



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl16>

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Version of record first published: 20 Apr 2011.

To cite this article: V. N. Putveenkov & E. A. Kirsanov (1984): Anisotropy of the Work of Adhesion for a Nematic Crystal on a Shaped Support, *Molecular Crystals and Liquid Crystals*, 102:8-9, 241-246

To link to this article: <http://dx.doi.org/10.1080/01406568408070534>

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ANISOTROPY OF THE WORK OF ADHESION FOR
A NEMATIC CRYSTAL ON A SHAPED SUPPORT

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(Received for Publication September 7, 1984)

Abstract: Under dynamic conditions, experimental data on contact angles of wetting for p-azoxyanizole on glass have been obtained. The contact angle of wetting is found to depend on support relief and the values of the contact angle are observed to change at the temperature of the liquid crystal phase transition. The value of energy required for turning a molecule of a nematic crystal by 90° on a shaped surface has been calculated.

1. Introduction. Practical applications of liquid crystals require, in most cases, preliminary orientation of molecules on pre-treated supports. To provide parallel orientation (planar texture of sample), shaped surfaces/1,2/ are generally prepared. The simplest procedure of formation of such a surface is polishing of glass supports in one direction with a diamond paste. Another procedure consists in deposition of SiO_2 by spraying at an oblique angle to the support. In both cases, a microrelief is obtained in a form of parallel bulges or grooves. Extended molecules of liquid crystals are orientated along the grooves. In theoretical calculations, a support

profile is assumed to be sinusoidal. To turn molecules by 90° , i.e. to the position perpendicular to the direction of polishing, the energy $W = (K/4)A^2q^3$ is needed, where K is the modulus of elasticity; A is the amplitude of the sinusoidal profile of the support; q is the wave number of surface distortion /2/.

Energy approximation to surface phenomena consists in determination of the surface tension of liquid crystal γ_L , work of adhesion W_a , interfacial tension γ_{SL} . In order to estimate the two latter values, contact angles for a sessile drop on the supports being concerned with are determined. On the shaped supports, the drop spreads better along the direction of grooves/3/.

Hirano et al./4/ determined by means of the Zisman method /5/ the critical surface tension γ_c for complete spreading of organic liquids by a SiO_2 layer on supports. They found the values of contact angles θ to differ insignificantly when investigating the drop in the perpendicular directions and obtained two values: 37 and 39 dyn/cm.

Proust /6/ determined the contact angle for drops of the methoxybenzylidene butylaniline liquid crystal on supports covered by surfactants (surface-active compounds). They found the angle θ to decrease spontaneously up to a certain stable value. The phenomenon of spreading was explained to be due both to the roughness of the support surface and to orientation of molecules near the surface.

Thus, the problem of anisotropy of contact angles

on a shaped support for isotropic and nematic phases of the same substance still remains unclear.

2. Experimental results. We studied the temperature dependence of contact angle for the p-azoxyanisole liquid crystal on a glass support (cover glass for microscopy). The support was polished in one direction by a diamond paste (the grain size of $10\mu\text{m}$). The glass purified from the paste was boiled for 20 minutes in distilled water and for the next 20 minutes in acetone followed by drying in a drying oven.

The contact angles were measured under heating conditions both in the nematic and isotropic phases when observing along the direction of polishing (θ_1) and perpendicular to the direction (θ_2). The values of $\theta(T^0)$ for the stable state of the drop are shown in Fig. 1.

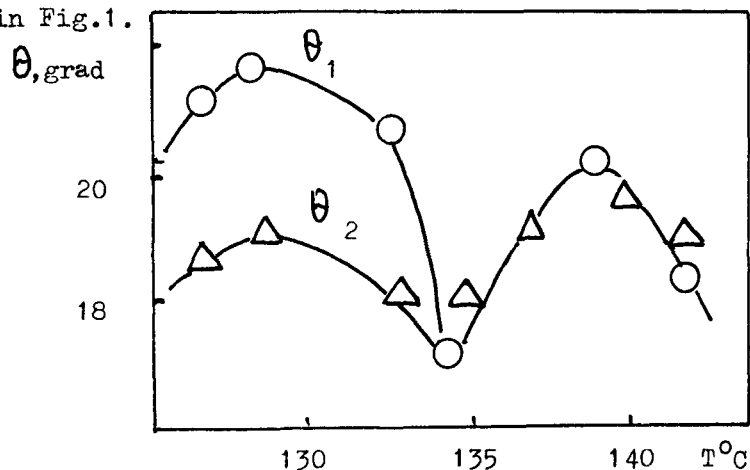


Figure 1. Temperature dependence of contact angles of wetting for p-azoxyanisole on glass (θ_1 and θ_2).

A heating rate was about $0.1^\circ\text{C}/\text{min}$. Since the measurements were carried out under dynamic conditions

then the contact angles θ_1 and θ_2 were determined at somewhat different temperatures.

The angle $\theta_1 > \theta_2$ in the region of the nematic phase ($T < T_c$); and above the transition point ($T_c = 135^\circ\text{C}$) the angles θ_1 and θ_2 are practically the same (Fig1).

The values of (T) for calculation of the work of adhesion were taken from the study/7/. The temperature dependence $W_a(T)$ is shown in Fig.2. In the anisotropic phase, there is some kind of anisotropy of the work of adhesion $W = W_a(2) - W_a(1) \approx 0.6$ dyne/cm. In the isotropic phase, $W_a(2) \approx W_a(1)$.

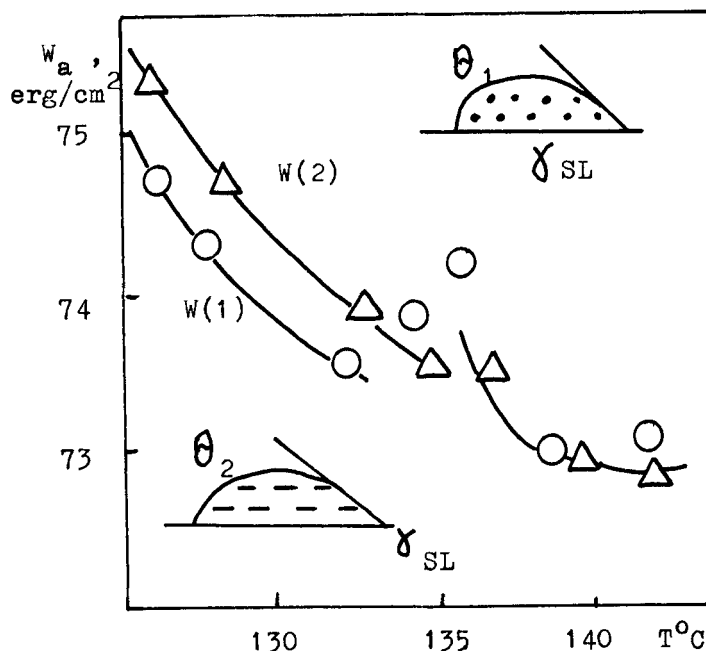


Figure 2. Temperature dependence for the work of adhesion $W_a(1)$ and $W_a(2)$.

3. Discussion. The experimental data obtained have shown that the nematic liquid is more sensitive to a support relief than the isotropic liquid. The anisotropy of the contact angles (and of the work of adhesion) may be related to orientation of the extended molecules of a nematic crystal with respect to the support relief. Orientations of molecules on the support surface for different positions of drops are shown in the insets (Fig. 2). The value of $\gamma' = \gamma_s - \gamma_{SL} = W_a - \gamma_L$ along the direction of polishing is larger than the one for the perpendicular direction.

The anisotropy of these values may be explained as follows. Upon spreading of a nematic drop, motion of molecules along the grooves occurs without considerable changes in orientation and is determined by the force of interaction of molecules of the liquid crystal, vapour and support. Then $W_a(1) = \gamma_L + \gamma_s - \gamma_{SL}$. In the other case, the molecules change their orientation when overcoming the surface non-uniformity which requires an additional energy δ . So, $W_a(2) = \gamma_L + \gamma_s - \gamma_{SL} - \delta$. Thus, we assume $\delta = W_a(1) - W_a(2)$ to be determined basically by the energy consumed for re-orientation of molecules upon spreading "over" the non-uniformities.

Such re-orientation of molecules near a shaped surface consists just in their turning in the support's plane. Theoretical estimation of energy consumed to turn molecules by 90° and the experimental values of W are given in /8/. For polished glass, $W(\text{calc}) \approx 0.08 \text{ dyne/cm}$; $W(\text{exp}) \approx 0.1 \text{ dyne/cm}$.

Data for the support with deposited SiO_2 (the grazing angle of 60°) are given in /9/: $W(\text{calc}) \approx 1$ dyne/cm; $W(\text{exp}) \approx 0.6$ dyne/cm.

The value we have obtained ($+\Delta\gamma' = \Delta W_a \approx 0.6$ dyne/cm) is of the same order of magnitude as the energy required for turning the molecules of nematic crystal near a shaped surface.

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