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## DETERMINATION OF THE SURFACE TENSION OF 5CB LIQUID CRYSTAL BY THE PENDANT DROP METHOD

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UDC 539  
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The surface tension  $\sigma$  of 5CB has been measured in a wide temperature interval at the free surface and 5CB/glycerine interface, using a pendant drop method. Both curves indicate an anomalous behaviour, which implies the positive slopes of  $\sigma(T)$  in the nematic and isotropic phases. Our experiments confirm the previous results [3, 5] that the isotropic boundary conditions influence not only the values of  $\sigma$ , but also the shape of  $\sigma(T)$ . The observed features are in a qualitative agreement with the theoretical predictions of Croxton and Chandrasekhar and may be explained by the existence of more ordered nematic states at the interface as compared with the bulk phase. The mechanisms, which are responsible for the interfacial molecular alignment of 5CB, are discussed.

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### 1. Introduction

The free (or interface) energy of a unit area or the surface tension  $\sigma$  is one of a few thermodynamical functions which are measured directly in experiment. For liquid crystals (LC),  $\sigma$  is an important parameter both from the physical point of view and from the technological one. For instance, a change of  $\sigma$  with temperature gives a certain information on the types of phase transitions and mechanisms responsible for the LC interfacial alignment [1].

However, the data on  $\sigma(T)$  of liquid crystals obtained in a true thermodynamic equilibrium is not yet numerous and relate mainly to free surfaces [1–4]. For LC/isotropic liquid interfaces, we know only few works [3,5,6]. Obviously, such a scarcity of results is connected with technical difficulties which accompany the measurements of  $\sigma(T)$  namely in equilibrium. It is these difficulties (from our point of view) that lead to the fact that there are even more theories of  $\sigma(T)$ , than experiments (their review can be seen in [7]). More novel experimental data on  $\sigma(T)$  are unknown to us, although  $\sigma$  of free-suspended films is now in the stage of intensive study. Relatively new conceptions of the surface tension are present in [8].

Thus,  $\sigma(T)$  measured in nonequilibrium is a subject of many experimental studies [7, 9]. Hence, the values of  $\sigma$  obtained by different authors are in conflict, and their divergence is far over the limits of usual errors [9]. In some cases, even the course of  $\sigma(T)$  is different. For example, for 5CB,  $\sigma$  changes from 28 to 40 dyn/cm [9]. The reasons for the difference of results may be various: the uncorrect choice of techniques; impurity effects; inhomogeneous boundary conditions; measurements of  $\sigma(T)$  in a nonequilibrium state, etc. If even one of these factors is present, this does not allow one to measure the true value of  $\sigma$ , true dependence  $\sigma(T)$ , and interfacial molecular orientation.

Our aim in this work was to study the behaviour of  $\sigma(T)$  under true equilibrium conditions. The measurements were carried out in the nematic (*N*) and isotropic (*I*) phase. To avoid above factors, we undertook the experimental study of the surface tension  $\sigma$  by the pendant drop method. It is single among the static methods, where the studied surface of a drop is not in contact with a solid substrate or wall. Hence, for LC possessing a great viscosity and a high sensitivity to the wall effect, this method is most suitable, as we believe. Since our aim in this work was also to understand qualitatively, what mechanisms are responsible for the LC interfacial alignment, we measured  $\sigma(T)$  both at the 5CB/vapor interface and at the 5CB/glycerine one. The interfacial molecular orientation (normal in the first case and tangential in the second one) was defined in the other experiment by using a polarizing microscope.

### 2. Experimental Method

The well-known liquid crystal — pentylcyanobiphenyl 5CB — is a representative of the homologous series of cyanobiphenyls. It possesses a good chemical stability and has a single nematic phase. Its structural formula is

as follows:



The liquid crystals are known to have large viscosity and orientational order towards the long axes. Hence, to obtain their equilibrium physical properties (under heating or cooling of rather large volumes), one requires a certain time. For this reason, the dynamic (capillary waves, etc.) and quasidynamic (Wilhelmy plates, ring isolation, etc.) methods are not suitable for liquid crystals, because the formation of an equilibrium surface in such systems requires much more time, than these methods allow. From the results for 5CB, we have already seen how essentially its surface tension depends on the method chosen. Therefore, after the studies of various techniques, we decided to use the pendant drop method. It is known to be suitable for viscous liquids and excludes any orienting influence of a solid surface. Its advantages before other methods are as follows:

- 1) the area of a drop, which is in direct contact with the solid surface, is very small as compared with the total area of the drop;
- 2) the values obtained are independent of a contact angle, as it is in other methods (sitting drop, capillary rise, etc.);
- 3) it is a static method so that the viscous spreading of a liquid does not play any role.

Thus, in the case of LC, this method can give absolute values of  $\sigma$  but under condition that a substance is highly pure. Moreover, it requires a small volume of a liquid and may be used at high temperatures. Applying precise optical devices, its accuracy may reach tenths of a percent.

We thus chose the pendant drop method, in spite of that there is some technical difficulties which complicate its application. First, a drop is to be formed under conditions excluding any external disturbances. Secondly, it is desirable that a shape of the drop be described by a certain value of  $S$  (see further). Thirdly, it is necessary that the experiment be carried out on a single drop, by ensuring that the drop was in a perfect equilibrium at each temperature. The complete experiment must involve about 20 temperatures and take nearly 10–12 hours. At each temperature, a shape of the drop must be controlled by fine movements of a micrometric piston. This may be achieved only handly. None other mechanical device gives such fine regulation of the drop.

In our experiments, 5CB was first heated up to the isotropic state, and the drop was formed at the end of a thin tube. Then it was cooled nearly with the same velocity. At a given temperature, it is necessary to wait for 30 min before a steady state is attained. To avoid a horizontal thermal gradient, a chamber was cooled not by heaters, but in a thermostat by a flowing liquid (the mixture of water and glycerine). The accuracy of measurements was 0.1 % °C.

A glass capillary tube (the internal diameter of 0.8–0.9 mm) filled with a liquid crystal was inserted strictly vertically in a copper chamber with two transparent windows. Its tip must be perpendicular to the axis of a capillary tube and be polished without cracks and jaggies, otherwise the drop will wet its edges. Before the beginning of the experiment, a chamber was filled with an inert gas (argon) or glycerine. In the first case, the glass tube is a straight line. In the second one, it is bent up to a top.

The surface tension was defined by a photographic profile of the drop [7]:

$$\sigma = \Delta\rho d_e^2 g / H, \quad (1)$$

where  $\Delta\rho$  is the density difference of 5CB and the isotropic medium;  $d_e$  is the maximum equatorial diameter of the drop;  $g$  is the gravitational constant;

$1/H = f(d_s/d_e)$  is the correction function depending on the drop shape [7];  $d_s$  is the horizontal diameter of the drop measured at the distance  $d_e$  from its vertex. The drop shape is characterized by a ratio  $S = d_s/d_e$ , and  $1/H$  is given in [7]. It is necessary to obtain empirical values  $S = d_s/d_e$  in the limits 0.8–0.9, since the error of measurements increases at smaller  $S$ . The densities for 5CB and glycerine were taken from [8] and [9], accordingly.

### 3. Results and Discussion

Fig. 1 shows our experimental results. As seen, the curves differ not only quantitatively, but also qualitatively. The main features of  $\sigma(T)$  are as follows.

In the isotropic phase, far from temperature  $T_{IN} = 35.1$  °C, a negative slope of  $\sigma(T)$  is observed, which is usual for isotropic liquids. The surface tension  $\sigma$  monotonously decreases with temperature. At  $T \geq T_{IN}$ , a positive slope of  $\sigma(T)$  is observed in both cases.

For a glycerine matrix, the curve  $\sigma(T)$  has a positive slope  $d\sigma/dT > 0$  near  $T_{IN}$  covering 5 °C of the  $N$ -phase and 2 °C of the  $I$ -phase. At  $T_{IN}$ , this slope has a break ( $\sim 1.2$  dyn/cm). At  $T - T_{IN} \geq 5$  °C, one more slope  $d\sigma/dT > 0$  is observed.

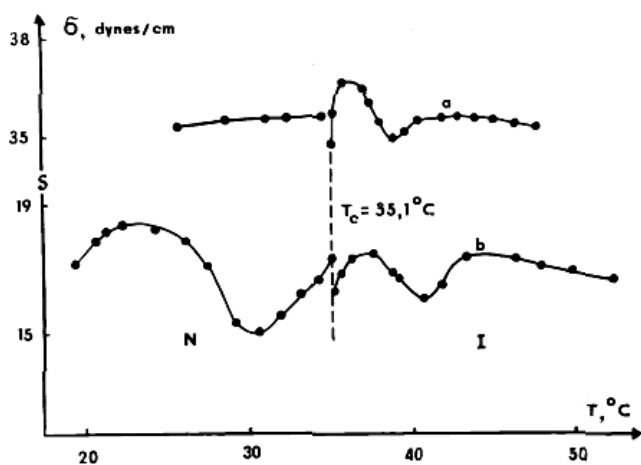


Fig. 1. Surface tension of 5CB: a) — at the free surface; b) — at the interface with glycerine

For the free surface, in the  $N$ -phase, the curve  $\sigma(T)$  is almost independent of temperature. At  $T = T_{IN}$ , it indicates a jump ( $\sim 2.2$  dyn/cm). At  $T \geq T_{IN}$  and  $T - T_{IN} \geq 4$  °C, two positive slopes  $d\sigma/dT > 0$  take place.

The features observed may be caused by three reasons: 1) a change of the interfacial molecular orientation with temperature; 2) the thermal expansion of 5CB with temperature; 3) different changes of the ordering degrees of the surface and the bulk with temperature.

Let us consider these mechanisms and clarify which of them is dominant.

The interfacial molecular orientation of 5CB was defined in the separate experiment by a polarizing microscope. For the free surface, we observed how the textures of thin films change with temperature. We studied the thin films (a thickness of 20–30 microns and a diameter of 250 microns) formed in the holes of polymeric plates. The character of the textures was found to indicate a normal orientation in the  $N$ - and  $I$ -phases. Observing the textures of spherical drops freely suspended in a glycerine matrix [10], we have also seen that the interfacial molecular orientation of 5CB is unchanged (tangential) in the whole temperature interval.

Thus, a molecular orientation cannot be the cause of  $\sigma(T)$  — anomalies, because it is independent of temperature. But even if such dependences take place, liquid crystals have usually  $\Delta\sigma \sim 10^{-2}$  dyn/cm [11] for the free surface and  $\Delta\sigma \sim 10^{-1}$  dyn/cm for the LC/glycerine interface [12]. ( $\Delta\sigma = \sigma_{||} - \sigma_{\perp}$ , where  $\sigma_{||}$  and  $\sigma_{\perp}$  are, respectively, the surface tension for the tangential molecular orientation and the normal one.)

Hence,  $\Delta\sigma$  is much more smaller, than the values of  $\sigma$  measured for liquid crystals.

The density of 5CB decreases monotonously, when temperature rises, with the exception of a small jump ( $\sim 0.4$  %) at  $T = T_{IN}$  [8]. A similar dependence is usual for liquid crystals [13,14]. Since  $\sigma \sim \rho$ , we can expect a decrease of  $\sigma$  with temperature (due to the thermal expansion) and a small jump of  $\sigma(T)$  at  $T = T_{IN}$ . The given mechanism thus explains only a single feature of  $\sigma(T)$ , namely, a general decrease of  $\sigma$  with rise of  $T$ .

Therefore, we suppose the excess nematic alignment in the surface layer (compared with the bulk) to be a main reason. In fact, the slope of  $\sigma(T)$  is proportional to the difference between the surface  $S_1$  entropy and the bulk  $S_0$  one on a unit surface area:

$$d\sigma/dT = -(S_1 - S_0). \quad (2)$$

There are many theories of the surface tension of liquid crystals. From our point of view, the Croxton—Chandrasekhar theoretical model [13, 14] describes experimental data in the best way. According to this theory,

$$d\sigma/dT \sim \int [\rho(z)\xi^2(z) - \rho_0\xi_0^2] dz, \quad (3)$$

where  $\rho_0$  and  $\xi_0$  are the bulk density and the orientational order parameter that are constant at a given temperature;  $\rho(z)$  is the profile density of particles across the surface;  $\xi(z)$  is the orientational order parameter in the interfacial layer which depends on the distance  $z$  to the interface, but  $\rho(-\infty) = \rho_0$ ,  $\xi(-\infty) = \xi_0$ . It follows from (2) and (3) that some effective parameter  $Q(z) = \rho(z)\xi^2(z)$  depends on two factors: a decrease of  $\rho(z)$  and an increase of  $\xi(z)$ . The latter is defined by interfacial torque forces. Thus,  $\rho(z)\xi^2(z)$  can exceed  $\rho_0\xi_0^2$  and thus can suppress a “classical” monotonous course of  $\sigma(T)$ . This leads to a positive slope of  $\sigma(T)$ , i.e.  $d\sigma/dT > 0$ . In the isotropic phase, far from the critical point, the spatial delocalization of the surface leads to a usual negative slope  $d\sigma/dT < 0$ , which is typical of isotropic liquids. Such negative slope is also observed in our experiments far from the phase transition.

Let us discuss the possible versions of the interfacial molecular alignment of 5CB which is present in a glycerine matrix. Here, at the surface of the  $I$ - and  $N$ -phase, we can expect the excess nematic alignment (with  $\xi'(z) \neq 0$ , but  $\xi'_0 = 0$  in the bulk) due to the interfacial polarization. The latter is caused by large longitudinal dipole moments of 5CB ( $\mu \sim 4.3$  D, see [18]). Since the liquid crystals are nonpolar, the dipoles of adjacent molecules compensate each other, and  $\xi'_0 = 0$ . But a polar

liquid such as glycerine directs them tangentially to the surface, and the excess nematic alignment arises at the 5CB/glycerine interface.

Such an alignment leads to a decrease of the surface entropy  $S_1$ , and, thus, a positive slope of  $\sigma(T)$  occurs. For the 5CB/glycerine interface, a positive slope  $d\sigma/dT > 0$  is observed near  $T_{IN}$  covering 5 °C of the nematic phase and 2 °C of the isotropic phase. There is still one such a slope in the  $I$ -phase. The appearance of positive slopes of  $\sigma(T)$  at  $T$  above  $T_{IN}$  means that the formation or destruction of a nematic alignment in the surface layer should not necessarily coincide with  $T_{IN}$ .

A similar discussion can concern the free surface of 5CB, where the molecular orientation is normal. Here, more ordered nematic states may exist at the surface of the  $I$ - and  $N$ -phases ( $\xi'(z) \neq 0$ , but  $\xi'_0 = 0$ ) due to the normal orientation of dipole moments (surface polarization). According to (2), this leads to positive slopes of  $\sigma(T)$ . At temperatures  $T < T_{IN}$ ,  $\sigma$  is almost independent of  $T$ . This means that  $S_0$  and  $S_1$  are nearly the same. The entropy balance predicts the equality of the degrees of molecular alignment at the surface and in the bulk phase.

Thus, we can assume that, at the cooling of 5CB towards  $T_{IN}$ , the nematic phase appears at the surface of the isotropic phase. Obviously, it arises, where the first positive slope of  $\sigma(T)$  takes place: at about 5 °C above  $T_{IN}$  at the free surface and, at about 7 °C above  $T_{IN}$ , at the 5CB/glycerine interface. Moreover, experiments have shown [18] that the so-called “surface nematic phase” of 5CB is located in separate regions of the surface. It, as it were, partially wets the free surface, and the wetting is complete below  $T_{IN}$ . A similar character of the “orientational wetting” was observed for 5CB/DMOAP-glass [20] and for other nCB ( $n=6\div 9$ ) [20]. Two positive slopes of  $\sigma(T)$  (above  $T_{IN}$ ) can indicate two discrete transitions corresponding to the formation of additional nematic layers at the surface. (The curves known to us [1–5, 9] do not have two positive slopes of  $\sigma(T)$ .)

At least, five discrete transitions were observed for 12CB at the free surface of the isotropic phase (by the X-ray reflection method) as the temperature approaches  $T_{IS}$  [19]. But we observed smectic layers, because 12CB has no nematic phase, but only a single smectic-A-phase. Smectic layers begin to develop at about 10°C above  $T_{IS}$ , and their number increases in quantized steps from zero to five.

For 80CB which has  $N$ - and  $S_A$ -phases, we have assumed [3] that the smectic alignment appears at the surface of the nematic phase. Smectic layers can provide

not only a greater translational order parameter, but also a greater orientational one as compared to the bulk. In this case, in formula (3), one should consider an excess translation order parameter. Following Croxton and Chandrasekhar [13,14], we then have

$$d\sigma/dT \sim \int [\rho(z)\xi^2(z) - \rho_0\xi_0^2 + \rho(z)\eta^2(z) - \rho_0\eta_0^2] dz, \quad (4)$$

where  $\rho_0$ ,  $\xi_0$ , and  $\eta_0$  are the volume density, orientational order parameter, and translational one;  $\rho(z)$  is the profile density of particles across the transition zone;  $\eta(z)$  and  $\xi(z)$  are the orientational and translational order parameters in the interface layer which depend on the distance  $z$  to the interface. Moreover,  $\rho(-\infty) = \rho_0$ ,  $\eta(-\infty) = \eta_0$ ,  $\xi(-\infty) = \xi_0$ . It follows from (2) and (4) that the sign of  $d\sigma/dT$  is defined by the competition between such factors: a decrease of the density profile  $\rho(z)$ , the degrees of orientational and translational alignments at the surface and in the bulk. The increase in  $\xi(z)$  and  $\eta(z)$  at the surface (as compared to the bulk) can suppress a “classical” monotonous course of  $\sigma(T)$ . This leads to a positive slope of  $\sigma(T)$ , i.e.  $d\sigma/dT > 0$ .

Thus, the surface tension  $\sigma$  of 5CB has been measured in a wide temperature interval at the free surface and the 5CB/glycerine interface. Both curves indicate an anomalous behaviour, which implies the positive slopes of  $\sigma(T)$ . The anomalies may be qualitatively explained by more ordered nematic states in the surface layer as compared to the bulk. One of the possible mechanisms of such an alignment is the surface polarization. For the complete understanding of a behaviour of  $\sigma(T)$ , it is necessary to study all mechanisms which are responsible for an excess nematic alignment at the interface. Further experiments may throw upon light on these mechanisms.

The work was partially financially supported by the project 1.4.1V/119 (under the guidance of Prof. Yu.P. Gnatenko). The author is also grateful to L.M. Bugajova for her valuable remarks.

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Received 22.04.05.

Translated from Ukrainian by V.V. Kukhtin

#### ВИЗНАЧЕННЯ ПОВЕРХНЕВОГО НАТЯГУ РІДКОГО КРИСТАЛА 5ЦБ РІВНОВАЖНИМ МЕТОДОМ ВИСЯЧОЇ КРАПЛІ

*Л.М. Таракхан***Р е з ю м е**

Методом висячої краплі виміряно поверхневий натяг рідкого кристала пентилціанобіфенілу (5ЦБ) в широкому температурному інтервалі на вільній поверхні й на межі з гліцерином. Обидві криві виявляють аномальну поведінку, яка полягає в наявності ділянок з додатним температурним коефіцієнтом  $\sigma$ . Аномалії якісно можна пояснити існуванням у поверхневому шарі, порівняно з об'ємом, більш впорядкованих нематичних станів. Вони передбачені теорією Крокстона—Чандрасекара. Цей експеримент підтвердив наші попередні результати стосовно того, що ізотропні межові умови впливають не лише на величину поверхневого натягу, але й на форму кривої  $\sigma(T)$ . Розглянуто механізми, які приводять до додаткового впорядкування молекул 5ЦБ в міжфазному шарі.