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Anisotropic Properties of the LC Surface Tension

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We have proposed a measurement technique for detection of the anisotropy of the surface tension (ST). A flat vertical capillary of glass substrates with transparent electrodes is split into 5 vertical sections. In each section a different LC orientation is set, such as planar, homeotropic, and homeoplanar. The open capillary end is placed into a vessel with LC. In each section the LC has a special level to ensure measurement of ST coefficients, while by varying temperature and applying driving voltage one can study how the ST is affected. The main results are: 1) The smallest rise (and the lowest ST) is observed for the homeotropic orientation, the highest for planar orientation, and average for the homeoplanar orientation. 2) Heating of the LC up to 30 to 50°C above isotropic point or application of orienting fields do not qualitatively change the picture of distribution of the rise levels. Interpretation of the results obtained and the ST coefficients for known LC are given.

Keywords: surface tension; anisotropy; influence electric field and temperature

INTRODUCTION

It is known that most physical parameters of LC have a certain degree of anisotropy. One can suggest that in this series there should also be surface

tension (ST). In the scientific literature information on surface tension is scarce and if any, it reports ST measured by the methods applied for normal isotropic liquids, i.e. without taking into account a possible anisotropy - see, for instance, review ^[1].

The authors have made an attempt to detect and measure ST anisotropy in the cases where it actually takes place. A simplest method described in any text book on physics was chosen based on rising of the liquid column in a flat or circular capillary. Surface tension is a product of interaction of three media, i.e. the liquid itself (1), gas medium (2) and solid restricting surface (3), see Fig. 1a. In generally, this is valid for an isotropic liquid.

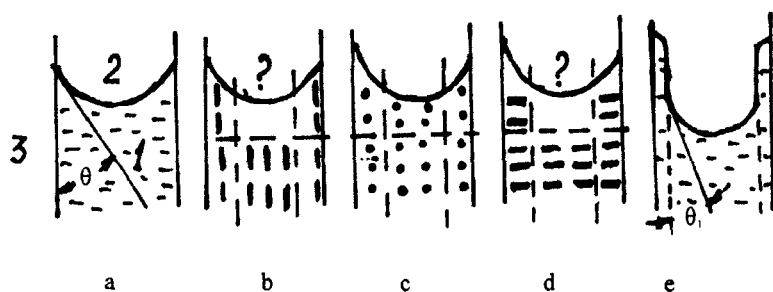


FIGURE 1 Determination of the wetting angle and schematic diagram of the menisca.

The height to which the liquid rises in the capillary, h , can be found from the expression $h = \sigma \times \cos \theta / \rho \times g \times \text{radius}$, where σ is surface tension coefficient; θ is wetting angle; ρ is specific weight of the liquid; g is free-fall acceleration; radius is capillary radius (for a flat capillary it is thickness of the capillary).

As can be seen from the above expression, the property of the solid surface of the capillary to orient LC is in no way taken into account. It is reasonable to expect that if the surface tension is anisotropic, the level of the LC rise should be different for different orientations.

Experimental

To verify this assumption, a flat vertical capillary was made of glass substrates with transparent ITO electrodes (Fig. 2).

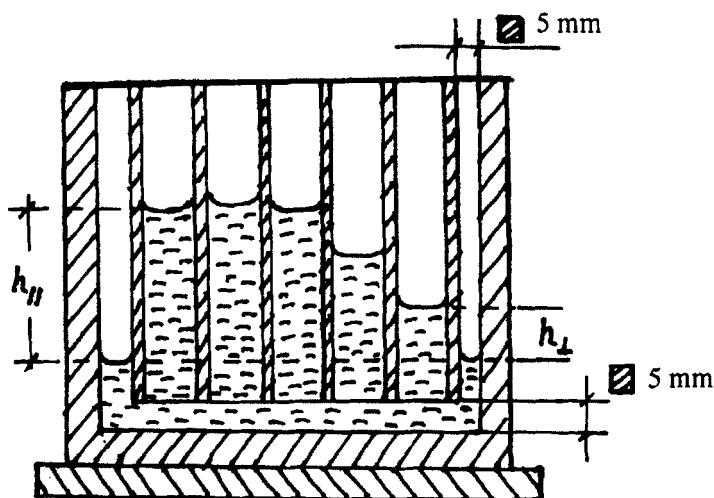


FIGURE 2 Design of the flat capillary.

The capillary's plane was divided into 5 sections and with 5 different orientations were provided within each of them, i.e. (left to right) planar vertical, twist, planar horizontal, homeoplanar (near one surface the LC

molecules had homeotropic orientation, near the other surface planar one) and homeotropic. The planar orientation was achieved by rubbing of the polymer film, homeotropic by either applying a special orienting agent on the same film or by polishing of the bare surface of the substrate with a polishing paste. The lower ends of the flat capillary were placed in a vessel with the liquid, the vessel being a square-section cavity at least 5 x 5 mm which means that the capillary effects in the «vessel» itself were eliminated. The capillary thickness in all sections was with a sufficient precision the same and equal to 100 μm .

The liquid measured (LC or control isotropic liquid) was transferred via the square cavity to the lower ends of the capillary sections and rose to a certain height wetting the dry surface of the capillary.

Result and discussion

1. The level of rising of the isotropic liquid, for instance, ethyl alcohol was the same in all sections of the capillary. The level of rising of the LC was different for different sections. Three orientations showed marked differences in the level of rising. The highest level of the LC MBBA rising (~ 75 mm) was observed for planar orientations near the substrates (planar vertical, planar horizontal and twist). The lowest level of rising was observed for the homeotropic orientation (65 mm) and the intermediate level for homeoplanar orientation (71 mm). Using the expression above for an anisotropic liquid, the coefficient of the surface tension for the planar orientation for the ideal wetting is 26.5 dyn/cm, for homeotropic 20.7 dyn/cm and for homeoplanar 24.2 dyn/cm.

The difference in the level of the LC rising was observed for all (more than ten) nematic LC studied and is a testimony of the explicit anisotropic character of the LC surface tension.

2. The levels of the LC rise in the three sections with planar orienting surfaces differ insignificantly (within 5%) without demonstrating of any clear regularity. This gives us a ground to use further the terms of the surface tension coefficient for planar orientation (along the molecule's long axes) $\sigma_{||}$, and the one for the homeotropic orientation (perpendicular to the molecule's long axes) σ_{\perp} . They can be measured using two round capillaries, one of which was not treated and has a random planar orientation while the other was treated with an orienting agent to get a homeotropic orientation. Subsequently the authors made a wide use of this procedure.

3. Quite naturally there occurs a question: is it possible that the difference in the level of the LC rising for planar and homeotropic orientations is due to the difference in the materials of the orienting surface contacting the LC? In the former case it is rubbed polymer film, in the latter it is a homeotropically orienting agent on the same polymer film. Two experiments were made. In a two-section capillary a planar orientation was provided by rubbing the bare surface while a homeotropic one was achieved by polishing the surface with a polishing paste. Though the material of the orienting surfaces was the same, the LC rise level in the planar section of the capillary was higher as compared to the homeotropic one but 10-15% lower than the one for the case of the planar orientation obtained by rubbing of the polymer substrate.

An insignificant lowering of the level of rising for the planar orientation obtained by rubbing of the uncovered surface could be due the imperfection of the latter.

In the second experiment, the homeotropic orientation in two sections of the capillary was obtained by different procedures, i.e. by application of the orienting agent and by polishing with the polishing paste. In the latter case, the level of rising was 10-12% lower which could be explained by a more perfect homeotropic orientation achieved.

The above experiments testify that the difference in the level of rising is mostly due to the ST anisotropy rather than different materials of the orienting surface.

4. Once the anisotropic character of the surface tension coefficients established, a study was performed on how they were affected by changes in the temperature and electric fields. It was established that heating of the capillary to temperatures exceeding isotropic point by 30-50°C leads to an insignificant (3-5%) reduction in the level of rising without any qualitative change in the pattern of the level distribution in the sections of different orientations. This is an evidence of the following facts:

- the surface tension is defined by the first layer of the LC molecules;
- the first layer of the molecules maintains the orientation not only in the LC phase but also in the isotropic one;
- probably, in the isotropic liquids having an elongated molecular shape, the first layer of molecules is also oriented by specially treated surfaces and this orientation can be translated at a certain distance leading to an ordering in the boundary layers which was observed by a group of researchers from the Odessa State University - see, for example,^[2].

5. Application of the electric fields close to breakdown does not lead to any recorded changes in the pattern of distribution of the LC layer rise levels in different sections in spite of the optically observed reorientation of the LC in these sections. This testifies to the fact that in the electrooptical effects at

least the first layer of the LC molecules retains its original orientation and this is why the ST remains unchanged.

6.The measurements made do not allow us to answer the question: what is the orientation of the LC molecules at the LC-air boundary? The answer seems to be interesting and ambiguous (possible versions are given in Fig 1b,c,d).

7.It should be noted that hysteresis phenomena are quite frequent. In many experiments the steady-state level of the LC rising in the same capillary section can be markedly different depending on how this level was achieved. If the level was attained by filling of the dry capillary, it can be 15-20% lower as compared with the one in the case when the steady-state level was achieved by lowering of the LC level in the make-up vessel. In the latter case, the steady-state level is observed in the capillary wetted by the LC; such level is higher than in the dry capillary. This situation remains stable for as long as tens of hours or days.

Evidently, in the capillary a structure is formed similar to that shown in Fig. 1e. The LC column is placed into the capillary whose walls are wetted with a film of the same LC. A more detailed investigation of the hysteresis phenomena may reveal further information on the forces of cohesion of the LC with the solid surface and the LC with the film of the same LC.

8.Finally, we present data on the anisotropic ST coefficients measured for a number of generally known LC (temperature 22-25°C)

LC	$\sigma_{ }$, dyn/cm	σ_{\perp} , dyn/cm
MBBA	26.5	20.7
E-7	23.7	14.5
ZLI-1132	26	13.6
ROTN-605	21.6	15.1
Lixon L-52	18.9	15.2
5 CB	24.3	15.2
ZhK-1289	24	16
ZhK-805	21.9	15.3
Ethyl alcohol	table value 22.03	measured value 21.52

Conclusion

The above data are a convincing evidence of the anisotropic character of the surface tension. The experimental procedure opens new possibilities to investigate subsurface phenomena on the LC-orienting surface boundary.

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