Surface tension of some liquid crystals in the cyanobiphenyl series

M. Tintaru; R. Moldovan; T. Beica; S. Frunza

PLEASE SCROLL DOWN FOR ARTICLE

Surface tension of some liquid crystals in the cyanobiphenyl series

M. TINTARU, R. MOLDOVAN*, T. BEICA and S. FRUNZA

National Institute for Materials Physics, Bucharest-Magurele CP Mg-07, R-76900,
Romania

The temperature dependence of the surface tension was measured by the pendant drop method for four compounds from the homologous series of alkylcyanobiphenyls (*n*CB), in the nematic liquid crystal and isotropic phases. For 8CB (octylcyanobiphenyl) the temperature dependence was also measured in the smectic range. Not very close to the isotropic transition temperature, and with the exception of 8CB, the surface tension decreases with increase in temperature in the nematic range. A downward jump at the transition temperature was observed for all liquid crystals studied. The shape of the drop in the smectic A phase of 8CB gives indications of stratification in a system of terraces.

1. Introduction

The surface tension of nematic and smectic liquid crystals has been the subject of a number of experimental studies [1–9]. It is discontinuous in most liquid crystals near the nematic–isotropic transition temperature, T_{NI} [1–3], with some exceptions [4]. The dispersion of the published experimental values for the surface tension for the same liquid crystal [5] can be attributed either to the measurement method or to the degree of purity of the substance. Concerning the former point, in our opinion a static method of measurement is best suited to liquid crystals because the equilibrium value of the surface tilt angle is reached. For smectics, where the equilibrium is reached even more slowly, the use of a static method is essential.

In this paper we present the results of determination of the temperature dependence of the surface tension and density for the liquid crystals of four members of the 4-alkyl-4′-cyanobiphenyl (*n*CB) homologous series. We used the static pendant drop method described in §2. In §3 the experimental data are presented and discussed. An anomalous behaviour around the isotropic transition temperature was observed for all the liquid crystals studied. The static method of measurement allows surface tension determination for 8CB (octylcyanobiphenyl) in the smectic range, although some small systematic deviations of the experimental drop shape from the theoretical shape were detected.

2. Experimental

The measurements were performed on four liquid crystals from the 4-alkyl-4′-cyanobiphenyl homologous

*Author for correspondence; e-mail: rodi@alphal.infim.ro

series: $C_nH_{2n+1}(C_6H_4)_2CN$ with $n = 5, 6, 7, 8$. The substances (Aldrich, purity 98%), were used without supplementary purification. The values of the transition temperatures we determined are listed in table 1.

The pendant drop method is based on exact theory [10] and is independent of the wetting angle. The method consists in taking images of a steady drop formed at the planar and horizontal end of a circular capillary tube with sharp edges. The one we used had a 4.035 ± 0.001 mm diameter. The images were taken by a digital capture system with a Kodak Megaplus Camera, Model ES 1.0. A Pascal code written by us processed the data, finding the outline of the drop image. The co-ordinates (x_e, z_e) of the drop edge were obtained using the edge detection algorithm [11] to be described in a future publication (sketched in the next). A window with a half-width of 8 pixels around the pixel of the x_c co-ordinate was used. We made a fitting of the light intensity for the pixels

Table 1. Liquid crystal materials used. T_{SmAN} = transition temperature from smectic A to nematic phase; T_{NI} = transition temperature from nematic to isotropic phase. M = molar mass, P = average value of the parachor.

Homologue no.	Transition temperature/°C		$M/$ g mol^{-1}	$P/$ CGS units
	T_{SmAN}	T_{NI}		
5	—	35.2	249	589
6	—	28.3	263	628
7	—	42.3	277	665
8	33.4	40.3	291	703

in the window, using the five parameter (a, b, c, x_e, w) formula:

$$I(x) = a + b(x - x_e) + \frac{2c}{\pi} \arctan\left(\frac{x - x_e}{w}\right). \quad (1)$$

If the x_e parameter obtained by the fitting process does not differ by more than 0.5 pixel from the x_c co-ordinate of the middle of the window, then the x_e value is considered as the x co-ordinate of the profile. If this is not the case, the window is moved toward the centre of the image until the condition is fulfilled or the image centre is reached (in this last case there is no drop at the considered z_e level). In this manner, neglecting diffraction effects, the drop profile co-ordinates are obtained with a precision better than 0.1 pixel.

The drop was enclosed in an airtight chamber filled with nitrogen. The chamber was thermostatted with a precision better than 0.02°C. The ratio of the surface tension to the density, γ/ρ, was computed at each temperature from the shape of the drop. Several determinations at the same temperature were performed until a reproducible and minimum value was obtained, indicating attainment of the equilibrium state. For 8CB in the smectic A phase, the waiting time was up to 2 h. We used the method of computation described in [12], but the number of measured points was significantly enlarged (from ≈ 10 to ≈ 700). As a test, we measured the surface tension of pure water and benzene, with results within 0.5% of the standard values.

In figure 1 we present deviation curves of the experimental results from the theoretical profile for the smectic
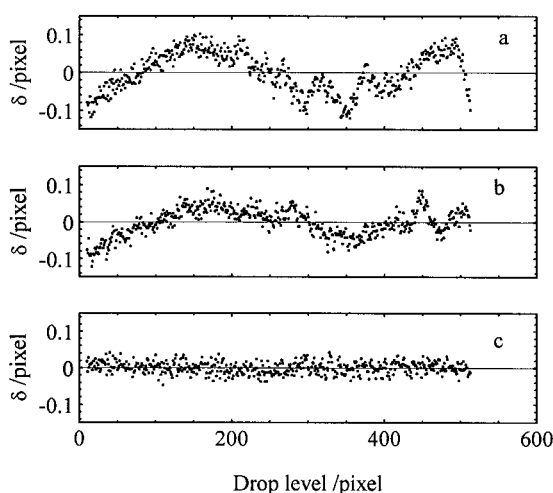

Figure 1. Curves describing the deviation δ of the experimental from the thoretical drop profiles. (*a*) Left side of the drop in the smectic phase; (*b*) right side of the drop in the smectic phase; (*c*) drop in the nematic phase. Image to objective plane magnification factor: 168.60 pixel/mm. Positive and negative values of δ correspond to the points outside and inside the theoretical drop profile, respectively.

phase, figures 1 (*a*) and (*b*), and the nematic phase figure 1 (*c*). The deviation δ is given by the distance, measured on the normal to the theoretical curve, between an experimental point and the curve. The drop image was analysed only after a chosen interval. It can be seen that for the nematic phase the very small deviations are almost uniformly distributed, while, for the smectic case, deviations that either alter or do not alter the axial symmetry of the drop are observed. We believe that the first type of deviation is a sign of drop stratification involving a system of terraces separated by steps (wedge disclinations) [13, 14] and that the second type are probably due to constraints caused by the solid-like behaviour in a direction normal to the smectic layers. We realize that the application of the theory used for the determination of the drop shape, adequate for isotropic as well as nematic liquids, is only an approximation when it is applied to smectics. Another error source for surface tension determination of smectics can arise from the fact that, on the drop surface the equilibrium orientation of the director, which is known to be homeotropic for nCBs [15], can be perturbed by the curvature. The surface tension of liquid crystals being anisotropic, the method can lead to higher values than the equilibrium value.

The density determinations needed for determinations of the surface tension were made by weighing and measuring a column of liquid crystal in a capillary of uniform and known diameter, enclosed in a thermostatted chamber (0.1°C precision). The error in determining the density was 0.3%.
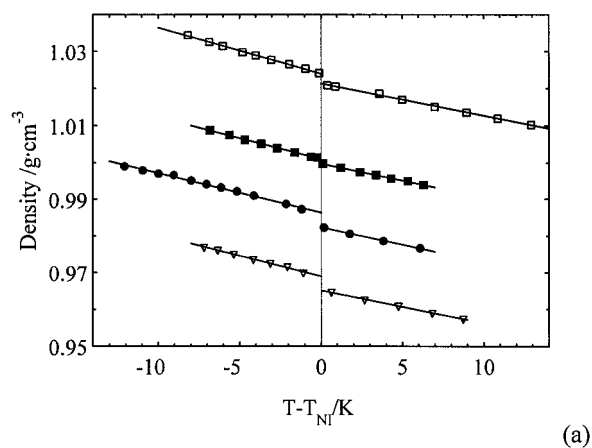
3. Results

The experimental results for the dependence of the density on the relative temperature ($\Delta T = T - T_{NI}$) are given in figure 2. The straight lines are the linear regressions (separately for each phase) which were used for computing the surface tension from the measured ratios, γ/ρ. The fitting parameters of the linear regressions, A, B, are given in table 2. As can be seen from figure 2, the nematic–isotropic transition is first order for all the liquid crystal materials. The density jump at the nematic–isotropic transition is downward for all the mesogens studied. The smectic–nematic transition of 8CB is second order or very weak first order, figure 2 (*b*).

The density value at the nematic to isotropic temperature and in the nematic and isotropic phases, decreases with increasing aliphatic chain length.
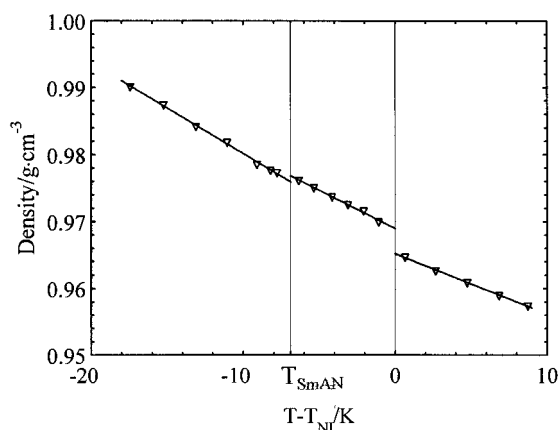
The dependence of the surface tension on the relative temperature for all the liquid crystal materials studied are given in figure 3. The behaviours around the nematic to isotropic transition point are shown in detail in figure 4, where the results are plotted as functions of the reduced temperature ($T/T_{NI} - 1$).

Table 2. The fitting parameters of the linear regression, $\rho = A + B(T - T_{NI})$, for the relative temperature dependence of the density for each liquid crystal phase.

Homologue no.	Smectic phase		Nematic phase		Isotropic phase	
	A	$B \times 10^3$	A	$B \times 10^3$	A	$B \times 10^3$
5	—	—	1.0239	− 1.243	1.0214	− 0.866
6	—	—	1.0014	− 1.130	1.0002	− 0.914
7	—	—	0.9859	− 1.065	0.9827	− 0.940
8	0.9665	− 1.359	0.9690	− 1.124	0.9652	− 0.895

(a)

(b)

Figure 2. The dependence of the density on the relative temperature for the *n*CB liquid crystals. The straight lines are linear regression results for the data in the corresponding phase. (*a*) Nematic and isotropic phases: □ 5CB; ■ 6CB; ● 7CB; ▽ 8CB. (*b*) Smectic, nematic and isotropic phases for 8CB. T_{SmAN} = smectic to nematic, T_{NI} = nematic to isotropic transition temperature, respectively.

The behaviour of the four compounds shown in figure 3 coincides with the most complex case described in [16]. As can be seen from figure 4, the curves present a negative discontinuity at the transition temperature in conjunction with a surface tension maximum above T_{NI}.

Recently, this experimental behaviour was theoretically explained by Braun [17]. He showed that in the case of partial nematic wetting, dampening of director fluctuations at the surface by anchoring at the nascent interface can reverse the sign of the surface tension discontinuity at the T_{NI}.

Our results for 5CB and 8CB were compared with data from the literature [2, 3, 5, 7]. For 5CB, our experimental value is greater than the literature values, using the same method [3, 5]. However, the capture technique of the drop image allowed us to choose the minimum γ value at each temperature. For the surface tension of 8CB at room temperature we found a 4% greater value than in [7]. We estimate also that this value is in agreement with that extrapolated from measurements of Mach *et al.* [9] for 12CB using their proposed model for the prediction of the surface tension of smectic liquid crystals.

In the literature, in the nematic range of both materials, temperature dependences of the surface tension, far from the transition, have positive slopes, while in our measurements there is a negative slope for 5CB and an almost zero slope for 8CB. Only near the transition points do the surface tension slopes become positive. Contrary to the data from the literature, a downward jump at $T = T_{NI}$ was observed by us for both liquid crystal materials. The same results were repeatedly obtained. We emphasize that our results were obtained using a static measurement method that is independent of wetting angle and more adequate for liquid crystals, contrary to the method used by Gannon and Faber [2]. Also, we used an improved technique of data capture and processing in comparison with that used by Krishnawamy [3]. In [3], the density values used are not specified, although we find that the behaviour of this parameter with temperature has an important influence on the surface tension trend.

Our experimental results for the homologous series of liquid crystal materials studied show that both in the nematic and isotropic phases, and not too close to the transition point, the surface tension slope decreases in absolute value when the alkyl chain length increases.
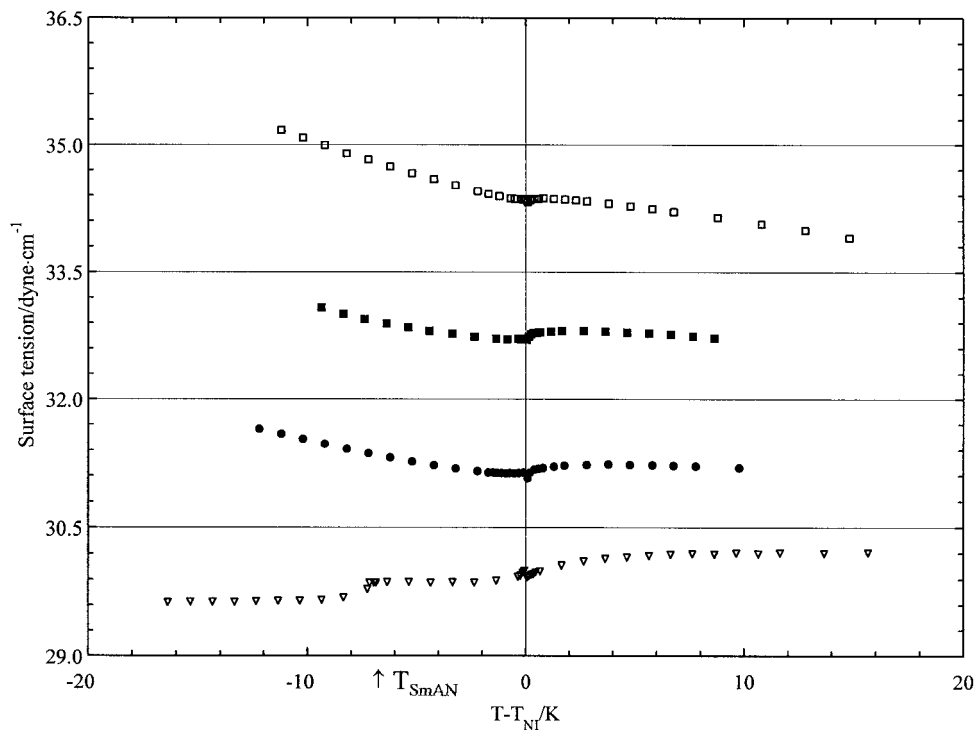
Figure 3. The dependence of the surface tension on the relative temperature for *n*CB. □ 5CB; ■ 6CB; ● 7CB; ▽ 8CB.
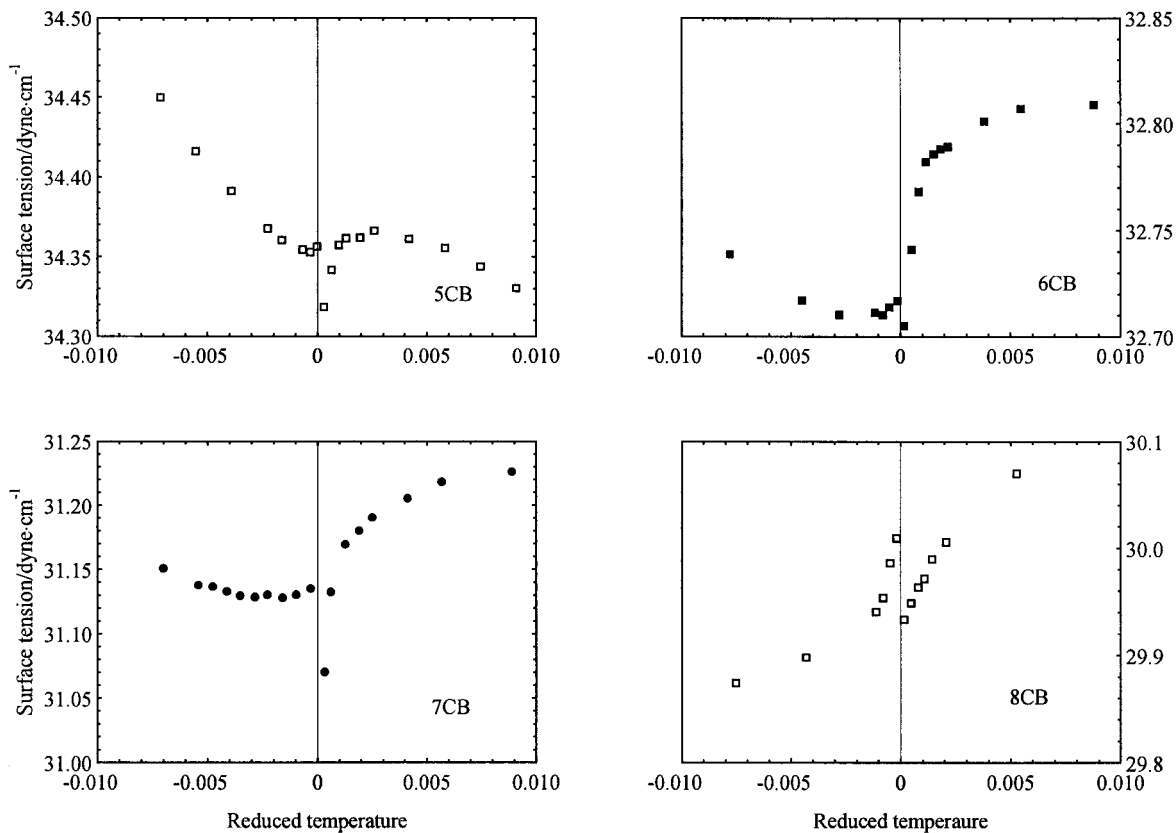

Figure 4. The temperature dependence of the surface tension for *n*CB in the nematic to isotropic transition range: plots using reduced temperature. □ 5CB; ■ 6CB; ● 7CB; ▽ 8CB.

This behaviour suggests that the role of the anisotropic contribution to the surface tension, appropriate to liquid crystals, becomes more important when the alkyl chain length increases. This can be supported by the experimental observation of a higher order at the surface in comparison with that in the bulk, with the increase in alkyl chain length [15]. This increasing order at the surface when passing from 5CB to 8CB also determines a more marked anomalous temperature dependence of the surface tension immediately above the T_{NI}.

We remark that in the smectic A phase of 8CB, the surface tension has a positive slope, and near the transition point it sharply increases. No jump at the smectic–nematic transition was observed.

At the same relative temperature, the surface tension decreases with increase in the alkyl chain length. This trend was found also for several homologous series in the smectic phase [9]. We checked our results with the theory of the parachor that predicts a decrease in surface tension with increase in aliphatic chain length. As is well known [18], the parachor, P is given by:

$$P = \gamma^{1/4} \; \frac{M}{\rho} \tag{2}$$

with M the molar mass. It describes the correlation between the surface tension and the chemical composition and, for normal liquids from a homologous series, the addition of a CH_2 group raises the parachor by a constant quantity (39 ± 1 CGS units). This rule is well followed by the series of liquid crystals studied, as can be seen from table 1, where P is the average value of the parachor calculated for the temperature range studied. The P deviations from the actual values are at the greatest 1.5%. From this table we can see that P increases by an average quantity of 38 CGS units when the aliphatic chain increases in length.

4. Conclusions

In this paper experimental results for the determination of the temperature dependence of the surface tension for four liquid crystal materials in the homologous series of nCBs are presented. Using the static pendant drop method, and images taken with a digital capture system, surface tension values for the equilibrium state were obtained. Contrary to the data from the literature for 5CB and 8CB [2, 3], a different trend of the surface tension in the nematic phase and a downward jump at the nematic to isotropic transition were obtained. To justify these differences some critical observations on the manner of surface tension determination in [2, 3], are made.

The surface tension of the four liquid crystal materials in the temperature range studied follows the parachor rule. The surface tension slopes decrease in absolute value with increase in the nCB alkyl chain length, both in the nematic and isotropic range, far from transition point. For the same increase in n, immediately above the T_{NI}, a more marked anomalous temperature dependence of the surface tension was observed. These observations are supported by the observed higher surface order when n increases [15].

The utilization of a static method of measurement also allowed determination of the surface tension in the smectic range of 8CB. While in the isotropic and nematic phases the experimental shape of the drop coincides with the theoretical shape (computed by isotropic hydrostatics), two types of small systematic deviation were observed in the smectic phase of 8CB.

References

[1] KRISHNASWAMY, S., and SHASHIDHAR, R., 1976, *Mol. Cryst. liq. Cryst.*, **35,** 253.
[2] GANON, G. J., and FABER, T. E., 1978, *Phil. Mag.*, **37,** 117.
[3] KRISHNASWAMY, S., 1980, in *Liquid Crystals*, edited by S. Chandrasekhar (London: Heyden), pp. 487–489.
[4] KORJENEVSKY, V. A., and TOMILIN, M. G., 1993, *Liq. Cryst.*, **15,** 643.
[5] COGNARD, J., 1982, *Mol. Cryst. liq. Cryst. Suppl.*, **1,** 1.
[6] STOEBE, T., MACH, P., GRANTZ, S., and HUANG, C. C., 1996, *Phys. Rev. E*, **53,** 1662.
[7] EBERHARDT, M., and MEYER, R. B., 1996, *Rev. sci. Instrum.*, **67,** 2846.
[8] STANNARIUS, R., and CRAMER, C., 1997, *Liq. Cryst.*, **23,** 371.
[9] MACH, P., HUANG, C. C., STOEBE, T., WEDELL, E. D., NGUYEN, T., DE JEU, W. H., GUITTARD, F., NACIRI, J., SHASHIDHAR, R., CLARK, N., JIANG, I. M., KAO, F. J., LIU, H., and NOHIRA, H., 1998, *Langmuir*, **14,** 4330.
[10] ADAMSON, A. W., 1990, in *Physical Chemistry of Surfaces*, 5th Edn (New York: Wiley-Interscience Publications), pp. 28–30.
[11] BEICA, T., *Rom. Rep. Phys.* (to be published).
[12] BEICA, T., TINTARU, M., MOLDOVAN, R., and FRUNZA, S., 1998, *Rom. J. Phys.*, **43,** 729.
[13] BROWN, G. H., and SHAW, W. G., 1957, *Chem. Rev.*, **57,** 1049.
[14] VAN DER VEEN, J., and HAANSTRA, H. B., 1976, *J. Physique Lett.*, **37,** L43.
[15] KASTEN, H., and STROBL, G., 1995, *J. chem. Phys.*, **103,** 6768.
[16] MARTINEZ-RATON, Y., VELASCO, E., SOMOZA, A. M., MEDEROS, L., and SLUCKIN, T. J., 1998, *J. chem. Phys.*, **108,** 2583.
[17] BRAUN, F. N., 1999, *Phys. Rev. E*, **59,** R4749.
[18] See for example BIRKEMAN, J. J., 1958, in *Surface Chemistry* (New York: Acad. Press), pp. 57–60.