaluated using the drop profile and the density of 7OCB at the corresponding temperature; density values were obtained from the literature [17].

2.2.2. *Contact angle measurements*

For contact angle determination, pellets of PS and VECTRA A-910 were moulded into discs of 25 mm diameter and 1 mm thickness, using a hot press between sheets of PET or aluminum foil. This procedure was used to obtain a smooth surface and non-oriented sample, in the case of VECTRA. A sessile drop of 7OCB was formed on the surfaces of the solid polymers. The temperature in the sample chamber was varied from 56°C to 89°C. The contact angles made by the drops on the surfaces of the polymers were measured 10 min after stabilization of the temperature inside the chamber. The accuracy of contact angle measurement was ±0.5°.

2.2.3. *Evaluation of interfacial energy between 7OCB and solid polymers*

The values of interfacial energy between 7OCB and PS, $\gamma_{7\mathrm{OCB/PS}}$, and between 7OCB and VECTRA, $\gamma_{7\mathrm{OCB/VECTRA}}$, were obtained using Young's equation. When a drop of a liquid rests on a solid surface it forms an angle θ with the surface, called the contact angle. In thermodynamical equilibrium conditions Young [18] showed that:

$$\gamma_{\mathrm{S}} = \gamma_{\mathrm{SL}} + \gamma_{\mathrm{L}} \cos\theta \tag{3}$$

where γ_{S} is the surface energy of the solid, γ_{SL} is the interfacial energy between the solid and the liquid and γ_{L} is the surface tension of the liquid. Therefore, if the angle formed by a drop of a liquid of known surface tension on a solid surface of known surface energy is measured, the interfacial energy between the liquid and solid can be evaluated. The contact angle values and the surface tension of 7OCB necessary for the calculations were measured experimentally as explained above. The values for the surface energy of PS, γ_{PS}, were obtained from a previous work [19]. As VECTRA is solid in the temperature range used in the experiments (there is no phase transition for VECTRA), the values for its surface energy, γ_{VECTRA}, were obtained assuming that γ_{VECTRA} decreases linearly as a function of temperature and adopting a value of 46 mN m^{-1} for γ_{VECTRA} at 20°C, and of -0.06 mN m^{-1} K^{-1} for $\mathrm{d}\gamma_{\mathrm{VECTRA}}/\mathrm{d}T$ [20].

3. Results

The pendant drops of 7OCB obtained had a typical drop shape and it was therefore possible to evaluate the surface tension of 7OCB using the pendant drop method. Similar behaviour has already been reported by Alexopoulos and Franses [21]. Figures 2(*a–c*) show typical pendant drops of 7OCB for three different temperatures (79.5, 67.0 and 74.0°C). The drop obtained at 79.5°C is transparent as can be seen from the clear area in the middle of the drop, corresponding to light crossing the drop coming from the light source of the pendant drop equipment. The drop obtained at 67.0°C is opaque. Although the intensity of the light source in the case of figure 2(*b*) was higher than in the case of 2(*a*), no clear area in the middle of the drop could be observed. This is because at 79.5 and 67.0°C the 7OCB is in the isotropic and nematic phases, respectively. The image of the drop at 74.0°C suggests the presence of a biphase: some shadow can be observed in the clear area in the middle of the drop; the shadow indicates a nematic phase and the clear area an isotropic phase.

Figure 3 shows the surface tension of 7OCB at 72°C, as calculated from the drop profile using the drop shape comparison, as a function of drop volume for volumes ranging from 5 to 11 mm^3. The quality of the fit of the theoretical drop to the experimental drop was equally good for all drop volumes. It was not possible to obtain drops with a volume of more than 11 mm^3: when the volume of the drop exceeded 11 mm^3 the surface forces were unable to support the drop mass and the drop would 'neck', causing detachment from the syringe. It can be seen from figure 3 that the value of surface tension increases as the volume of the drop increases. For drop volumes greater than 9 mm^3, the surface tension seems to be constant; a similar behaviour was observed at each temperature. The variation of surface tension with drop volume has already been observed by other researchers [11, 12] using different drop algorithms. The

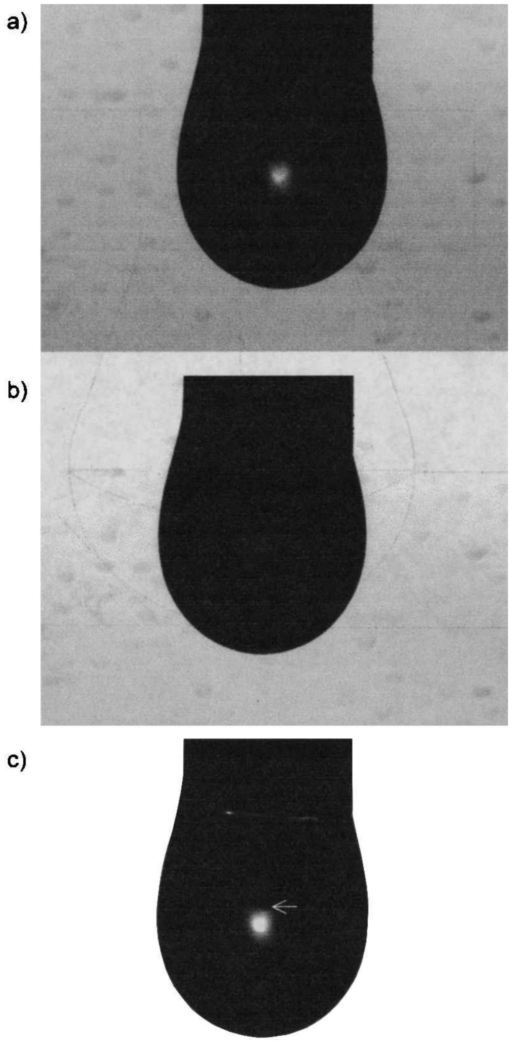


Figure 2. Typical pendant drop of 70CB: (*a*) $T = 79°\mathrm{C}$, (*b*) $T = 67°\mathrm{C}$, (*c*) $T = 74°\mathrm{C}$.

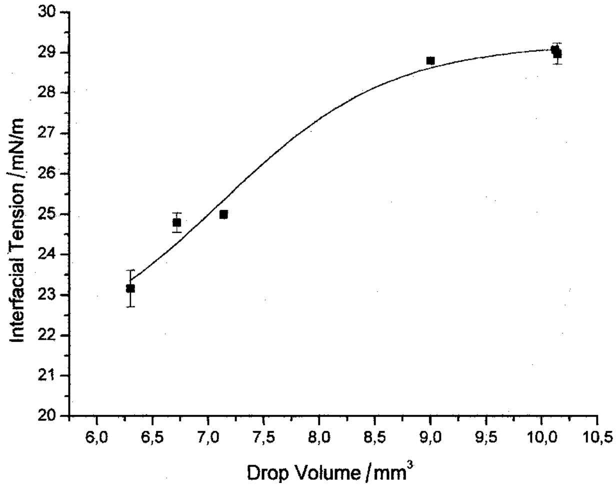


Figure 3. Surface tension of 70CB at 72°C as a function of drop volume.

authors concluded that a minimum drop volume is necessary for the method to be valid. However, such a dependence was not observed for drops of Glycerin using the shape comparison algorithm used in this work [13]. The dependence of surface tension on volume drop size could therefore be due to the nature of the LMMLC. When the drop is too small the syringe tip could have more influence on the orientation of the molecules and therefore influence the value of surface tension. Therefore, in this work only drops with volume equal to or greater than 9 mm^3 were considered for surface tension analysis.

Figure 4 shows the surface tension of 7OCB, γ_{7OCB}, as a function of temperature, for drops of volume equal to or greater than 9.0 mm^3. Figure 5 shows the contact angle made by a sessile drop of 7OCB on surfaces of PS (circles), θ_{PS}, and VECTRA (square), θ_{VECTRA}, as a function of temperature. Figure 6 shows the interfacial tension between 7OCB and PS (circles), $\gamma_{\mathrm{7OCB/PS}}$, and between 7OCB and VECTRA (squares), $\gamma_{\mathrm{7OCB/VECTRA}}$, as a function of temperature, evaluated using equation (2). The values of γ_{7OCB}, necessary for the calculation of $\gamma_{\mathrm{7OCB/PS}}$ and $\gamma_{\mathrm{7OCB/VECTRA}}$, were obtained from figure 2.

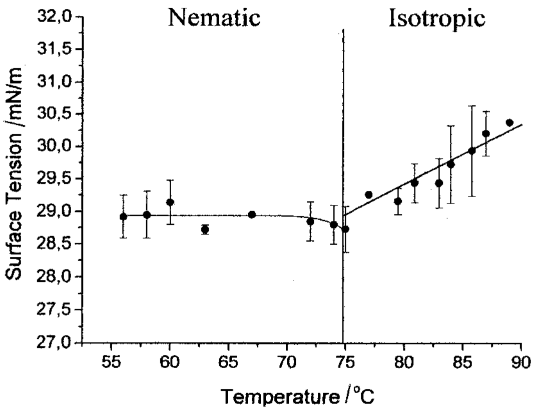


Figure 4. Surface tension of 70CB.

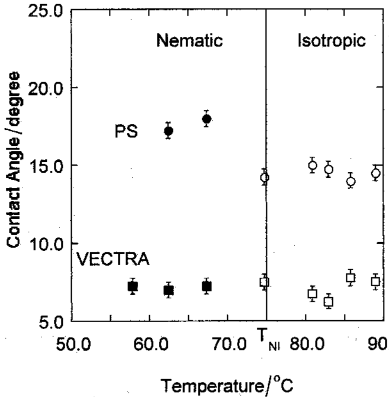


Figure 5. Contact angle formed by a sessile drop of 70CB on PS and VECTRA.

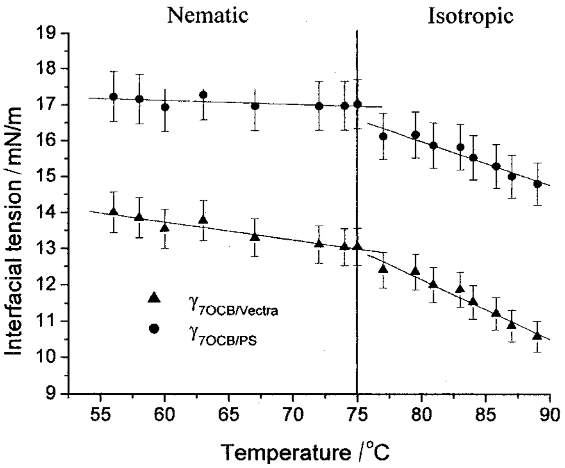


Figure 6. Interfacial tension between 70CB and PS, and between 70CB and VECTRA.

The filled and open symbols in figures 4–6 correspond to the experimental data in the nematic and isotropic phases of 7OCB, respectively. The solid lines shown in figure 4 are a guide for the eye; in figure 6 they correspond to the best fit obtained by linear least square regression of the data.

4. Discussion

4.1. *Surface tension of 7OCB*

To our knowledge there are no reported data for the surface tension of 7OCB, with which to make a direct comparison. The values obtained in this work are of the same order of magnitude as those obtained by Song and Springer [22, 23] who evaluated the surface tension of 5CB by the pendant drop method, but are slightly higher than those reported by Gannon and Faber [24] who evaluated the surface tension of 5CB and 8CB using the Wilhelmy plaque method. Such a discrepancy could be due to the different method used by Gannon and Faber or to the difference in chemical structure between the CB and OCB family.

Recently, Mach *et al.* [25, 26], used the properties of a LMMLC in the smectic phase (in the smectic phase the LMMLC can be spread into a free standing film) to develop an elegant method to measure its surface tension. A film with a thickness ranging from 2 to 30 layers of LMMLC is spread across a hole, its boundary formed on three sides by the hole itself and on the remaining side by a string. The surface tension of the film deforms the string into an arc to minimize the film surface. Once thermodynamical equilibrium is obtained, the surface tension can be measured from the radius of curvature of the string. Due to the smectic character of the LMMLC, the molecules are arranged perpendicular to the free surface. Using this method, Mach *et al.* were able to tailor the chemical group at the surface and study the dependence of surface tension on specific terminal groups and to evaluate the surface tension of various LMMLCs in the smectic phase. They observed that the values fell into major categories according to chemical structure. Values of 27, 24, 21, 13 and 11.5 mN m^{-1} were obtained. The values obtained for 8OCB and 12OCB were of the order 26 mN m^{-1} lower than those obtained here for 7OCB which were of the order 29–30 mN m^{-1}. The discrepancy between the results obtained by Mach *et al.* and those obtained here may be due to the difference of experimental method used and the fact that 7OCB does not exhibit a smectic phase. The method developed by Mach *et al.* for the smectic phase induces a layered structure that leads to a free surface containing CN or CH_3 groups. In the pendant drop a variety of molecular orientations is possible at the free surface (including alignment of the long axis parallel to the surface leading to the presence of CH_2 and phenyl groups at the surface) that can lead to higher values of surface tension [27].

It can be observed from figure 4 that γ_{7OCB} decreases as temperature increases, for temperatures ranging from 56.0 to 75.0°C. A clear discontinuity of γ_{7OCB} can be observed near the nematic to isotropic transition temperature, T_{NI}. This transition is a first order transition and discontinuities of physical properties such as specific volume, heat capacity, index of refraction and surface tension are expected for those temperatures [28]. Discontinuities of LMMLC surface tension at T_{NI} of the same order of magnitude have already been observed by other researchers [23, 24]. For temperatures ranging from T_{NI} to 89.0°C, γ_{7OCB} increases with increasing temperature.

Due to the lack of data for the surface tension of 7OCB, no direct comparison with other results could be done. The influence of temperature on LMMLC surface tension has been reviewed extensively by Song and Springer [22]. They reported a large discrepancy between the different experimental studies reported in the literature. While some studies report a 'normal behaviour' of the LMMLC surface tension as a function of temperature (i.e. $d\gamma/dt < 0$ for both the nematic and isotropic state), other studies report that close to the nematic to isotropic transition $d\gamma/dt$ can be positive, and that the surface tension may show a discontinuity.

In order to clarify this puzzling issue, Song and Springer [23] measured the surface tension of various LMMLCs as a function of temperature using the pendant drop method. They observed basically three types of behaviour, corresponding to the theoretical predictions of Martinez *et al.* [29], depending on the nature of the LMMLC. For EBBA (4′-ethoxybenzylidene-4-*n*-butylaniline) it was observed that the surface tension decreases as a function of temperature in the nematic phase and increases for temperatures ranging from $T_{NI} - 10°$ to T_{NI} showing a discontinuity at T_{NI}. For temperatures corresponding to the isotropic state of EBBA, Song and Springer observed that the surface tension decreased with increasing temperature. For M11CN and M11CH$_3$ the authors observed that the surface tension increased with increasing temperature for temperatures corresponding to the nematic phase and temperatures just above the nematic to isotropic transition. For temperatures much above T_{NI} they observed that the surface tension decreased with increasing temperature. For 5CB the authors observed a decrease of surface tension with increasing temperature for temperatures corresponding to both the nematic and isotropic phase and a discontinuity at T_{NI}. The behaviour they observed for 5CB was different from that seen by Gannon and Faber [24] who observed an increase of surface tension with increasing temperature for temperatures corresponding to the nematic phase. Song and Springer attributed this discrepancy to the possible presence of impurity in their sample. They also observed that a positive value of $\mathrm{d}\gamma/\mathrm{d}T$ for temperatures just below T_{NI} seems to be more common for LMMLC for which the melting temperature is close to the T_{NI}, because the existence of a nearby low temperature high ordered phase could favour the formation of high ordered structures at the surface. This observation corroborates the results obtained here. The surface tension of 7OCB was shown to decrease for the whole range of temperatures corresponding to the nematic phase and did not show an 'anomalous' behaviour (i.e. $\mathrm{d}\gamma/\mathrm{d}T > 0$) for temperatures corresponding to the nematic phase.

The entropy of surface or interphase formation can be easily inferred [5] from the values of surface tension or interfacial tension, respectively, as functions of temperature [5]. At constant volume the entropy per unit area of interphase formation, $\Delta S''$, is given by:

$$\Delta S'' = -\frac{\mathrm{d}\gamma}{\mathrm{d}T}. \tag{4}$$

It can be seen from figure 1 that for temperatures corresponding to the nematic phase of 7OCB, the entropy of surface formation, $(\Delta S'')_{7OCB}$, is positive, meaning that there is an increase of disorder ongoing from the bulk to the surface of the drop. Such a behaviour corroborates the observations of Song and Springer [23]. It can also be seen that $(\Delta S'')_{7OCB}$, and therefore the difference in order between bulk and surface, increases with increasing temperature. This may be explained by a probable increase of disorder of the surface caused by an increase in temperature and by the proximity of a phase transition. For temperatures ranging from T_{NI} to 89°C, $(\Delta S'')_{7OCB}$ is negative. The same type of behaviour has been observed by George *et al.* who measured interfacial tension between 7OCB and glycerine using a spinning drop apparatus [15, 30].

The results obtained here can be explained by the theoretical considerations of Croxton and Chandrasekhar [31]. For normal liquids $\Delta S''$ is positive. This suggests that the molecules at the surface are less ordered than those in the bulk, most likely due to the freedom of molecules at the surface. According to Croxton and Chandrasekhar, for liquid crystalline systems $-\mathrm{d}\gamma/\mathrm{d}T$ and therefore $\Delta S''$ results from a competition between the orientational ordering and the spatial disorder developed at the surface of the liquid crystal. Just above the melting temperature, the spatial disorder may be sufficiently low that the order at the liquid surface may be higher than in the bulk region, resulting in a negative value of $\Delta S''$. As the temperature increases, the spatial disorder at the surface increases, and the relaxation of the molecules at the surface decreases the surface order more than of the bulk and therefore $\Delta S''$ becomes positive. At T_{NI} the bulk order parameter suffers a discontinuity (first order transition), whereas a small residuum of orientational order at the isotropic phase can be observed. This implies a discontinuous change of absolute value of surface tension and a second region of negative $\Delta S''$, which is observed in the experimental results reported in this work. The increase of surface tension with increasing temperature for temperatures just above T_{NI} can be explained by a nematic wetting of the isotropic vapour surface [32, 33]. For temperatures much above T_{NI} the surface tension is expected to decrease when temperature increases. The negative value of $\Delta S''$ for temperatures close to the melting temperature was not observed here, within experimental error. However, it can be seen from figure 4 that $\Delta S''$ increases as temperature increases, corroborating the theoretical predictions of Croxton and Chandrasekhar. The increase of surface tension with increasing temperature for temperatures just above T_{NI} was observed here, indicating that there might be a nematic wetting of the isotropic vapour surface. However, for temperatures much above T_{NI} the experimental results showed that the surface tension still increases as a function of increasing temperature. This anomalous behaviour could be due to the increasing disorder of the molecules which would enhance the presence of CH$_2$ and phenyl groups at the surface at the expense of CH$_3$ or CN groups that have a lower surface energy.

4.2. *Contact angles formed by drops of 7OCB on solid polymers*

Figure 5 shows the values of contact angle formed by drops of 7OCB on a surface of PS, θ_{PS}, and VECTRA, θ_{VECTRA}, as functions of temperature. For both polymers the contact angle is constant for temperatures corresponding to the nematic and isotropic phases of 7OCB. The average values of contact angle formed by drops of 7OCB on the surfaces of PS and VECTRA, for both the nematic and isotropic phases of 7OCB are reported in table 1. These values show that θ_{PS} depends on the phase of 7OCB (17.6° for the nematic phase and 14.5° for the isotropic phase) and that θ_{VECTRA} is constant (7.2° for both phases), independant of the phase of 7OCB. This suggests that the nematic order of the molecules of 7OCB at the interphase between 7OCB and the solid polymers has less influence on θ_{VECTRA} than on θ_{PS}. This is probably due to the higher affinity between 7OCB and VECTRA which are both polar. In the case of PS a smaller affinity, evidenced by a higher value of the contact angle, could allow the molecular order to have more influence on θ_{PS}.

4.3. *Interfacial energy between 7OCB and the solid polymers*

It can be seen from figure 6 that the value $\gamma_{7OCB/VECTRA}$ and $\gamma_{7OCB/PS}$ are quite high when compared with values of interfacial tension between two molten polymers. It should be remembered that in order to evaluate interfacial tension energy between 7OCB and PS and between 7OCB and VECTRA, the value of surface energy of PS and VECTRA had to be used; see equation (3). Due to the methods used to measure surface energy of solids there is a great discrepancy between the values published in the literature [19]. This discrepancy could affect the absolute value of interfacial energy but not its behaviour as a function of temperature.

It can also be seen from figure 6 that for both the nematic and isotropic phases of 7OCB, $\gamma_{7OCB/PS}$ and $\gamma_{7OCB/VECTRA}$ decrease linearly with increasing temperature. The coefficients of the linear least square regression of the data (obtained by fitting the interface energy as a function of temperature) for both states of 7OCB and both polymers are shown in table 2. For temperatures approaching T_{NI}, both $\gamma_{7OCB/VECTRA}$ and $\gamma_{7OCB/PS}$ show a clear dicontinuity, most likely due to the first order transition from the nematic to the isotropic phase of 7OCB.

Even allowing for the discrepancies for the surface energy of PS and VECTRA, it can be seen from figure 6 that the values $\gamma_{7OCB/VECTRA}$ are lower than $\gamma_{7OCB/PS}$. These results are probably due to a better affinity between 7OCB and VECTRA than between 7OCB and PS. Similar behaviour has been seen by Runke *et al.* [34] who measured a much smaller value of interfacial energy between a side group LCP and polymethylmethacrylate than between the same LCP and polyethylene.

Table 1. Contact angles θ (degrees) made by drops of 70CB on the surfaces of PS and VECTRA in the nematic and isotropic phases.

Phase	PS	VECTRA
Nematic	17.6 ± 0.5	7.2 ± 0.5
Isotropic	14.5 ± 0.5	7.2 ± 0.5

Table 2. Influence of temperature on interfacial energy ($mN\,m^{-1}$): linear regression coefficients of $\gamma = a - bT$.

Phase	γ7OCB/PS	γ7OCB/VECTRA
Nematic	$\gamma = 17.15 \pm 0.01T$	$\gamma = 16.72 - 0.05T$
Isotropic	$\gamma = 27.02 - 0.137T$	$\gamma = 25.30 - 0.16T$

For temperatures corresponding to the nematic phase of 7OCB, $(\Delta S'')_{i/j}$ is positive for both systems and very small for PS/7OCB. This suggests that there is a decrease in the order of the molecules of 7OCB going from the bulk of the drop to the interphase. The highest value of $(\Delta S'')_{i/j}$ is probably due to the highest affinity of 7OCB with VECTRA and also to a higher value of $-\partial\gamma/\partial T$ for VECTRA than for PS [19, 20]. It should be noted here that the liquid crystalline nature of VECTRA has no influence on the interfacial tension since VECTRA was solid all the time. For temperatures corresponding to the isotropic phase of 7OCB, $(\Delta S'')_{i/j}$ is positive for both systems, showing behaviours similar to those reported for polymer pairs or other pairs of liquid [35–37].

5. Conclusions

The experimental results presented here show that the value of surface tension of a liquid crystal obtained from the analysis of a drop profile depends on the volume of the drop, and that a drop as large as possible (close to detachment) should be used in order to obtain accurate values by this method.

It has been shown that the entropy of surface formation of 7OCB is positive in the nematic phase, increasing with increasing temperature; and that for the isotropic phase it is negative, most likely due to a nematic wetting of the isotropic vapour surface and to an increase of disorder of the molecules that could enhance the presence of CH_2 and phenyl groups at the surface at the expense of CH_3 or CN groups. A discontinuity of the surface tension was observed near the nematic to isotropic transition temperature, T_{NI}.

The contact angles formed by sessile drops of 7OCB on surfaces of PS and VECTRA were constant as a function of temperature for ranges of temperature corresponding to the nematic and isotropic phases of 7OCB. The contact angle formed by drops of 7OCB on PS surfaces was greater for nematic phase temperatures than for isotropic phase temperatures. The contact angle formed by drops of 7OCB on VECTRA surfaces did not depend on the 7OCB phase.

For both 7OCB/PS and 7OCB/VECTRA systems the entropy of interphase formation, $(\Delta S'')_{i/j}$, was positive for the nematic and isotropic phases of 7OCB. $\gamma_{7\mathrm{OCB/VECTRA}}$ was lower than $\gamma_{7\mathrm{OCB/PS}}$, and the absolute values of the entropy of interphase formation, for both phases of 7OCB, were larger for 7OCB/VECTRA system than for 7OCB/PS system. This was probably due to a better affinity between 7OCB and VECTRA than between 7OCB and PS.

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