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. Matveeiwo & E. A. Kirsanov (1984): The Behaviour of Contact Angles of Wetting for Liquid Crystalline Drops on Glass Near the Phase Transition, Molecular Crystals and Liquid Crystals, 102:8-9, 235-240

To link to this article: http://dx.doi.org/10.1080/01406568408070533

Mol. Cryst. Liq. Cryst. Vol. 102 (Letters), pp. 235-240
0140-6566/84/1028-0235$15.00/0

THE BEHAVIOUR OF CONTACT ANGLES OF WETTING FOR LIQUID CRYSTALLINE DROPS ON GLASS NEAR THE PHASE TRANSITION.

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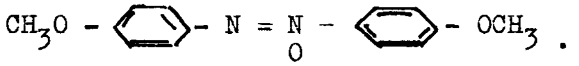
(Received for Publication August 31, 1984)

ABSTRACT: The experimental values of contact angles of wetting for p-azoxyanisole - glass in the nematic and isotropic phase have been obtained. At the point the phase transition, a change in the value of contact angle of wetting is observed. The values of adhesion energy, have been calculated for different orientation of molecules with respect to the glass support.

It is well-known /1/that contact angles of drops on solid supports enable an information on interfacial energy γ_{SL} to be obtained. A change in the structure of liquid results in alteretion of the contact angle as it a has been shown recently for polymer solutions /2/. It seems to be quite possible that orientational ordering of liquid crystals has to affect the value of conyact angles of wetting. Nevertheless, this value was not found to very upon phase transition from the isotropic to liquid crystalline state /3/.

We studied the behaviour of contact angle of wetting for a drop of a classical liquid crystalline compound p-azoxyanisole (PAA) in its nematic and isotropic phases.

PAA is known /4/ to be transformed from the solid state to the nematic state at 118°C and from nematic to isotropic state at 135°C.The structural formula of the compound is



The angle between the long axis of the molecule and a free surface in the nematic phase is almost equal to zero and does not depend on temperature.

Measurements of the contact angle were carried out visually by means of a microscope equipped with a degree scale. A glass support(cover glass for microscopy) was treated directly before the experiment according to the following procedure:20 min. of boiling in distilled water,20 min. of boiling in acetone("pure for analysis" grade),drying oven.The glass was placed on a heat-insulating mount inside a metallic thermochamber.A termistor adjusted near the support was used to measure temperature.

The substance was melted in a porcelain crucible and transferred in a form of a drop on the support heated to the temperature of about 130°C.After formation of a stable contact angle θ ,the sample was heated in the thermostat chamber at a heatin rate of about 0.1°C/min. Contact angles were measured for several drops of different dimensions.Though the absolute values of the angles were somewhat different, the type of the temperature dependence was similar for different drops.The differences are apparently caused by pre-treatment of the glass surface(some non-uniformity).The values of cosθ(T^{o}) for a drop of a medium size are given in Fig.1.

During a heating cycle,the value of cos θ depends practically linearly on temperature.At the point of the phase transition (135°C) the linearity is distorted and the angle θ is considerably larger than the values extrapolated to the isotropic phase. At the temperature of 139°C,power supply of the thermochamber was switched off and it was cooled to room temperature.Heat inertia of the set-up resulte in some additional heating of the drop(to 140.5°C) for about ten minutes. Under these conditions,the contact angle θ increased (as shown by the curved arrow in Fig.1). This phenomenon may be explained by the fact that a thin layer between the drop and the support remains partially orientated upon the transition though the critical point i.e., it posesses a liquid crystalline order. After some time,this boundary layer disappears which results in the change in θ .

During a cooling cycle,the contact angles increase though the dependence cos θ(T) appears to be much more complex after transition to the nematic phase. Thus,the contact angles vary upon the "nematic crystal - isotropic liquid" phase transition or, at least,the shape of the curve cos (T) changes. Such a behaviour does not agree with the data obtained by Proust and Ter-Minassian-Saraga/3/ for a nematic compound methoxybenzylidenebutylaniline on a surface treated with a surfactant (surface active substance). The authors/3/ noted a uniform decrease of θ with increasing temperature without any change with in the phase transition region.

It is worth to consider the temperature dependence of the work of adhesion $W_a(T)$. The value of $W_a(T)$ is determined experimentally out of the relationship $W_a = \gamma_L(\cos\theta + 1)$. The values of surface tension γ_L for different temperatures were obtained from the data of study /5/.

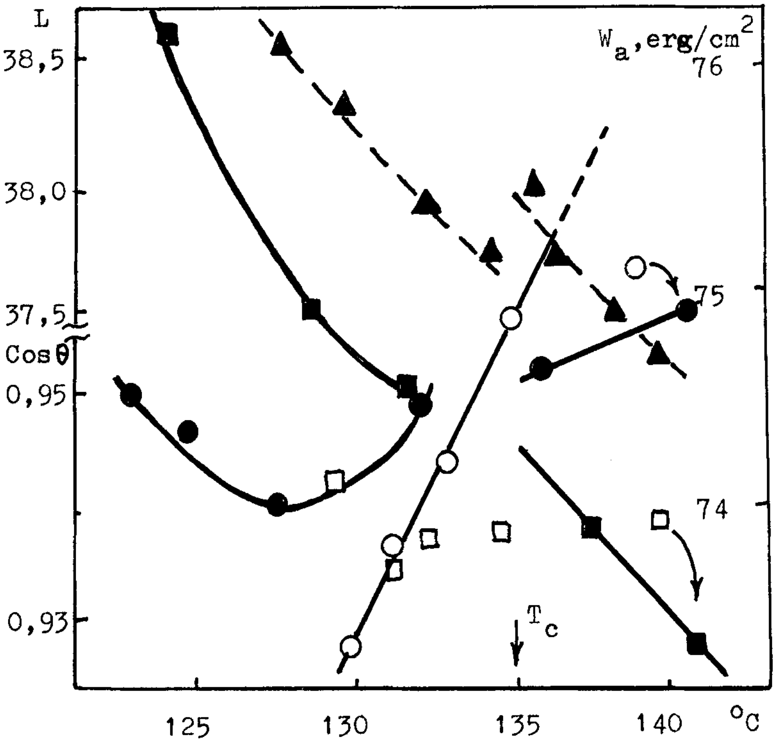


Fig.1 Temperature variations of of the cosine of contact angle cos θ (o – heating; ● – cooling), of work of adhesion W_a(□ – heating; ■ – cooling) and of the surface tension γ_L (▲).

Apparently, during a heating cycle, W_a chages only slightly on the trasition though T_c (Fig.1) though the data immediately close to T_c are needed for more grounded conclusion. The value of W_a is equal to 73.7 erg/cm^2. The physical meaning of the work of adhesion is represented by the formula $W_a = \gamma_S + \gamma_L - \gamma_{SL}$, where γ_S is the surface energy of a support; γ_{SL} is the interfacial energy; γ_L is the surface tension of a liquid. The value of γ_S was equal to 45 erg/cm^2 for the glass support kept under low humidity. Within yhe temperature interval studied (130°-140°C), γ may be considered to be constant. Then $\gamma_{SL}(132.5^\circ) \approx 8.75$ erg/cm^2; $\gamma_{SL}(134.5^\circ) \approx 9.0$ erg/cm^2; $\gamma_{SL}(139^\circ) \approx 8.8$ erg/cm^2. The value of γ_{SL} 8 erg/cm^2 for liquid crystals is in agreement with the approximate estimation /6/.

During a cooling cycle, the work of adhesion increases dramatically with increasing temperature. Perhaps, this is related with formation of an adsorbed liquid layer near the drop.

The values of $W_a(\parallel) = 77.8$ erg/cm^2 and $W_a(\perp) = 85.0$ erg/cm^2 were calculated /7/, correspondingly, for molecular orientation parallel and perpendicular to the glass support. Assuming $\gamma_S = 45$ erg/cm^2, $\gamma_{SL}(\parallel) = 4.9$; $\gamma_{SL}(\perp) = 4.55$ erg/cm^2 can be obtained.

The above values are of the same order of magnitude as the ones obtained in our experiment.

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