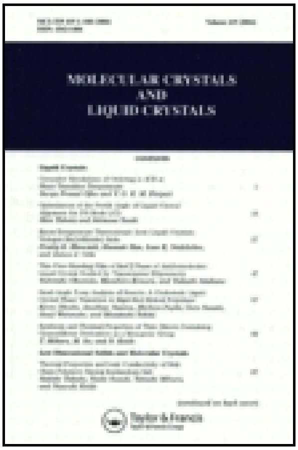

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Influence of Temperature on Surface Tension of Liquid Crystals in the Cyanobiphenyl and Cyano-oxybiphenyl Series

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The surface tension of low molar mass liquid crystals from the nCB and nOCB series was evaluated for temperatures, T, corresponding to the different phases of the materials, using the pendant drop method. With the exception of the materials which presented a smectic phase, and far from the transition temperatures the surface tension was shown to decrease with increasing temperature. The atypical behaviors (discontinuities of surface tension, γ, and of $\partial\gamma/\partial T$, upward jump, and increase of surface tension with increasing temperature) that were observed for temperatures in the proximity of the transition temperatures and for the materials that presented a smectic phase, was explained in light of the ordering of the molecules.

Keywords: OCB and CB liquid crystals; pendant drop method; surface tension

INTRODUCTION

The surface tension of low molar mass liquid crystals (LMMLCs) has been the subject of intense research [1–27], due to the importance of these materials in displays and electro-optical devices areas [28–29]. The study of surface tension of LMMLC and interfacial energy between LMMLC and thermoplastics can be of great interest, because

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it will help understanding the influence of the ordering of the liquid crystal at the interface between liquid crystals and thermoplastics which can be important for composite materials. For example, microdroplets 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, they can switch from a transparent state to a light scattering state when submitted to a low voltage [28]. 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 [28].

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 method, etc [30]. It has been reported that the pendant drop method may be the most appropriate to measure the surface tension of a liquid crystal [11], 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 which is extremely sensitive to wall effects. The pendent drop method involves the determination of the profile of a drop of liquid suspended in air at mechanical equilibrium [31]. The profile of the drop is determined by the balance between gravity and surface forces. The equation of Bashforth and Adams [32] which is based on Laplace's equation, relates the drop profile to the surface tension through a non-linear differential equation [33].

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

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

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

In this work, the effect of temperature on the surface tension of low molar mass liquid crystals (LMMLCs) from the cyanobiphenyl (nCB) and cyanoxybiphenyl (nOCB) series (n = 5, 6, 7 and 8) was evaluated for ranges of temperatures corresponding to the different mesophases

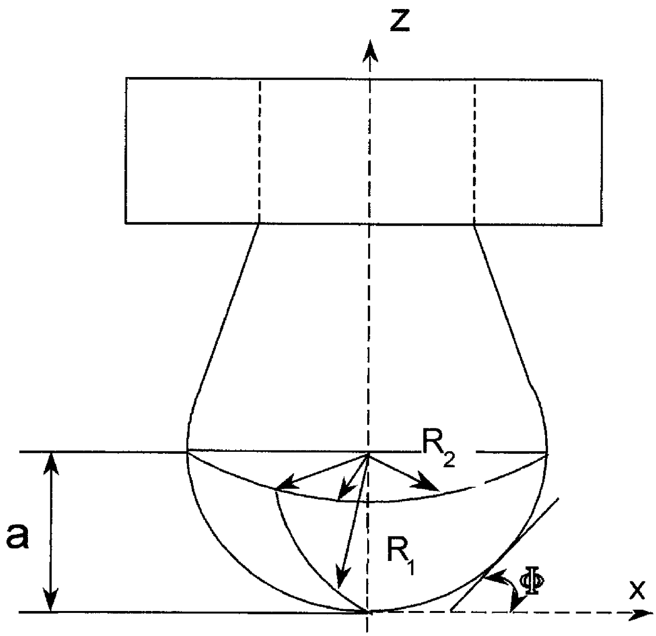


FIGURE 1 Geometry of a pendant drop.

(nematic, smectic and isotropic) of the materials, using the pendant drop method.

EXPERIMENTAL

Materials

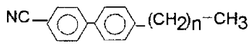
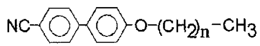
Liquid crystals (LMMLCs) from the cyanobiphenyl (nCB) and cyanoxybiphenyl (nOCB) series (n = 5, 6, 7 and 8) were used in this work to study the influence of temperature, of alkyl chain length and the presence of oxygen atom on the surface tension of these liquid crystals. The chemical structure and the values of the transition temperatures of the liquid crystals used in this work are reported in Table 1.

Experimental

Surface Tension Measurements

The surface tension of the LMMLCs studied in this work was evaluated using the pendant drop method. The apparatus used in this work is very similar to the one used by Demarquette and Kamal

TABLE 1 Chemical Structure Transition Temperatures of the Liquid Crystals used in this Work

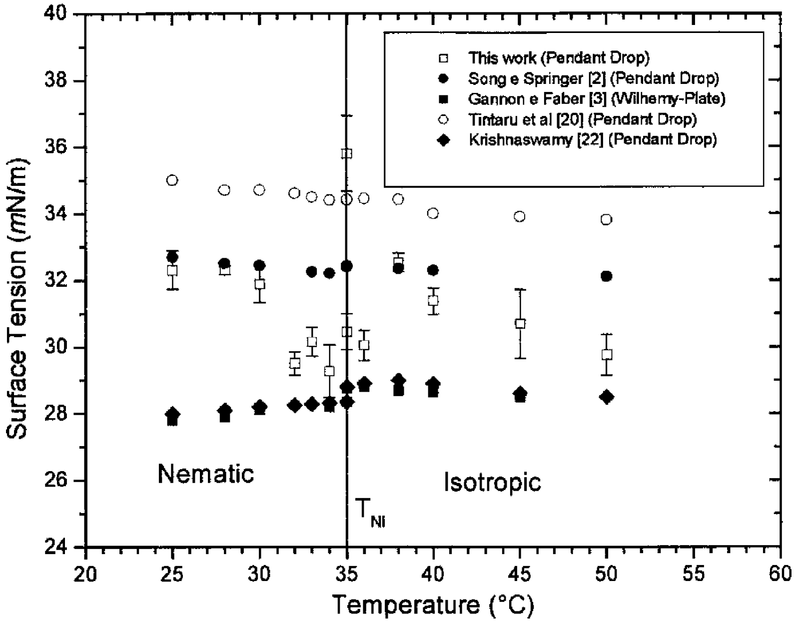
Liquid crystals	Chemical Structure	n	T_{SSm}	T_{SN}	T_{SmN}	T_{NI}	Supplier
nCB		5	–	23,0°C	–	35,0°C	
		6	–	14,5°C	–	29,5°C	
		7	–	31,0°C	–	44,0°C	
		8	20,0°C	–	34,0°C	41,0°C	
nOCB		5	–	54,0°C	–	68,0°C	Sigma Aldrich
		6	–	57,0°C	–	76,0°C	
		7	–	55,0°C	–	75,0°C	
		8	52,0°C	–	67,0°C	80,0°C	

[34]. 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*. [35], 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 [36]. The algorithms and apparatus used in the present study have been described in detail by Arashiro and Demarquette [33]. Pendant drops of liquid crystals were formed in the sample chamber. A temperature controller was used to maintain the sample at the temperature at which it was desired to measure surface tension with a precision of ± 0.3. For each temperature, a new (single) drop was formed. The drops were formed in an argon atmosphere. The values of surface tension were obtained when the drop reached mechanical equilibrium (about 5 minutes). The surface tension of liquid crystals were then evaluated using the drop profile and the density of LMMLCs at the corresponding temperature. The density for nCBs, 6OCB and 7OCB were obtained from the literature [20,37,38]. The density for 5OCB and 8OCB values were inferred from PVT measurements which were obtained using a dilatometer manufactured by Gnomix. The experimental procedures have been described in another work [39].

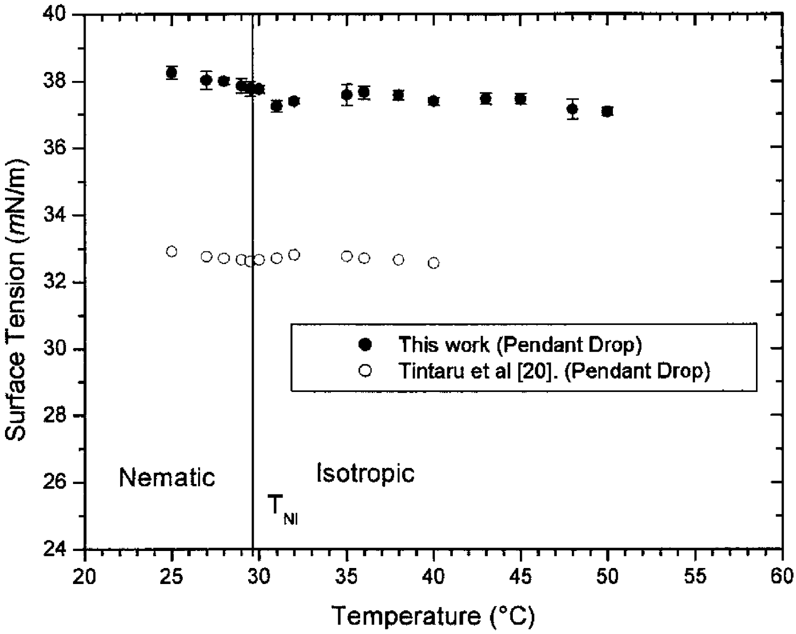
RESULTS AND DISCUSSION

Figures 2a–h show the surface tension of nCBs and nOCBs as a function temperature. The different symbols in Figures 2a–h correspond to the experimental data in smectic, nematic and isotropic phases of nCBs and nOCBs obtained in this work and data reported in literature.

It can be seen from Figures 2a–h that the values of surface tension obtained in this work are in relatively good agreement with the ones reported in the literature considering the large range of data reported by other authors (see Fig. 2a). The results seem to indicate that a) For the LMMLC containing an odd number of CH_2 group, a clear discontinuity of the values surface tension can be observed at T_{NI}. Similar behavior was observed by other researchers [2,3,20,22] for 5CB although the magnitude of the discontinuity observed was much smaller (see Fig. 2a). In some cases, (5CB), it was even observed that the surface tension could adopt two distinct values at the T_{NI}. This behavior could to due to the dual structure that can observed at the

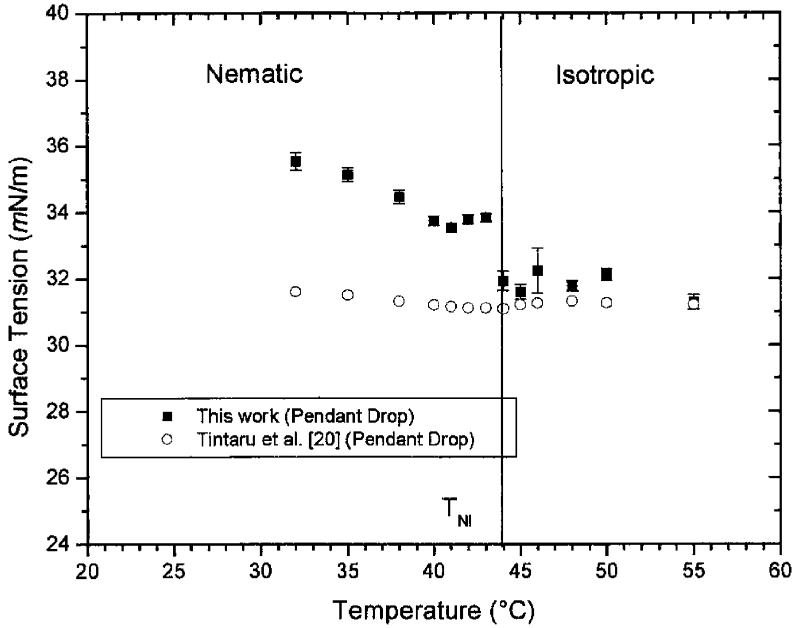


(a)

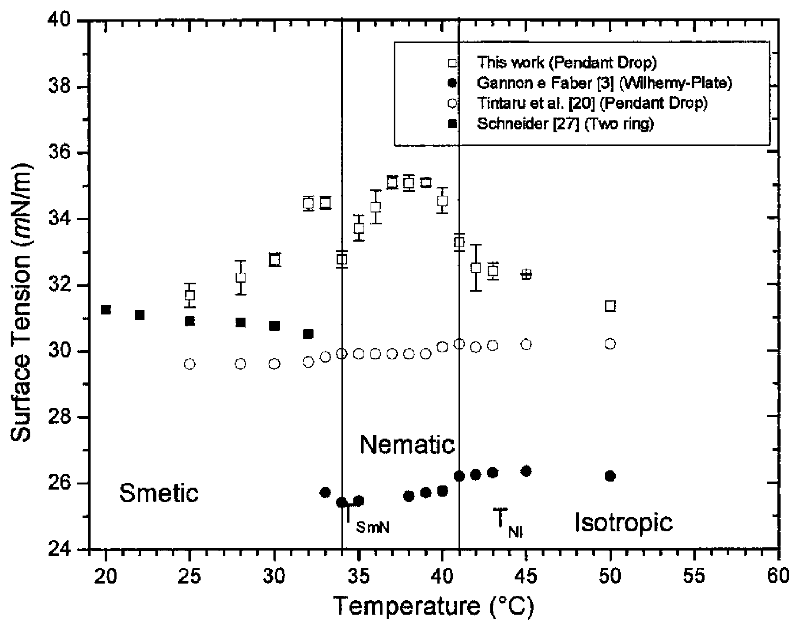


(b)

FIGURE 2 Surface tension of nCBs and nOCBs: a) 5CB, b) 6CB, c) 7CB, d) 8CB, e) 5OCB, f) 6OCB, g) 7OCB, h) 8OCB.



(c)



(d)

FIGURE 2 Continued.

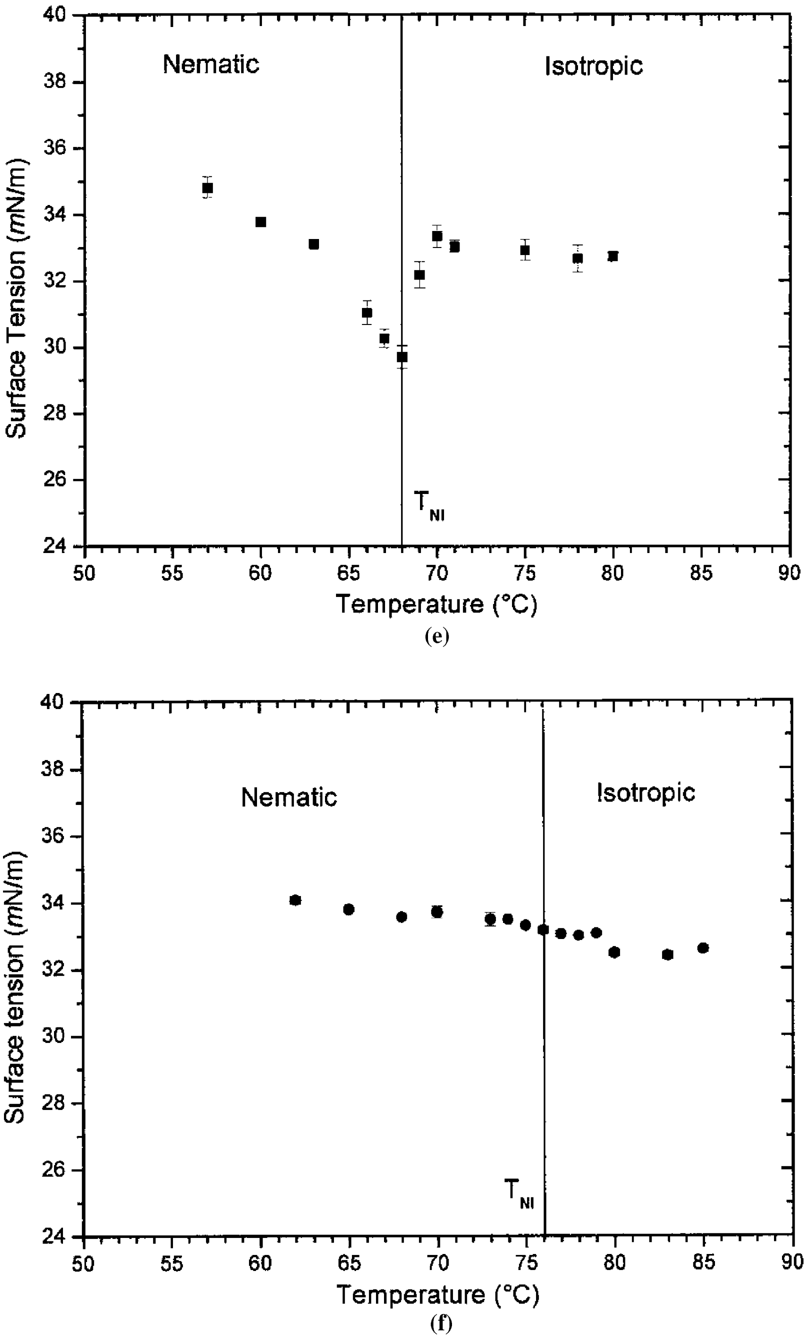
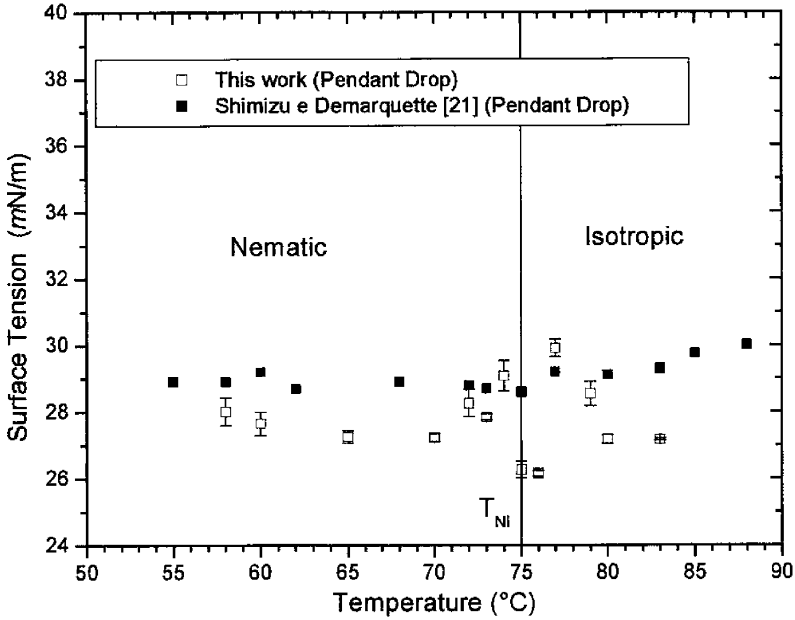
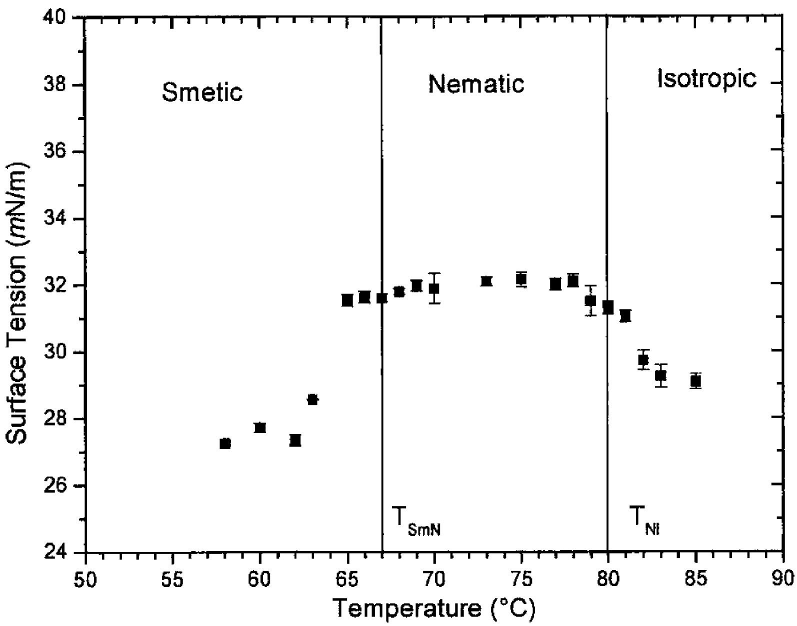


FIGURE 2 Continued.



(g)



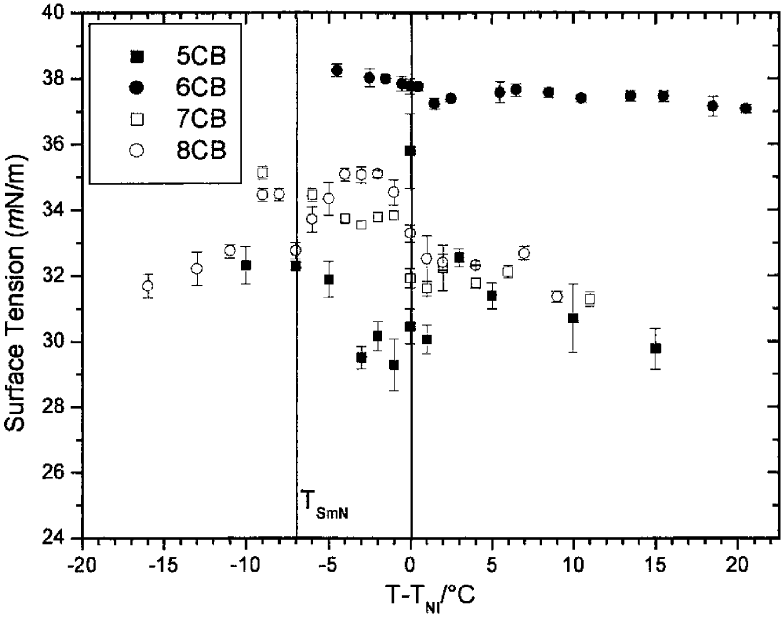
(h)

FIGURE 2 Continued.

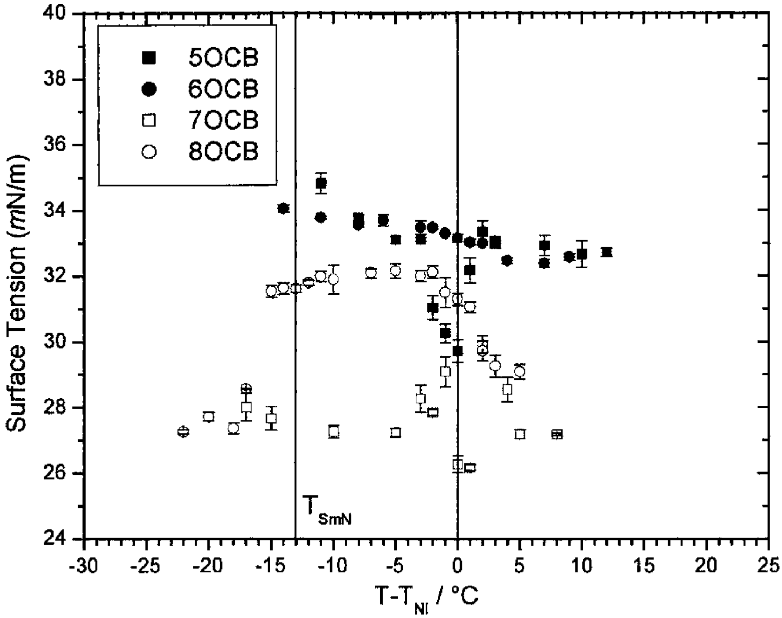
transition temperature [21]. b) For the LMMLCs containing an even number of CH_2 group, only a change of $\partial\gamma/\partial T$ without a discontinuity of γ can be observed. This transition (transition temperatures nematic–isotropic) is a first order transition and discontinuities of physical properties such as specific volume, heat capacity, index of refraction and surface tension are expected for those temperatures [40]. An upward jump of surface tension can also be observed at temperatures at the proximity of T_{NI} for the LMMLCs containing an odd number of CH_2 group. This jump may be explained by a possible presence of an order of the LMMLC molecules at the surface of drop, most likely due to a nematic wetting of the isotropic vapour surface at temperatures close T_{NI} [41, 42]. The results presented in Figures 2d and 2h show that at T_{SmN} the surface tension of both 8CB and 8OCB also present a discontinuity. This behavior has never been reported before.

For all LMMLC studied in this work, with the exception of 8CB and 8OCB which present three phases, the surface tension decreases with increasing temperature for temperatures corresponding to both the nematic and isotropic phases and far from the transition region ($T < T_{NI}$ –4°C and $T > T_{NI} + 4$°C). Similar behavior was reported by Song and Springer [2] and Tintaru *et al*. [20] as can be seen in Figure 2a. For temperatures just above of T_{NI}, the surface tension of the LMMLC containing an odd number of CH_2 group increases with increasing temperature. These results are in good agreement with the studies of Tintaru *et al*. [20] and Krishnaswamy [22] although once again the magnitude of the increase observed in the present work is larger than the one observed by the other authors. This increase of surface tension cannot be seen for 6CB and 6OCB, for which the mild increase that can be observed in Figures 2b and 2f is within experimental error. The increase of surface tension with increasing temperature indicates that the entropy of surface formation, $\Delta S'' = -d\gamma/dT$, is negative. $\Delta S'' < 0$ corresponds to presence of an order of the molecules at the surface so that there is an increase of order ongoing from the bulk to the surface of the drop.

In the case of 8CB and 8OCB, the surface tension increases with increasing temperature for temperatures which correspond to the smectic phase. For temperatures corresponding to the nematic phase, the experimental data seem to indicate that for both substances, the surface tension increases presents a maximum and then decreases. For temperatures corresponding to the isotropic phase, the surface tension decreases. The discrepancy that can be observed between the values obtained in this work for 8CB and the ones of Gannon and Faber [3] and Schneider [27] could be attributed to the use of



(a)



(b)

FIGURE 3 Surface tension of nCBs and nOCBs as a function of relative temperature: a) nCBs, b) nOCBs.

the different methods to evaluate the surface tension. However, no explanation could be found to explain the discrepancy between our data and the ones Tintaru *et al*. [20].

Figures 3a and 3b show the surface tension of the different cyano-biphenyl (nCBs) and cyano-oxybiphenyl (nOCBs) studied in this work as a function relative temperature.

It can be seen that the value of surface tension of the different LMMLCs, at T_{NI}, can be ranked in the following order: $\gamma_{5CB} < \gamma_{7CB} < \gamma_{8CB} < \gamma_{6CB}$ and $\gamma_{7OCB} < \gamma_{5OCB} < \gamma_{8OCB} < \gamma_{6OCB}$. The observed phenomenon may be related to the odd–even effect that can be observed for some of the properties of homologous series of LMMLC [43].

CONCLUSIONS

In this work, the surface tension of low molar mass liquid crystals (LMMLCs) from the cyanobiphenyl (nCB) and cyanoxybiphenyl (nOCB) series ($n = 5$, 6, 7 and 8) was evaluated for ranges of temperatures corresponding to the different mesophases (nematic, smectic and isotropic) of the materials, using the pendant drop method.

A clear discontinuity of value of surface tension but only of the value of $\partial\gamma/\partial T$ was shown for LMMLC with an odd and even number of CH_2 groups respectively. For temperatures just above T_{NI} an upward jump of the values of surface tension, which was explained by a nematic wetting of isotropic vapour surface, was observed for the LMMLC with an odd number of CH_2 groups. Discontinuities of values of surface tension were also observed at T_{SmN} for 8CB and 8OCB.

For the LMMLC which only presented a nematic and isotropic phases, and far from T_{NI} ($T < T_{NI} - 4°C$ and $T > T_{NI} + 4°C$) the surface tension was shown to decrease with increasing temperatures. In the case of 8CB and 8OCB, the surface tension was shown to increase with increasing temperature for temperatures corresponding to the smectic phase, show an atypical behavior for temperatures corresponding to the nematic phase and decrease for temperatures corresponding to the isotropic phase. An odd–even effect was observed for the surface tension values at T_{NI} of the LMMLC studied in this work.

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