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Interfacial tension of some liquid crystals in the cyanobiphenyl series at the interface with glycerol

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The temperature dependence of the interfacial tension for three compounds from the homologous series of alkylcyanobiphenyl (nCB), 5CB, 7CB and 8CB, at the interface with glycerol was measured in a temperature range from mesomorphic to isotropic phase. The drop shape method of measure was used. The interfacial tension of all the studied liquid crystals presents an anomalous behaviour with maximum and small upward jumps at the phase transitions, in rising temperature.

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1. Introduction

The interfacial phenomena in liquid crystals are studied on account of their technological importance and their interest as a fundamental problem in the statistical mechanics of non-uniform, ordered fluids. They have been the subjects of a number of experimental studies [1-13], most of them at the boundary with air. The measurements of interfacial tension at the boundary with an isotropic liquid are rather scarce [1-8].

The interfacial tension between a liquid crystal and an isotropic liquid often exhibits unusual features as compared to the interfacial tension between two isotropic phases. In many cases it presents a relative maximum or minimum near the nematic to isotropic transition temperature and a jump at this temperature [1-4].

The interfacial tension between two isotropic liquids monotonically varies with increasing temperature, often with negative slope [14]. Various means have been developed for predicting the interfacial tension γ_{12}. An early empirical relation, known as Antonoff's rule [15], states that:

$$\gamma_{12} = \gamma_{1(2)} - \gamma_{2(1)} \quad (1)$$

Here $\gamma_{1(2)}$ is the surface tension of liquid (1) with an adsorbed film of substance (2) and vice versa for $\gamma_{2(1)}$. The liquid (1) is that with higher surface tension. The rule is approximately obeyed by a large number of systems.

In the paper we present the results of determination of the temperature dependence of the interfacial tension of three members of the 4-alkyl-4'-cyanobiphenyl (nCB) homologues series in contact with glycerol. We used the drop shape static method that is sketched in Section 2 and is largely described in ref.[10, 18]. In Section 3 the experimental data are presented and discussed. All the obtained curves present anomalous behaviours with maximum and upward jumps at phase transitions.

2. Experimental

The measurements were performed on three liquid crystals from the 4-alkyl-4'-cyanobiphenyl homologous series: $C_nH_{2n+1}(C_6H_4)_2CN$ with n=5, 7, 8. The liquid crystals (Aldrich, purity 98%) and glycerol (Aldrich, purity 99.5%) were used without supplementary purification.

The interfacial tension liquid crystal/glycerol was measured using the drop shape method [15]. Among the methods to determine the interfacial tension, the drop shape method (sessile or pendant) presents some advantages and is well suited for liquid crystals because it needs small quantity of liquid, is based on an exact theory and is a static method. The method consists in taking images using a digital capture system of a steady drop of liquid crystal formed below or above a circular capillary tube situated in the second fluid. Details of the experimental set-up and of the measuring cell for measurements are given in ref. [10, 18]. As it can be seen from Fig.1 in ref. [10], in the case of nematics and isotropic liquids, the detection method of the drop boundary, as well as the fitting method, gives results much more precise than 1 pixel. In fact, from this figure we can see deviations between theory and experiment less than 0.1 pixels. We can also see a qualitative difference of error distribution in the case of a nematic and of a smectic, putting in evidence the existence of a structure of the smectic drop surface.

The equatorial extension of the drop image used in measurements (when it was the case) was of the order of 600 to 800 pixels. The value of the apex radius of the drop (obtained by fit) was in the range of 300 to 400 pixels. The magnification factor was 195 pixels/mm. The drop volume estimation lead to the result that its value is enough large (15-30 μl) so that a random volume change do not affect the measured interfacial tension [13].

Since the glycerol density is higher than that of the investigated liquid crystals, the droplets, profile of which are determined, are stable only when they are formed

above the tip. The cell containing the liquid drop was thermostatted. A linear variation of 0.05 K/min in the range of transition temperature and of 0.1 K/min out of this range was used. This corresponds to a separation of experimental points of about 0.02 K and 0.05 K, respectively, as a drop image was analyzed every 30 s. The temperature variations were enough small to ensure a thermal quasi-equilibrium. Even so, a small difference between the transition temperatures for the curves obtained in heating and cooling was observed (see Fig. 1).

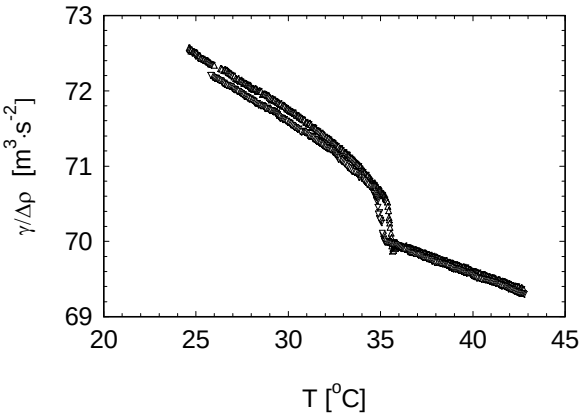

Fig. 1. Experimental results for γ/Δ vs. temperature for 5CB in (Δ) heating and (∇) cooling.

The experiments lead to the determination of the ratio between the interfacial tension and the difference of the densities of the two media in contact, $\gamma/\Delta\rho$. The temperature dependence of the densities of the liquids was measured in independent experiments.

In Fig. 1 the determination of $\gamma/\Delta\rho$ for 5CB in rising and descending temperatures is given as an example. We remark the displacement of the transition temperature of 0.5 K between the two curves. It is due to the fact that the temperature was slowly but continuously changed. Moving each curve by 0.25 K in the necessary direction, the calculated curves for γ are well overlapped in the isotropic phase and enough well in the nematic phase. This indicates that the aging of the surface layer of the liquid crystal in contact with glycerol is very small during the time of the experiments (about 8 hours).

The interfacial tension for the three liquid crystals was determined considering that the thermodynamical state of the liquid crystal corresponds to a temperature delayed with 0.25K in comparison with the indication of the sensor and we used the density for this corrected temperature. In the transition range, we eliminated the experimental points corresponding to a mixture of phases as visually observed on the droplet photos.

The estimated error in the determination of the absolute value of the interfacial tension was $\pm$ 0.05 mN $\cdot$ m^{-1} [19]. We mention that in this estimation of the error we considered that the errors in the determination of density are negligible. The relative deviations of the experimental points, as the fitting program for the determination of the interfacial tension gave, were evaluated at $\pm$ 0.025 mN $\cdot$ m^{-1}.

3. Results and discussions

The temperature dependence of interfacial tension of the three studied liquid crystals in the cyanobiphenyl series at the interface with glycerol is given in figure 3. We mention that for 7CB and 8CB we were able to make measurements only in cooling. Indeed, at room temperature 7CB is in solid state (melting point 30°C) and 8CB is in the smectic phase (SmA – N transition temperature 33.5°C) and so, for the later it is easier to reach the equilibrium shape of the drop at a temperature in the isotropic state and make the measurements in cooling.
As previously mentioned, for the calculation of the temperature dependence of interfacial tension it is necessary to know the temperature dependence of density for liquid crystals and glycerol. The liquid crystals densities, in the mesomorphic and isotropic phases and glycerol, were measured using an Anton Paar densitometer (Model DMA 4500). The precision of the determinations, $\pm$ 0.00001 g $\cdot$ cm^{-3}, was assured by a dedicated program for the acquisition of the data, made by us. The results are presented in Fig.2 and table 1. The glycerol density and its temperature dependence are well described by the equation:

$$\rho_{gl} = 1.27386 - 0.63433 \cdot 10^{-3}T,$$

where ρ_{gl} is glycerol density in g $\cdot$ cm^{-3} and T is the temperature in Celsius degrees.

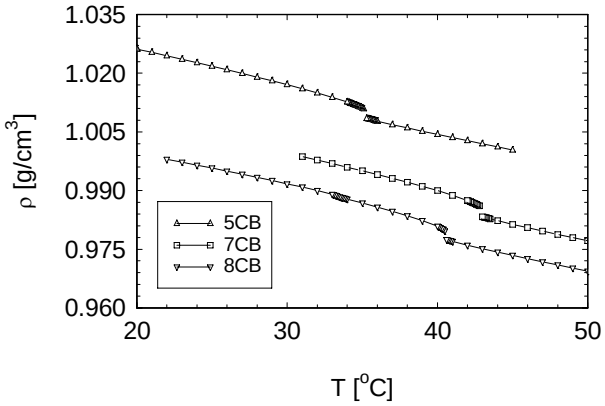

Fig. 2. Temperature dependence of the density for the nCB liquid crystals.Δ 5CB, □ 7CB, ∇ 8CB.

Table 1. The fitting parameters for the regression, $\rho = A(T - T_{NI})^3 + B(T - T_{NI})^2 + C(T - T_{NI}) + D$, for the relative temperature dependence of the density of each liquid crystal phase, in $g \cdot cm^{-3}$.

Liquid crystal	T_{NI} (ºC)	Phase	Fitting parameters			
			A	B	C	D
5CB	35.2	N	-1.95×10^{-6}	-5.75×10^{-5}	-1.43×10^{-3}	1.01094
		I	-1.02×10^{-6}	$+2.22 \times 10^{-5}$	-9.53×10^{-4}	1.00853
7CB	42.9	N	-2.78×10^{-6}	-7.28×10^{-5}	-1.54×10^{-3}	0.98608
		I	-2.6×10^{-6}	$+4.24 \times 10^{-5}$	-1.05×10^{-3}	0.98342
8CB	40.55	SmA	-1.24×10^{-6}	-5.75×10^{-5}	-1.65×10^{-3}	0.97926
		N	-1.46×10^{-6}	-1.84×10^{-4}	-1.82×10^{-3}	0.97989
		I	-1.33×10^{-6}	$+2.94 \times 10^{-5}$	-1.02×10^{-3}	0.97751

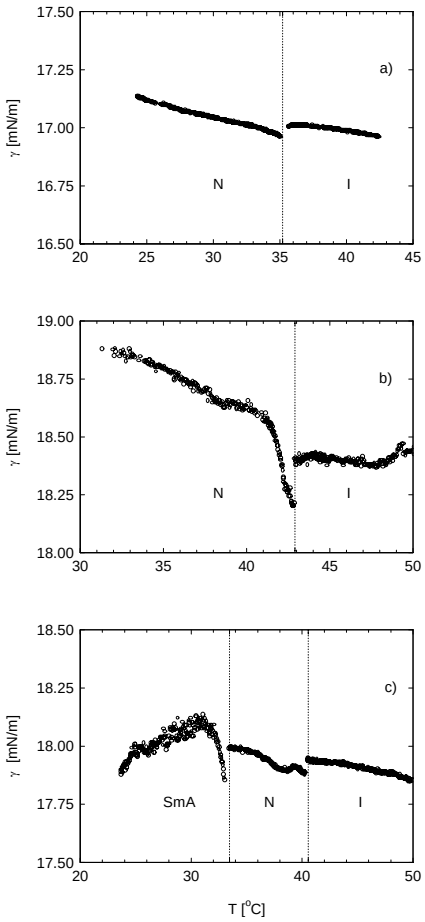

Fig. 3. Temperature dependence of glycerol/liquid crystal interfacial tension for a) 5CB obtained in heating, T_{NI} =35.2ºC; b) 7CB obtained in cooling, T_{NI}=42.9ºC; c) 8CB obtained in cooling; SmA, N and I are the smectic, nematic and isotropic phases, respectively. T_{SN}=33.45ºC T_{NI}=40.55ºC

From the results in figure 3 we observe that the liquid crystal/glycerol interfacial tensions are smaller than the highest surface tension of the two liquids (glycerol, $62.6\, mN \cdot m^{-1}$ at 24°C [15]), in accordance with Antonoff's rule. Examining the temperature variation of the liquid crystal/glycerol interfacial tensions in comparison with the corresponding variation of the surface tension curves previously obtained by us [10], it results that the trend of curves qualitatively follows the Antonoff's rule as the two trends usually have opposite curvatures, in the same phase.

The $\gamma(T)$ curves for the three liquid crystals put in evidence an anomalous behaviour of γ as function of temperature, but the interfacial tension variations in the studied interval of temperature are small. In the nematic phase, the curve 7CB has a maximum. For all the studied liquid crystals, the curves are decreasing before the nematic to isotropic transition. In rising temperatures all the liquid crystals present an upward jump at the transitions. Its value is small for all the liquid crystals. In the isotropic phase, the curves for 5CB and 8CB are slowly decreasing, while for 7CB we can consider that the curve γ is rather indifferent to temperature.

In literature there are results for interfacial tension glycerol/5CB [2] and glycerol/8CB [3]. The value for 5CB at the nematic to isotropic transition that we obtained is the same with that found by Lavrentovich ($17 mN \cdot m^{-1}$ [2]), although the curve aspect is different due probably to the fact that in [2], the drop shape method with a photo technique was used. This technique leads to much higher errors from point to point. Not the same thing can be said about the results for 8CB for which we obtained a nematic to isotropic jump from 17.88 to 17.94 $mN \cdot m^{-1}$ instead of 71 to 77 $mN \cdot m^{-1}$ in [3]. We remark that the results in [3] are not plausible as the values of the liquid crystal/glycerol interfacial tensions are higher then that of glycerol ($62.6\, mN \cdot m^{-1}$ at 24°C).

As indicated in literature [1-2, 20, 21], the anomalous character of γ(T) liquid crystal curves can have as main cause the difference between the degree of order in the surface layer in comparison with that in the bulk of the liquid crystal. The slope of $\gamma(T)$ curve is proportional with the excess entropy of the surface layer, given by:

$$\frac{d\gamma}{dT} \sim \int_{-\infty}^{\infty} \left[\rho(z)\xi^2(z) - \rho_0\xi_0^2 + \rho(z)\eta^2(z) - \rho_0\eta_0^2\right] dz \quad (2)$$

$\rho(z)$ is the density of the liquid crystal, dependent on the distance from the separation surface between the two phases in contact; $z<0$ in the liquid crystal phase; ξ and η are the translational and orientational order parameter, respectively; $\rho_0 = \rho(-\infty)$ is the density in the bulk of the liquid crystal; $\xi_0 = \xi(-\infty)$ and $\eta_0 = \eta(-\infty)$ are the bulk order parameters. Increased values of ξ and η (in the surface layer) in comparison with ξ_0 and η_0 (from the bulk) lead to $d\gamma / dT > 0$ and vice-versa. We observe that the interfacial tension curves in the nematic phase mainly decrease with temperature. This can be explained by the disordering of the liquid crystal surface layer due to the diffusion of glycerol. In the smectic phase of 8CB and for 7CB far from the transition to isotropic point, a more ordered surface layer is possible despite the glycerol presence due to diffusion. In the isotropic phase after the transition point, the decreasing behaviour observed for 5CB and 8CB is due to the spatial delocalisation of the surface.

4. Conclusions

The paper presents the experimental results for the determination of the temperature dependence of interfacial tension for three liquid crystal materials, 5CB, 7CB and 8CB at the boundary with glycerol. Measurements were made using the drop shape method with images taken with a digital capture system, in quasi-static regime of temperature. Anomalous temperature dependences for interfacial tensions, presenting a maximum, were obtained. However, the range of the interfacial tension variation of the three liquid crystals is enough small with a small up jump at the phase transitions in rising temperatures. The obtained results are in qualitatively agreement with the phenomenological Antonoff's rule for interfacial tensions.

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[19] The errors at the determination of $\gamma / \Delta\rho$ are composed from those of the apex radius of the drop (b) expressed in pixels, of the shape factor $\beta = (g\Delta\rho b^2)/\gamma$ and of the conversion factor from pixels to standard units of length. The fitting program for the determination of interfacial tension gave the first two and we evaluated the third one at 0.1%. The result is an error of about 0.3%. The error for the density measurement is two order of magnitude lower and it was neglected. We obtain an error of $\pm 0.05\, mN \cdot m^{-1}$ for the determination of the absolute value of the interfacial tension.
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