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Experimental investigation of the surface energy of a nematic liquid crystal†

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The temperature dependences of surface tension, $\gamma=f\neq(t)$, are experimentally studied and discussed for homologous series of liquid crystalline 4-alkyl-4′-cyano biphenyls, 4-alkyl-4′-cyanophenylbenzoates, 4-alkyloxy-4′-cyanophenylbenzoates and also for several nematic liquid crystals of other chemical classes. The surface energy anisotropy of 5CB is measured at fixed temperature.

1. Introduction

The surface tension of nematic liquid crystals (NLCs), γ, and its anisotropy, $\Delta\gamma$, are important physical characteristics which are required both for theoretical calculations and for the solution of practical problems. It should be noted that using the more general term 'surface energy', F, to emphasize the origin of the parameter we actually mean 'surface tension', i.e. $\gamma=F$, in the context of the present paper, considering only individual LCs, although the latter term applies more exactly to the surface tension anisotropy. The necessity to study the LC surface tension arises from the NLC orientation required in various devices [1], wetting of the surfaces in LC based non-destructive tests, encapsulation of the LCs in polymers, providing the controlled boundary conditions at the NLC–substrate interface and many other LC applications. The reported experimental surface tension measurements [1–3] are rather contradictory even for the same compounds not only because of the difference in the samples degree of purification but also due to the specific technique employed. Hence, the present work is aimed at measuring the temperature dependence of the surface tension for NLCs of different chemical structures within the mesophase range, using a single technique that permits a proper comparison of the obtained results for different LCs.

2. Experimental

2.1. *Choice of compounds*

To study the dependence of surface tension on LC structure, we chose three homologous series: the 4-alkyl-4′-cyanobiphenyls, the 4-alkyl- and the 4-alkyloxy-4′-cyanophenylbenzoates (see the table). The chemical formulae and physical parameters for several other investigated nematogens are also given in the table. All those NLCs showing a relatively wide nematic phase and low nematic–isotropic transition temperature (T_{NI}), were supplied from the laboratory of Dr P. Adomenas of Vilnius University. All the examined samples were purified by recrystallization. The conductivity was to within $1\times10^{-11}\ \Omega\times\mathrm{cm}^2$. The surface tension depends on the concentration

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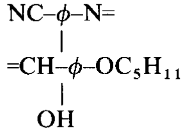
The basic physical characteristics of the samples under investigation.

No.	Chemical formulae	Homologue No.	Transition temperature/°C	d/g cm^{-3}	μ/D	$\Delta b \times 10^{-25}$/ cm^{-1}
1	$C_nH_{2n+1}-\phi-$	5	C 22·5 N 35·5 I	1·010	5·1	130
2		6	C 13·5 N 27·0 I	1·005	5·1	130
3	$-\phi-CN$	7	C 28·5 N 42·0 I	0·990	5·1	130
4		8	CM 33·5 N 40·3 I	0·950	—	—
5	$C_nH_{2n+1}-\phi-$	5	C 44 N 48 I	1·063	6·1	130
6		7	C 43 N 55 I	1·052	6·1	142
7	$-COO-\phi-CN$	8	C 47 N 53 I	1·028	6·1	148
8	$C_nH_{2n+1}O-\phi-$	5	C 88 N 96 I	1·083	6·6	130
9		7	C 72 N 83 I	1·055	6·6	138
10	$-COO-\phi-CN$	8	C 77 N 86 I	1·037	6·6	142
11		10	CM 83·5 N 89·5 I	1·017	6·6	160
12	$C_4H_9-\phi-COO-$ $-\phi-OC_6H_{13}$		C 29 N 51·5 I	1·107	2·3	130
13	$C_4H_9-\phi-N=N-$ $-\phi-OC_5H_{11}$		C 55 N 72 I	0·968	1·2	240
14	 $NC-\phi-N=$ $=CH-\phi(OH)-OC_5H_{11}$		C 82 N 127 I	0·828	5·3	210
15	$=CH-\phi-OC_6H_{13}$		C 37·5 N 48 I	1·099	3·8	210

of impurities which are mostly surfactants and are concentrated in the surface layer. To eliminate most of these impurities we removed a thin surface layer of the LC before conducting measurements.

2.2. *Choice of technique*

The reported discrepancies in the surface tension measurements essentially arise from the technique used. One is the static technique, i.e. a dynamic equilibrium between the LC and its vapour should be maintained during all the measurements. In our measurements we used a modified version of a well-known 'pendent drop' method, the LC volume being 0·5–1 ml, and when the LC volume was enough to fill a vessel (2–3 ml) we used the so-called 'meniscus near the wall' method, whose principle is shown in figure 1. These two methods yield identical results, provided that the dynamic equilibrium is ensured. It is rather difficult to state a criterion of the dynamic equilibrium, but in practice it takes more than half an hour to obtain one point on the curve. We describe only the latter less-known technique.

2.3. *The technique of surface tension measurements*

2 to 3 ml of the LC was placed in the vessel (see figure 1) so that it makes a meniscus at the vertical wall. The complete wetting of the wall by liquids and LDs in our experiment was ensured by the choice of the material. Wetting angles were optically checked. So that the LC should wet the wall of the vessel and the He–Ne laser beam

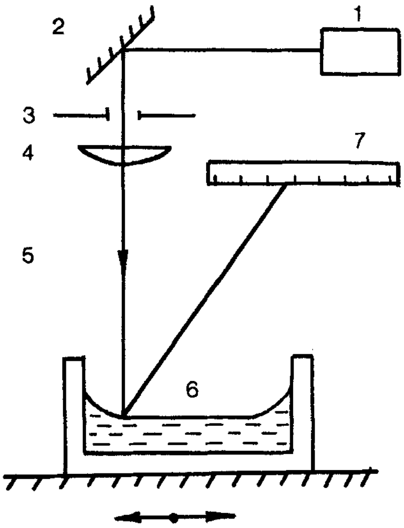


Figure 1. Schematic diagram of the experimental set-up for the LC surface tension measurements: (1) He–Ne laser; (2) mirror; (3) aperture; (4) lens; (5) laser beam.

should be focused on the curved LC surface not too close to the wall, a gap of about 1 mm avoids the influence of the wall on the LC orientation. The beam is reflected from the meniscus and its position, X_1, is marked on the scale. Then the vessel is moved relative to the laser beam and the second position X_2, is recorded on the scale. The difference $\Delta X = X_1 - X_2$ is measured by a micrometer. The surface tension is calculated by the formula

$$\gamma = A(\Delta X^2)d + B, \tag{1}$$

where A and B are the calibration coefficients, obtained with the vessel filled by the liquids with known surface tensions and d is the LC density. The accuracy of this method is within $\pm 0{\cdot}3\,\mathrm{mN\,m^{-1}}$. The thermal stabilization and temperature measurement accuracies are about $\pm 0{\cdot}2$°C. The measurements were made only after the γ value drift was excluded and this ensured the LC–vapour equilibrium was established. All our results correspond to the cooling process when the isotropic phase changes to the crystal one via the LC phase. The direction of the temperature change is essential in this case, because of a slight hysteresis of the $\gamma = f(T)$ dependences in the mesophase before T_{NI}. The F values are slightly higher in the case of heating than those in the case of cooling. One possible explanation is that the LC–vapour interface has a different structure at the same temperature depending on the previous process in the system. The $D = f(T)$ dependences for the NLCs were measured by a two-capillary picnometer with an accuracy of $0{\cdot}005\,\mathrm{g\,cm^{-3}}$. For most of the benzoates the D values were taken from [5].

3. Results and discussion

Figure 2 illustrates the general characteristics, d–T behaviour (the dependence of density on temperature). For all the NLCs and d–T characteristics are the same as for liquids except for a small dip in the region of the nematic–isotropic transition. The negative slope and proportionality are general features of characteristic d–T behaviour for all LCs. It should be noted here that to obtain the correct results the magnitudes of the surface densities should be substituted in equation (1), but because of their unavailability the bulk densities were used. Therefore, the calculated surface tension will exceed the real value.

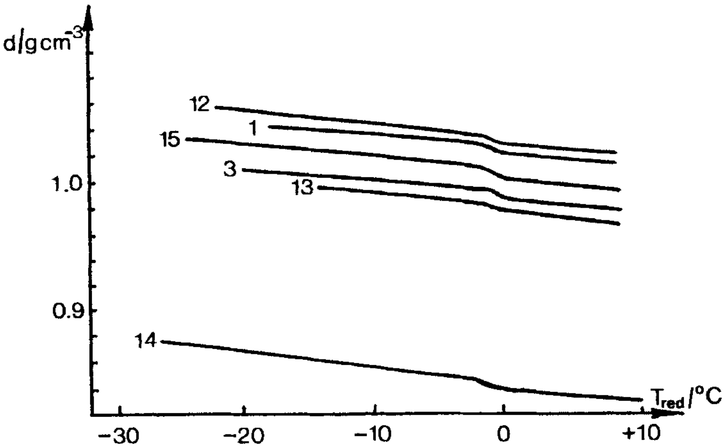


Figure 2. The dependence of density on the reduced temperature for NLCs of different structures (see the table).

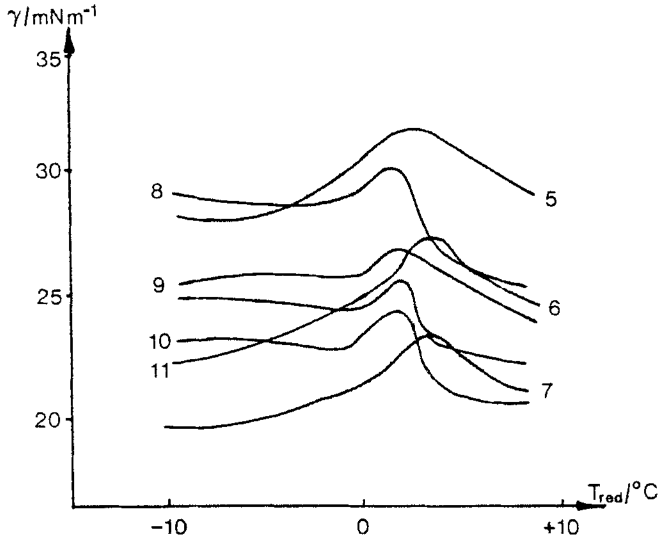


Figure 3. The dependence of the surface tension on the reduced temperature for nematogens of the 4-alkyl- and 4-alkyloxy-4′-cyanophenylbenzoates homologous series (see the table).

Figure 3 shows the $\gamma = f(T)$ dependences for two homologous series of 4-alkyl- and 4-alkyloxy-4′-cyanophenylbenzoates. This figure illustrates the similarity of the $\gamma = f(T)$ curves for nematics of the same homologous series and shows the γ values to decrease with the homologue number. This fact can be easily explained: the growth of the side chain length with homologue number leads to the increase of the molar volume, $V = M/d$, and, hence, to a decrease in molecular interactions which is equivalent to a decrease in the surface tension. We assume here that this consideration in terms of the bulk value remains valid for the relevant surface values. The results for the 4-alkyl-4′-cyanobiphenyl series are shown in figure 4.

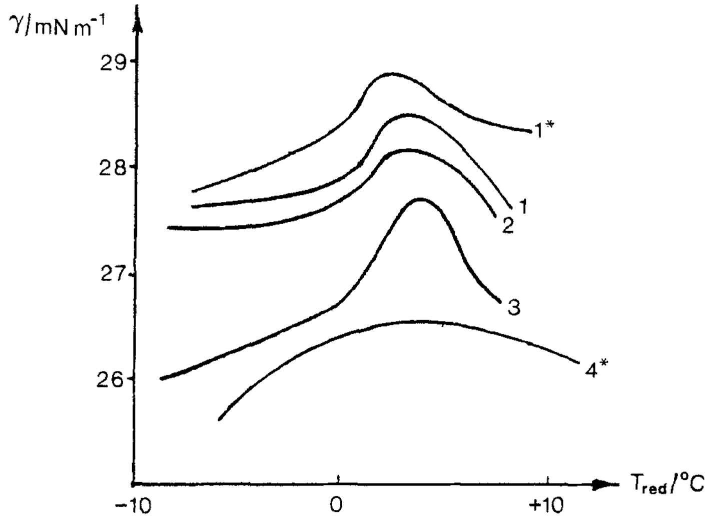


Figure 4. The dependence of surface tension on reduced temperature for the pentyl (1*, 1) 4-hexyl; (2) 4-heptyl; (3) and 4-octyl-4′-cyanobiphenyls; (4*) in the nematic and isotropic phases. Curves labelled by (*) are taken from [3].

As we can see from figures 3 and 4, all the investigated homologous show maximum surface tension in the isotropic phase, as was predicted by Parsons in [5]. The peak in the γ value is about 5 per cent with an accuracy of about 1 per cent. Moreover, according to Barbero [10] our results correspond to the case in which bulk and surface, S, values differ only at the critical temperature (the case of a first order phase transition).

It is known that surface tension is directly proportional to density. Thus there are only two parameters that can increase surface tension with temperature: the order parameter, S, and the orientation of the LC molecules on the free surface.

Our measurements of the $\Delta\gamma$ value for 5CB, along with the measurements of other authors, show that the surface tension anisotropy is too small to change the surface tension. According to [7], the positive slope of the $\gamma = f(t)$ curves, for example, for 5CB and other 4-alkyl-4′-cyanobiphenyl nematics near T_{NI}, results from an increase in the parameter $Q = S_S/S_V$, where S_S and S_V are the surface and volume order parameters, respectively (figure 4). We agree with the conclusion of [3] and [7] that this effect can be explained by the highly ordered smectic-like organization of the cyanobiphenyl interface layers.

Figure 5 illustrates the behaviour of γ–T characteristics for the nematogens 12–15 in the table. All the curves have negative slopes and two of them have no peaks in the T_{NI} region or the peaks are too small to be measured. The experimental investigation of these four nematogens together with previous studies made it possible to plot the $\gamma = f(\mu)$ curve, where μ is the dipole moment of the LC molecule (see figure 6). To eliminate the density effect, we normalized the surface tension by dividing it by the density. The normalized data are plotted in figure 6, the values of Δb and V being also indicated. Apparently, the direct proportionality between γ/d and μ can take place only under the condition that parameters V and Δb are approximately equal and that all the quantities depending on temperature are measured at the same $T_{red} = -1$, where $T_{red} = T - T_{NI}$. At this temperature the order parameters, S, are approximately equal for all nematics and thus the influence of S on g is ruled out.

4. Surface energy anisotropy measurements

The essence of the method is to calculate $\Delta\gamma$ from a direct measurement of ΔH, i.e. the difference between the heights to which the LC rises in a plane capillary with planar and homeotropic alignment of the LC molecules. To achieve this effect, two glass plates covered with transparent electrodes were rubbed along the electrodes to achieve good planar alignment of the 5CB molecules and were then connected to the plane capillary. The spacing between the plates, or capillary opening, could be changed to an accuracy of 10^{-6} m. The orientation of the LC molecules and the spacing were checked by an optical method. The height to which the LC rose in the capillary (width $d=4{\cdot}5\times10^{-4}$ m) was measured also optically by a cathetometer with an accuracy of $0{\cdot}5\times10^{-6}$ m. After the LC rose up the capillary to the height H_1 a voltage with magnitude $U=100$ V was applied to the transparent electrodes causing an optically checked reorientation of the LC molecules and the height changed to H_2. $\Delta\gamma$ was then calculated by the formula

$$\Delta\gamma=\gamma(H_1-H_2)/H_1, \tag{2}$$

where γ is the LC surface tension.

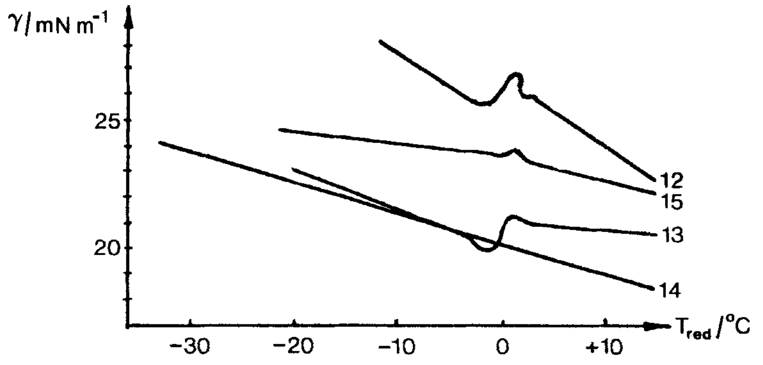


Figure 5. The dependence of surface tension on the reduced temperature for NLCs of different structure (see the table).

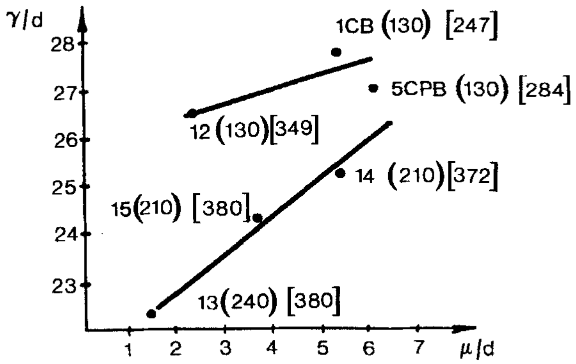


Figure 6. The $\gamma/d=f(\mu)$ dependence. The Δb and V values for the corresponding LCs in the table are given in parentheses and square brackets, respectively.

The temperature was measured by a thermocouple with an accuracy of 0·2°C. The accuracy of the thermostabilization was the same. The experiment was carried out at $T = 30°C$. The same experiment performed at $T = 40°C$ showed an orientation H_1-H_2 value only within experimental error.

This technique has the advantage that the determination of the surface tension anisotropy avoids an accurate determination of the absolute density and surface tension values. But if necessary, the technique can be converted from the 'relative' to the 'absolute' mode with a simultaneous measurement of the LC surface tension. Our experimental results for 5CB, $1{\cdot}5 \times 10^{-5}\,\mathrm{mN\,m^{-1}} = 1{\cdot}5 \times 10^{-7}\,\mathrm{J\,m^{-2}}$, are considerably higher than those of Nersisian [6] $(2{\cdot}5$–$0{\cdot}5) \times 10^{-8}\,\mathrm{J\,m^{-2}}$ but much less than those calculated for PAA ($\sim 7 \times 10^{-3}\,\mathrm{J\,m^{-2}}$, and are practically the same as those obtained for PAA by experiment [9]. A shortcoming of our method is the assumption of the validity of the contact angle and wetting properties of the LC during experiment. It is known that the electric field can affect the contact angle but our experimental evidence showed no change in the rise height to occur in the isotropic phase after the electric field was applied to the electrodes. Therefore we can assume that no change in the wetting angle occurs or that the change is negligible. Although the authors have no experimental evidence about reorientation of the LC molecules on the surface, we must point out that the value of ΔH does not change upon achieving the $U = 100\,\mathrm{V}$ point, which is the so-called 'saturation effect'. This means that no more changes in molecular orientation occur. One of the drawbacks of this technique is the absence of a theoretical investigation of a real, physical picture of the LC molecules orientation at the curved surface of the meniscus and the absence of a model than can describe what happens at the curved interface when the electric field is applied to it.

5. Conclusion

The experimental data obtained makes it possible to conclude that the $\gamma = f(T_{\mathrm{red}})$ curves are similar for NLCs of the same homologous series and the values of F decrease with homologue number. In the mesophase near T_{NI}, the $\gamma = f(T)$ curves of some NLCs have a positive slope with the maximum in the isotropic phase. Using the plane capillary technique the surface tension anisotropy for the 5CB NLC was determined to be $\Delta\gamma = 1{\cdot}5 \times 10^{-5}\,\mathrm{mN\,m^{-1}}$ at 30°C. Theoretical studies are critically needed in this field of LC research.

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