Translated from *Uspekhi Khimii*, **55**, 1319-1343 (1986) U.D.C. 541.182.183:539.2

Surface Phenomena in Nematic Liquid Crystals

V.N.Matveenko and E.A.Kirsanov

The characteristic features of the surface tension, adhesion, and ordering of the molecules, and their orientation in the surface layers of the liquid-crystal phases of nematogenic compounds in relation to the anisotropic intermolecular interaction have been examined.
The bibliography contains 95 references.

CONTENTS

I.	Introduction	743
II.	Basic theories of the liquid-crystal state	743
III.	The surface tension of liquid-crystal materials	744
IV.	The energy of adhesion of a liquid crystal to a solid support	748
V.	The surface order parameter	749
VI.	The orientation of the director on the free surface of a nematic liquid crystal	751
VII.	Criteria for determining the nature of the orientation of liquid crystals on supports	753
VIII.	The influence of the azimuthal anisotropy of the support on surface phenomena	754

I. INTRODUCTION

An understanding of the mechanism of the production of a given orientation of the molecules of liquid crystals between specially treated supports is of considerable practical importance for creating improved electro- and thermo-optical devices based on liquid crystals. The problem has been dealt with to some extent in familiar monographs.[1-5] Most studies, however, have been predominantly experimental and empirical in character, and the discussion of the results has been restricted to general physicochemical considerations, borrowed from the physics of the surface phenomena of ordinary liquids. The few theoretical studies have been devoted to specific chemical compounds, and do not claim to be general in their approach.

It therefore seems appropriate to examine the available experimental results (often contradictory) and various existing theoretical models.

II. BASIC THEORIES OF THE LIQUID-CRYSTAL STATE

Liquid crystals (LC), or anisotropic liquids, are formed by the molecules of organic compounds which have an elongated shape. Like ordinary liquids, nematic LC are characterised by short-range translational order, but there is no long-range translational order; they can form droplets, and can be drawn into capillaries; and different types of flow are produced in them. At the same time, the long-range orientational order in the arrangement of the long axes of the molecules of nematic LC is preserved, although thermal fluctuations partly deflect the molecules from the predominant direction (denoted by the unit vector **n**, which has been called the "director").

The present examination will be restricted to nematic LC (NLC or nematics). For these, the order parameter

$$Q = {}^1/_2(3\langle\cos^2\theta\rangle - 1),$$

has been introduced, where θ is the angle of inclination of an individual molecule to the director **n**, and the brackets denote averaging over all possible orientations of the molecules in the macroscopic volume of the material. If the long axes of the molecules are arranged randomly, as in an isotropic phase (or in an ordinary organic liquid), $\langle\cos^2\theta\rangle = 1/3$ and $Q = 0$. The value $Q = 1$ corresponds to 100% parallel mutual orientation of the molecules. In practice, Q can take values of 0.3–0.4 at a temperature close to the transition point from the nematic to the isotropic phase $T \cong T_c$.

The order parameter Q appears in the expression for the total free energy of the liquid-crystal phase, and it is used to describe phase transformations and the changes in the optical, electrical, and magnetic properties of LC with change in temperature. The parameter Q naturally retains its importance in the description of surface phenomena. A typical curve giving the temperature dependence of Q, obtained from magnetic susceptibility measurements, is shown in Fig.1.

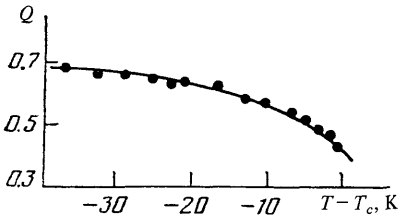


Figure 1. Temperature dependence of the order parameter in the nematic phase of p-azoxyanisole.[4]

In addition to the nematic phase, there exist a large number of other liquid-crystal phases, of which the smectic *A* phase must be mentioned. In it, the molecules are grouped in layers, and the long axes of the molecules are approximately perpendicular to the plane of the layer. The layers can move relative to one another, and the molecules within a layer have short-range translational order. In a nematic phase obtained after heating a smectic LC, clusters with smectic order (or cybotactic groups) are preserved.

For experimental studies, an LC specimen is placed between two glass plates subjected to special treatment. The molecules in the thin layers of the LC are oriented under the influence of the walls of the cell, leading to the formation of the required structures. Rubbing the glass (with paper or diamond paste), the production of a special relief on the glass by applying coatings with an obliquely incident beam, or the deposition of a stepped lattice (by photolithography) create a unique direction in the NLC layer, along which the director **n** is oriented. This direction is called the axis of easy orientation, or the "easy" axis. The methods of treating the support described above lead to the orientation of the director **n** parallel to the support (for example in the direction of rubbing). In the case of thoroughly cleaned glass surfaces or plates covered with surface-active substances, the axis of easy orientation is arranged at right angles to the surface of the support. Thus the orientation of the director close to the support depends on its treatment; the influence of the support extends into the bulk of the specimen, creating a uniform "single-crystal" state (from the viewpoint of optics, nematic crystals behave as monoaxial crystals, whose optical axis coincides with the director **n**). As a result, in a thin layer of LC between treated plates, one of three possible uniform textures is produced: planar with parallel orientation of the molecules with respect to the support, homeotropic with normal orientation of the molecules, or tangential with sloping orientation; the latter exists in the case of a complex relief on the support. The orientation of the director **n** within a specimen relative to the support is generally described using a system of coordinates with the z axis at right angles to the plane of the plates; the x axis is usually directed along the projection of the director **n** (for parallel and sloping orientations).

Table 1. The surface tension of various nematic LC.[10]

Compound	γ, erg cm^{-2}	T, °C	Method	Refs.
MBBA	38	23	—	[11]
MBBA	35.8	—	I	[12]
MBBA	30	—	II	[13]
MBBA	35.3	—	—	[14]
PAA	38	125	III	[15]
PAA	37	120	—	[14]
PAP	31.2	145	III	[15]
5CB	28.1	31.5	II	[8]
5CB	27.9	20	II	[8]
8CB	26.2	41	II	[8]

Notes: I—pendant drop method, II—measurements using a Wilhelmy plate, III—capillary rise method; the dash indicates that the method or the temperature of the specimen were not given. Compounds: MBBA = methoxybenzylidenebutylaniline, PAA = *p*-azoxyanisole, PAP = *p*-azoxyphenetol, 5CB = 4-pentyl-4′-cyanobiphenyl, 8CB = 4-octyl-4′-cyanobiphenyl.

Various external influences bring about orientational deformation, associated with the rotation of the local director $\mathbf{n}(x, y, z)$, leading to an increase in the elastic component of the free energy F_d. In a magnetic field, for example, the molecules are oriented in the direction of the field **H**. The orientation in an electric field **E** depends on the sign of the dielectric anisotropy ε_a of the specific LC. Various forms of orientational deformation have been described in detail.[1-5]

Close to the free surface of a liquid-crystal layer (in the case of a freely suspended film or drop on a support), different orientations of the director relative to the normal **N** to the free surface are produced for different substances. For example, for nematic *p*-azoxyanisole (PAA), the angle ψ between the normal **N** and the director **n** on the free surface is 90°,[6,7] whereas for nematic materials of the series of 4-C_nH_{2n+1}-4′-cyanobiphenyls, $\psi = 0$.[8] For methoxybenzylidenebutylaniline (MBBA) and ethoxybenzylidenebutylaniline (EBBA), the angle ψ changes with change in temperature.[6,9]

III. THE SURFACE TENSION OF LIQUID-CRYSTAL MATERIALS

1. Experimental Data

The magnitude of the surface tension γ for the free surface of the nematic and isotropic phases of liquid-crystal compounds has been measured by different methods at various temperatures. The values of γ for individual temperatures are given in Table 1.

The temperature dependence of the surface tension for a given substance, obtained by different authors, often shows lack of agreement, and differences are observed not only in the magnitude of the surface tension, measured at the same temperature by different methods, but also in the nature of the change in γ in the region of the phase transformation from the nematic to the isotropic phase (Fig. 2).

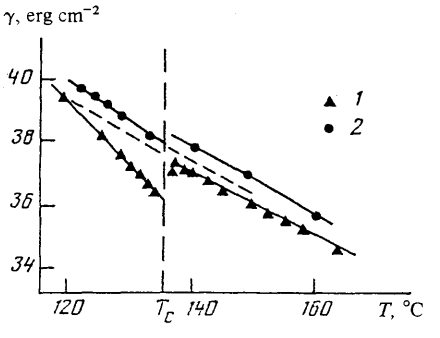


Figure 2. Temperature dependence of the surface tension of PAA, measured by the capillary rise method (*1*),[15] the ring lifting method (*2*),[16] and the maximum gas-bubble pressure method (broken line).[17]

The observed differences in the experimental data are apparently due to differences in the degree of purification of the materials, but the choice of the method used to determine the surface tension also has an extremely significant influence on the results of the experiments; this can be seen, in particular, for the case of PAA (see Fig. 2). In spite of the considerable differences, the curves nevertheless demonstrate important characteristic features of the $\gamma(T)$ relationship for PAA; at a distance from the transition point T_c, γ changes approximately linearly with increase in the temperature of both the nematic and the isotropic phases; in the region of the transition, the linearity of $\gamma(T)$ breaks down to some extent (depending on the method of measurement); γ increases smoothly or abruptly. A

similar non-smooth $\gamma(T)$ relationship in the region of the phase transformation was obtained by the pendant drop method under equilibrium conditions for PAA (Fig. 3*a*) and *p*-anisaldazine (Fig. 3*b*), and also for MBBA.[18]

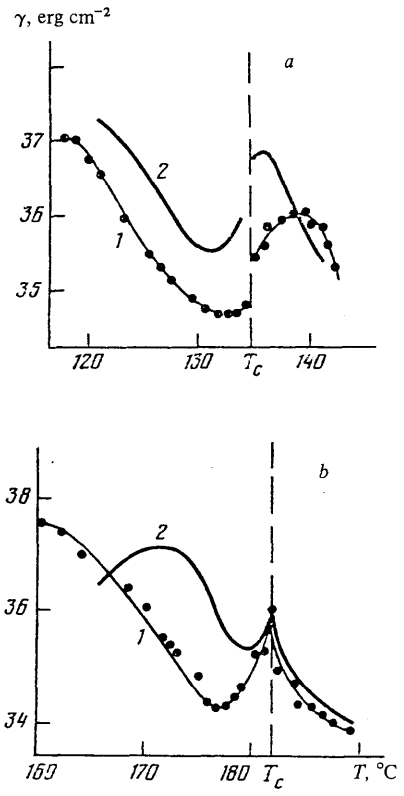


Figure 3. Temperature dependence of the surface tension of *p*-azoxyanisole (*a*) and *p*-anisaldazine (*b*):[18] *1*) experiment (pendant drop method), *2*) theoretical curves.[34]

For both MBBA [19] and PAA,[17] the maximum gas-bubble pressure method gives a linear decrease in γ with increase in temperature in both phases; on going from the nematic to the isotropic phase, γ undergoes a positive jump for both substances.

When the method of detachment (of a plate or ring) from the free surface is used for PAA [16] and MBBA,[20] a linear decrease in γ with increase in T is observed, and there is no unique feature (jump) in the region of the transition. Measurements by the Wilhelmy method in an experiment of the continuous type gave $\gamma = 35.0 \pm 0.2$ erg cm^{-2} for MBBA at $T = T_c$.

The same method (Wilhelmy plate), however, gave an appreciably non-linear $\gamma(T)$ relationship close to T_c for 5CB and 8CB.[8] The measurements were made under conditions close to equilibrium, and the rate of displacement was 5–50 mdyne cm^{-1} per day. Measurements with a good accuracy were achieved in this way; for example, for 6CB, $\gamma = 28.1 \pm 0.3$ erg cm^{-2} at 31.5 °C. γ increases with increase in temperature, both below and above T_c (Fig. 4). The slope of the $\gamma(T)$ curve is positive close to T_c in both phases (Fig. 4*a*). The maximum on the curve (Fig. 4*b*) was calculated theoretically.[8]

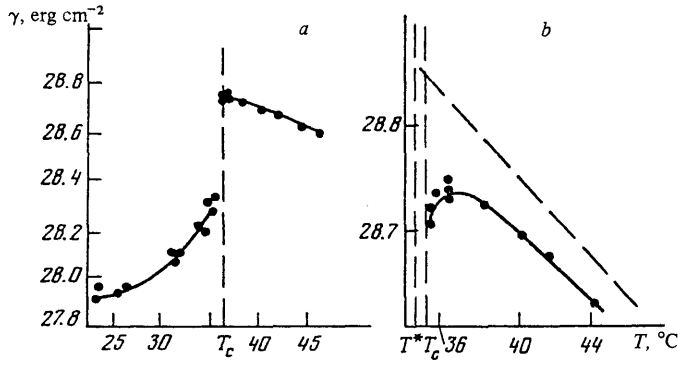


Figure 4. Temperature dependence of the surface tension for 5CB in the nematic and isotropic phases (*a*) and in the isotropic phase on an expanded scale (*b*).[8] The thick line gives the theoretical curve, and the broken line the values of $\gamma(0)$, extrapolated from the distant isotropic range.

The fundamental importance of ensuring equilibrium conditions for the reliable determination of $\gamma(T)$ can be proved indirectly for the method involving light scattering from the free surface, in which the shear viscosity and the surface tension are measured simultaneously by generating surface waves and studying their characteristics. The scattering of light from the thermal fluctuations (~10 kHz) of the free surface of MBBA made it possible to calculate γ with a relatively low accuracy[21] (Fig. 5*a*). Low-frequency ($\lesssim$1 kHz) running surface waves with a relatively high amplitude (~100 Å) have been used;[22] the temperature dependence of γ obtained for the nematic and smectic phases of *p*-cyanobenzylidene-*p*-octyloxyaniline (CBOOA) is shown in Fig. 5*b*. Similar values for the nematic phase of CBOOA were obtained from an experiment on light scattering on the thermal fluctuations of the free surface.[23] It was concluded that within experimental error, γ remains constant within the nematic phase; this does not agree with other data.[17,18,34]

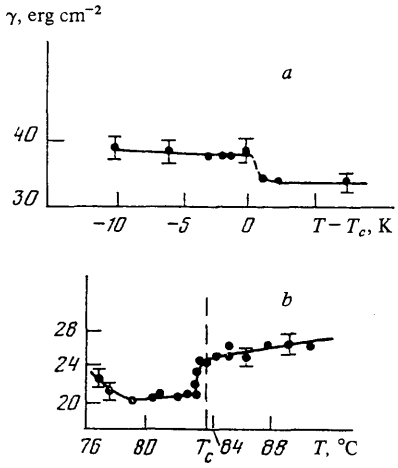


Figure 5. Temperature dependence of the surface tension, obtained by light scattering on surface waves: *a*) MBBA in the region of the transition from the nematic to the isotropic phase,[21] *b*) CBOOA in the region of the transition from the nematic to the smectic phase.[22]

The spectra of the autocorrelation functions of surface waves of low amplitude were recently studied and used to calculate the surface tension of PAA.[24] The large scatter in the experimental points (uncertainty ±1 erg cm^{-2}) makes possible only a crude estimate, $\gamma \cong 36$ erg cm^{-2}, throughout the range of existence of the nematic phase studied.

Thus the non-equilibrium surface-wave method gives values of γ with a fairly high uncertainty, so that it is practically impossible to determine the temperature dependence of γ.

2. Theoretical Models of the Surface Tension of Liquid Crystals

Existing calculations of the surface tension γ and its temperature dependence have been carried out only for the limiting cases of the orientation of the director next to the phase interface, that is for $\psi = \pi/2$ and $\psi = 0$.

The surface tension γ at the free surface of a liquid-crystal material whose molecules are joined by van der Waals interaction has been calculated.[25] The degree of order Q and the angle of inclination of the director ψ do not appear in explicit form in the expression for the interaction potential. In the macroscopic approximation, in which the material is regarded as a continuous medium, it was assumed[25] that two semi-circumferential volumes of the given substance interact with one another through a vacuum gap of thickness l. The specific (per unit area of the surface) additional energy of the system due to the van der Waals interaction will then have the form:

$$U(l) = \frac{\hbar}{4\pi}\int_0^{\infty} d\omega \int_0^{k_c} k\, dk \ln[1 - \Delta^2(i\omega)] \exp(-2kl)$$

Here, k is the wavenumber; ω the frequency of the electromagnetic field; k_C the limiting wavenumber of the fluctuating electric field, directed parallel to the surface; and

$$\Delta(\omega) = [\varepsilon(\omega) - 1]/[\varepsilon(\omega) + 1],$$

where $\varepsilon(\omega)$ is the complex dielectric constant of the liquid.

It is assumed that the free energy $U(\infty) = 0$. Decrease in the gap l to zero gives the quantity $U(0)$, which is equal to the work of cohesion with sign reversed. Thus the free energy of each of the two surfaces is equal to

$$\gamma = -{}^1/_2 U(0)$$

A calculation carried out according to this scheme for the free energy of an isotropic liquid[26,27] gave the following expression:

$$\gamma = -\frac{\hbar}{16\pi^2} k_c^2 \int_0^{\infty} d\omega \ln[1 - \Delta^2(i\omega)]$$

This method can be extended to nematic liquids, taking account of the fact that the dielectric constant of the interacting media is an anisotropic quantity. A rectangular system of coordinates with z axis perpendicular to the surface is used. The dielectric constant of the NLC will then be described by the tensor:

$$\varepsilon(\omega) = \begin{pmatrix} \varepsilon_x(\omega) & 0 & 0 \\ 0 & \varepsilon_y(\omega) & 0 \\ 0 & 0 & \varepsilon_z(\omega) \end{pmatrix}$$

The components of the complex dielectric constant parallel to and perpendicular to the director will be denoted $\varepsilon_\parallel(\omega)$ and $\varepsilon_\perp(\omega)$. In this case, for parallel orientation of the director on the free surface,

$$\gamma_\parallel = -\frac{1}{2}\frac{\hbar}{16\pi^2} k_c^2 \int_0^{\infty} d\omega \int_0^{2\pi} d\varphi \ln \frac{4[\varepsilon_\parallel \varepsilon_\perp \cos^2\varphi + \varepsilon_\perp^2 \sin^2\varphi]^{1/2}}{[\varepsilon_\parallel \varepsilon_\perp \cos^2\varphi + \varepsilon_\perp^2 \sin^2\varphi]^{1/2} + 1} \qquad (1)$$

where ϕ is the azimuthal angle of the orientation of the director relative to the x axis. For the orientation of the director normal to the surface, the oscillating electromagnetic field is directed at right angles to the director, and in Eqn.(1) the angle ϕ can be put equal to zero. Thus:

$$\gamma_\perp = -\frac{1}{1}\frac{\hbar}{8\pi^2} k_c^2 \int_0^{\infty} d\omega \ln \frac{4(\varepsilon_\parallel \varepsilon_\perp)^{1/2}}{(\varepsilon_\parallel \varepsilon_\perp)^{1/2} + 1} \qquad (2)$$

In the calculation in Ref.25, the boundary wavenumber was taken as $k_C = 2\pi/10$ Å^{-1}. Published data[28] on the complex dielectric constant of PAA, and Eqns.(1) and (2), were used to calculate the values $\gamma_\parallel = 37.8$ erg cm^{-2} and $\gamma_\perp = 44.6$ erg cm^{-2}.[25] It can be seen that the lowest surface energy corresponds to the parallel orientation of the director on the free surface. Experiment has in fact shown that PAA molecules are arranged in the surface layer parallel to the free surface,[6,7] and the experimental values of γ lie in the range 38–39 erg cm^{-2}.[15,17] The surface tension γ at the boundary between nematic PAA and glass has been calculated similarly; the value

$$\Delta\gamma_{LS} = \gamma_{LS}(\pi/2) - \gamma_{LS}(0) = 0.36 \text{ erg cm}^{-2}$$

was obtained,[25] that is on a clean glass surface the PAA molecules tend to adopt the perpendicular orientation, in agreement with experiment.[29]

A molecular-statistical theory of the surface tension of liquid crystals was developed[30] by examining the anisotropic paired interaction between the LC molecules. It used a general expression for the surface tension of a polyatomic liquid, previously obtained[31] in a calculation of the dipole–dipole contribution to the surface tension of water at a low vapour pressure. If the interaction potential of a pair of molecules U_{12} depends only on the vector of the centres of mass $\mathbf{R} = \mathbf{r}_2 - \mathbf{r}_1$ ($\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of the centres of mass of molecules *1* and *2*) and the orientation of the molecules relative to the direction of the director $\mathbf{n}$, given by the unit vectors $\mathbf{e}_1$ and $\mathbf{e}_2$, the expression for the surface tension has the form:

$$\gamma = -\frac{1}{2}\int_{-\infty}^{+\infty} dz \int d^3R\, d^3e_1 d^3e_2 \left(Z\frac{\partial U_{12}}{\partial Z} - X\frac{\partial U_{12}}{\partial X}\right)\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{e}_1, \mathbf{e}_2) \qquad (3)$$

(in the system of coordinates x, y, z where the plane xy coincides with the free surface, and the z axis is directed into the depth of the LC layer). In Eqn.(3), Z and X are the coordinates appearing in the expression for the potentials U, and $\rho^{(2)}$ is the binary distribution function, defined in such a way that the quantity $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{e}_1, \mathbf{e}_2) \cdot d^3\mathbf{r}_1 d^3\mathbf{r}_2$ gives the average number of pairs of molecules present in the corresponding states *1* and *2*. Instead of $\rho^{(2)}$ it is more convenient to introduce the distribution function $g^{(2)}$, such that $\rho^{(2)} = \rho^{(2)} g^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{e}_1, \mathbf{e}_2)$, where ρ is the density of the liquid.

For the calculation of the surface energy of a nematic LC,[30] U_{12} was taken as the van der Waals interaction potential in the form used[32] to describe the phase transformation from the nematic to isotropic phase, with the assumption that the molecules are monoaxial and rod-shaped, and that the induced dipole moments are produced along the long axes of the molecules. For a pair of molecules it is possible to introduce the polar angles θ_1 and θ_2 relative to the director $\mathbf{n}$ in a spherical system of coordinates. All the azimuthal angles of these molecules are equally probable, so that the first averaging is carried out with respect to the azimuthal angles. In accordance with the monoaxial symmetry of the nematic phase, it is possible to introduce an order parameter Q from the distribution function $f(\theta)$ of the single molecule:

$$\theta = {}^1/_2 \int_0^{\pi/2} (3\cos^2\theta - 1)\sin\theta \cdot f(\theta)\, d\theta$$

In the average-field approximation, the distribution function of two molecules with respect to the corresponding angles is $f(\theta_1, \theta_2) = f(\theta_1)f(\theta_2)$. Under these conditions, the binary function $g^{(2)}$ takes the form:

$$g^{(2)}(\mathbf{R}, \mathbf{e}_1, \mathbf{e}_2) = g^{(2)}(R)f(\theta_1)f(\theta_2)$$

Thus Parsons' approach[30] includes the following assumptions: the vectors of the centres of mass **R** are distributed isotropically within the meso-phase, the local correlation between the orientations of the molecules can be neglected, and the distribution function $f(\theta)$ is independent of z, that is the order parameter Q has the same value in the bulk and on the surface. The calculation gives the expression

$$\gamma = \rho^2/2 \int\limits_{z>0} d^3R Z g^{(2)}(R) \left[Z \frac{\partial}{\partial Z} - X \frac{\partial}{\partial X} \right] \langle W \rangle \qquad (4)$$

The quantity $\langle W \rangle$ represents the averaging of the Maier–Saupe potential[32] over all azimuthal and polar angles of the vectors **R** under conditions of cylindrical symmetry (the z axis coincides with the director **n**). Thus

$$\langle W \rangle_{\mathbf{e}_1, \mathbf{e}_2, R} = -\frac{2\nu}{3R^6} \left[1 + \frac{Q^2}{5} \right]$$

where ν is a constant.

Parsons' calculation leads to the following expressions for the parallel and perpendicular orientations of the director relative to the free surface:

$$\gamma_\parallel = \gamma_0 \left(1 - \frac{4}{9} Q + \frac{8}{27} Q^2 \right) \qquad (5)$$

$$\gamma_\perp = \gamma_0 \left(1 + \frac{2}{3} Q + \frac{1}{6} Q^2 \right) \qquad (6)$$

where

$$\gamma_0 = (3\pi\rho^3\nu/4) \int\limits_0^\infty \frac{dR}{R^3} g^{(2)}(R) \qquad (7)$$

According to Eqns.(5) and (6), $\gamma_\parallel < \gamma_\perp$ for all values of Q usually realised in the nematic phase.[30] This means that the molecules of the surface layer should be oriented parallel to the surface. The magnitude of the abrupt change in the surface tension at the temperature of the phase transformation T_C is readily determined from Eqns.(5)–(7):

$$(\gamma_0 - \gamma_\parallel)/\gamma_0 = \frac{4}{9} Q_c - \frac{8}{27} Q_c^2$$

where Q_C is the value of the order parameter of the nematic phase at the transition point. For a typical value $Q_C \cong 0.44$,[2] Parsons' model[30] predicts an abrupt increase in γ on going to the isotropic phase, in agreement with the experimental data.[15–17]

An obvious merit of Parsons' calculation[30] is that an analytical expression is obtained for the dependence of the surface tension γ on the order parameter Q. However, it describes sufficiently correctly only the case of rigorously parallel orientation of the director on the free surface, realised, for example, for PAA.

A theory of surface tension for a nematic liquid has been proposed,[34] taking account of the continuous change in the density of the liquid $\rho(z)$ and in the order parameter $Q(z)$ with increase in the distance from the interphase surface along the z axis (coinciding with the normal to the surface N). The theory[34] is not associated with any dependence of γ on the orientation of the director on the free surface. The local order parameter $Q(z)$ reaches the value of the bulk order parameter Q_ν at a sufficient distance from the surface of the liquid. Because of the mathematical difficulty of the problem, only qualitative $\gamma(T)$ relationships were obtained.[34] Variation of some of the parameters appearing in the theoretical equations makes it possible to obtain satisfactory agreement between the theoretical curves and the experimental data in the region of the phase transformation (see Fig.3). At a distance from the transition point T_C, the $\gamma(T)$ curves have a negative slope, and close to T_C the quantity $d\gamma/dT$ may be positive. The model of Ref.34 is described in more detail in Ref.2.

To describe the nematic liquids 5CB and 8CB, for which the long axes of the molecules are perpendicular to the free surface, a theory was proposed[8] in which two order parameters were introduced: in the bulk (Q_0) and on the free surface (Q_1), and $Q_1 - Q_0 \ll 1$. The surface energy is introduced in the form of an expansion with respect to powers of $(Q_1 - Q_0)$ and (dQ/dz) with coefficients A and B which depend on temperature:

$$\gamma = \gamma_0(Q_0) + \left(\frac{\partial \gamma_0}{\partial Q} \right)(Q_1 - Q_0) + \int\limits_0^\infty \left[A(Q - Q_0)^2 + B \left(\frac{dQ}{dz} \right)^2 \right] dz$$

The minimisation of γ with respect to Q and Q_1 leads to the expression

$$\gamma = \gamma_0(Q_0) - (\xi/4B)(\partial\gamma_0/\partial Q)^2$$

where $\xi = (B/A)^{1/2}$. Since no detailed microscopic theory exists, the authors cited[8] introduced a simple linear relationship of the form $\gamma_0(Q) = \gamma_0(0) - \alpha Q$, where α is independent of temperature. This gives the expression

$$\gamma = \gamma_0(0) - \alpha Q_0 - (\alpha^2\xi/4B) \qquad (8)$$

which includes only the "bulk" order parameter Q_0.

In the Landau–de Gennes theory,[1] the free energy of a nematic is decomposed in powers of Q. A critical temperature T^*, corresponding to a phase transformation of the second kind, is introduced, with $T_C > T^*$. Using the average-field approximation and the Landau–de Gennes phenomenological model, the authors cited[8] obtained for the isotropic phase ($T > T_C$):

$$\xi = \xi_c [(T_c - T^*)/(T - T^*)]^{1/2} \qquad (9)$$

For the nematic phase ($T < T_C$) the following relationship was obtained:

$$\xi = \xi_c [(T^{**} - T_c)/(T^{**} - T)]^{1/2} \qquad (10)$$

where

$$T^{**} = T_c + {}^1/_8 (T_c - T^*).$$

Substituting Eqns.(9) and (10) in Eqn.(8) gives the following expressions for the surface energy: in the isotropic phase:

$$\gamma \approx \gamma_0(0) - \beta [(T_c - T^*)/(T - T^*)]^{1/2} \qquad (11)$$

and in the nematic phase:

$$\gamma \approx \gamma_0(0) - \alpha Q_0 - \beta [(T^{**} - T_c)/(T^{**} - T)]^{1/2}$$

where

$$\beta = ({}^1/_2)\alpha(Q_1 - Q_0)_{T=T_C} = \alpha^2\xi_c/4B.$$

The relationship

$$\gamma_0(0) = 28.86 - 0.0023\,(T - T_c)$$

was obtained by extrapolating the values from the range of high temperatures of the isotropic phase (broken line in Fig.4*b*). To calculate the value of $\gamma(T)$ in the isotropic phase from Eqn.(11), the value $T_C - T^* = 0.7$ K [35] was used, and the value of β/α^2 was taken as 0.65 dyne^{-1} cm [8] (Fig.4*b*). Good agreement was obtained between the experimental values and theoretical curve, but it should be noted that β/α^2 is essentially an arbitrary parameter. It is also

not clear why the authors cited[8] did not carry out a comparison with experiment for the nematic phase, although the temperature dependence of the order parameter $Q_0(T)$ for 5CB is known.

IV. THE ENERGY OF ADHESION OF A LIQUID CRYSTAL TO A SOLID SUPPORT

Treatment of the surface of glass supports in different ways leads to the production of different liquid-crystal textures (homeotropic and planar).[29,36,37]

In the examination of the orientational deformation of a liquid-crystal specimen, it is usually assumed[1-4] that the orientation of the director n on the supports remains constant, in spite of the change in the orientation of n in the bulk of the specimen. These boundary conditions correspond to so-called strong or rigid anchoring to the support (infinite energy of anchoring of the LC to the support). In the case of a finite energy of anchoring W_S, the molecules on the surface of the support change their orientation, and this is expressed in a rotation of the director (weak anchoring). In the simplest case, the potential of the anchoring forces is introduced[37-40] in the form $W_\theta = B \sin^2 \theta_0$, where $B = \frac{1}{2}W_S$.

A fairly large number of studies in which the energy of anchoring was determined experimentally by various methods have now been published. For greater clarity, the orientational effects in LC cells whose nature is influenced by the quantity W_S will be examined separately.

1. The Frederiks Transition in an External Field

The Frederiks transition involves the reorientation of LC molecules, having dielectric ε_α or diamagnetic χ_a anisotropy, under the influence of an external electric E or magnetic H field.[1-3] Orientational deformation of the entire LC specimen takes place. In the general case, the expression for the elastic orientational energy of the specimen per unit volume has the form:[1]

$$F_d = {}^1/_2 K_{11} (\mathrm{div}\, \mathbf{n})^2 + {}^1/_2 K_{22} (\mathbf{n} \times \mathrm{rot}\, \mathbf{n})^2 + {}^1/_2 K_{33} (\mathbf{n} \times \mathrm{rot}\, \mathbf{n})^2$$

where K_{11}, K_{22}, and K_{33} are the Frank elastic constants for transverse bending, twisting, and longitudinal bending respectively.

The free energy of an original homeotropic specimen is the sum of the bulk elastic energy, the surface anchoring energy, and the energy due to the influence of an external electric or magnetic field of the following form (in the one-dimensional approximation):[38]

$$F = 2B_\theta \sin^2 \theta_0 + {}^1/_2 \int_{-d/2}^{+d/2} [K_{11} \sin^2 \theta + K_{33} \cos^2 \theta] \left(\frac{d\theta}{dz}\right)^2 dz - {}^1/_2 \int_{-d/2}^{+d/2} \chi_a H^2 \sin^2 \theta \, dz$$

Here, θ is the angle between the director n at an arbitrary point of the specimen and the normal to the supports (the z axis), and d the thickness of the specimen. For strong anchoring, the threshold of the Frederiks transition is given by:[1]

$$H_c' = \frac{\pi}{d} \left(\frac{K_{33}}{\chi_a}\right)^{1/2}$$

The existence of a finite anchoring energy, as calculated in Refs. 38–41, leads to a decrease in the threshold H_C, and the $H_C(d^{-1})$ relationship becomes non-linear. For MBBA, the following values were obtained[38,41] for $W_S \times 10^{-3}$ (erg cm^{-2}): 11.0 for surface-active substances on glass covered with In_2O_3 and 6.1 on clean glass; 5.9 for lecithin on glass covered with In_2O_3 and 3.1 on cleaned glass.

In the one-constant approximation ($K_{11} = K_{33} = K$), the calculation of the orientational deformation is simplified,[40] and H_C for the Frederiks transition becomes directly proportional to the quantity $(d + 2\xi)^{-1}$, where $\xi = 2K/B_\theta$ has been called the extrapolation length. The Frederiks threshold in an electric field for weak anchoring of the molecules to the walls of the cell is described by the following equation:[42]

$$V_c = V_c' (1 + 2K_{11}/W_s d)^{-1}$$

where the threshold for strong anchoring is

$$V_c' = 2\pi (\pi K_{11}/\varepsilon_a)^{1/2}.$$

The Frederiks transition in an electric field has been studied for 5CB. When ordinary glass supports covered with a layer of lecithin were used, strong anchoring of the LC to the support was detected.[43]

The phase difference of polarised light passing through a cell containing an NLC deformed by a magnetic field has been calculated and determined experimentally.[44] To obtain better agreement between the theoretical curves and the experimental data, a new potential of the anchoring forces was introduced, namely:[44,45]

$$W_\theta = C \cos^2 \theta_0 + C_4 \cos^4 \theta_0$$

In an attempt to reconcile the results obtained experimentally in studies of the Frederiks transition and the flexoelectric effect, a potential for the anchoring forces was introduced[46] in the form of the square of the elliptical sine, where the argument $0 \leq k \leq 1$:

$$W_\theta = \frac{1}{2} W_s \mathrm{Sn}^2 (\theta_0, k)$$

Table 2. Coefficients of azimuthal anchoring B_ϕ of nematic MBBA to a support.[10]

Method of producing the relief	B'_φ, J m^{-2}	B_φ, J m^{-2}
Rubbing with diamond paste	$8 \cdot 10^{-5}$	$7 \cdot 10^{-6}$
Depositing SiO_2 at an angle of 30°	$5 \cdot 10^{-4}$	10^{-3}
Depositing a film of trimethylchlorosilane	—	$5 \cdot 10^{-6}$

Notes: B'_ϕ—calculated from Eqn. (12), B_ϕ—measured experimentally from the Frederiks transition.

The case of the orientational deformation of an NLC on rotation of the director in the plane xy parallel to the walls of the cell can be considered. In this case the potential of the anchoring forces is given by the expression

$$W_\varphi = B_\varphi \sin^2 \varphi_0$$

where ϕ_0 is the angle of deviation of the director from the axis of easy orientation (the y axis). Rubbing of the glass support, and the oblique deposition of SiO_2, were used to obtain a planar texture.[10,47] The magnitude of the azimuthal anchoring coefficient B_ϕ was determined from measurements of the rotation of the molecules in a magnetic field oriented parallel to the support.[10] The orientation of the molecules along the direction of rubbing is usually attributed to the geometric factor, that is it is assumed that the orientation of the rod-shaped molecules along the grooves is energetically favourable, since elastic orientational deformation does not take place. For the simplest case of a sinusoidal surface relief with wave vector q, rotation of the director in a

position perpendicular to the grooves increases the elastic energy by an amount[47]

$$W(\varphi) = {}^1/_4 KAq^3 \sin^2 \varphi_0 \qquad (12)$$

The experimental values of B_ϕ and the values calculated from this equation are given in Table 2. The lack of agreement between the experimental and theoretical values is apparently related to the simplification of describing the surface by a sinusoidal function.

2. The Flexoelectric Effect

The flexoelectric effect (FE) is related to the asymmetry of the shape of the molecule (for example the "banana-shaped" MBBA) and its constant dipole moment. When an external electric field is applied, polarisation is produced in the specimen as a result of the deformation of the bend, leading to the stabilisation of the orientational deformation in the cell.[1,2] Since the greatest deviation of the director is observed close to the walls of the cell, the flexoelectric effect is very sensitive to the magnitude of the energy of anchoring of the LC to the support.

The fullest theoretical description of the uniform flexoelectric effect is given in Ref. 48. For symmetrical boundary conditions, the value of the angle θ (between the director n and the z axis) is equal to

$$\theta = (e_3 + p) E \left(W_s \operatorname{sh} \frac{d}{2\zeta} + \frac{K_{33}}{\zeta} \operatorname{ch} \frac{d}{2\zeta} \right)^{-1} \operatorname{sh} \frac{z}{\zeta}$$

where e_3 is the flexoelectric coefficient for the geometry of the experiment described above and the "banana-shaped" molecules of MBBA,

$$\zeta = E^{-1} (4\pi K_{33} / |\varepsilon_a|)^{1/2}$$

the dielectric coherence length, and p the surface polarisation at the boundary between the solid support and the LC (possibly produced as a result of the difference in the values of the interaction of the support with the two different ends of the elongated LC molecule). The induced birefringence of the specimen is calculated from the equation:[49]

$$\Delta n = \frac{1}{4d} n_0 \left(1 - \frac{n_0^2}{n_e^2} \right) \left(\frac{e_3 + p}{K_{33}} \right)^2 E^2 \zeta^3 \left(\operatorname{sh} \frac{d}{\zeta} - \frac{d}{\zeta} \right) \times \times \left\{ \operatorname{ch}^2 \frac{d}{2\zeta} \left[1 - \frac{\zeta W_s}{K_{33}} \operatorname{th} \frac{d}{2\zeta} \right]^2 \right\}^{-1} \qquad (13)$$

In most experimental studies,[49-51] the calculations were carried out using different simplified versions of Eqn. (13); thus W_S, p, and ε_a (in different combinations) were neglected; the expansion of the hyperbolic functions in a series with respect to powers of (d/ξ) was carried out only as far as the first or second order of smallness. In fact, the experimental $\Delta n(d, E^2)$ relationship gave the effective flexoelectric coefficient e_3^*:

$$e_3^* = \frac{e_3 + p}{1 + dW_s / 2K_{33}} \qquad (14)$$

Eqns. (13) and (14) were used to determine the energy of adhesion between MBBA molecules and a support treated with an aqueous solution of decyltrimethylammonium bromide.[49] The value was 3.74×10^{-3} erg cm^{-2} in a cell with a thickness of 30 μm for $T_C - T = 16$ K and 2.48×10^{-5} erg cm^{-2} for a thickness of 90 μm and $T_C - T = 4.5$ K.

These results indicate that the energy of anchoring depends markedly on the temperature of the specimen. Nevertheless, order of magnitude agreement (10^{-3} erg cm^{-2}) is observed with the data obtained from the Frederiks transition.[38,41]

3. The Spontaneous Frederiks Transition

In nematics with negative dielectric anisotropy ($\varepsilon_a < 0$), the effect of spontaneous breakdown of the homeotropic orientation at a certain critical thickness of the layer is observed.[52] This effect can be attributed[53] to polarisation in the regions of the homeotropic nematic next to the surface, and hence to an electric field E_S existing in a region of thickness δ next to the surface. A new term is therefore introduced into the expression for the free energy of the specimen to take account of the energy next to the surface

$$(\varepsilon_a E^2 \delta / 4\pi) \sin^2 \theta_0.$$

Solution of the corresponding equations[53,54] shows that there exists a certain critical cell thickness

$$d_c = 2K | W_s + \varepsilon_a E_\delta^2 / 4\pi |^{-1}.$$

For $d < d_C$, the layer is energetically more favourable in the non-deformed state; for $d > d_C$, on the other hand, the layer is deformed according to the law $\theta = \theta_C = (z - d/2)$. Thus the mechanism of the spontaneous transition is attributed[54] to competition between electric forces of different character next to the surface, facilitating planar orientation of the nematic with $\varepsilon_a < 0$, and the elastic energy of the NLC, which favours the homeotropic orientation. This effect obviously decreases the threshold of the ordinary Frederiks transition.

The orientation of an NLC is influenced considerably by long-range dispersion forces,[46,55] which often stabilise the homeotropic orientation of the director. A theoretical examination of a one-dimensional stabilising field has been carried out.[56] At a layer thickness $d < d_1$, the predominating van der Waals forces lead to homeotropic orientation on the surface of the nematic layer; for $d_1 < d < d_2$ the planar orientation on the surface is ensured by short-range surface forces with a potential $\gamma \cos^2 \theta_0$; for $d > d_2$, the most important role is played by the elastic energy of orientational deformation.[55]

Theoretical calculations[57,58] have shown that shielding of the supports by amorphous films with thickness l leads to a local Frederiks transition in the NLC close to the boundary with a support. The moment of the van der Waals forces is described by the expression

$$\lambda c \sin \theta_0 \cos \theta_0 / (\lambda + z + l)(z + l)^2,$$

where c is a constant, and $\lambda \cong 1000$ Å, and the moment of the short-range surface forces has the form $W_S \sin \theta_0 \cos \theta_0$. An experimental study of a local Frederiks transition was carried out[59] on fragments of crystalline mica with a shielding covering in the form of stepped monolayers of stearic acid. The mica support produces planar orientation of the NLC, and the Langmuir layers produce homeotropic orientation, so that for a Langmuir film of sufficient thickness, a change from planar to homeotropic texture is observed experimentally for liquid-crystal droplets of MBBA and 5CB.

V. THE SURFACE ORDER PARAMETER

The order parameter Q is an important characteristic of the meso-phase, and is widely used to describe the temperature dependence of various physical characteristics of LC.[2,4] It may be assumed that the values of Q in the volume of a specimen (Q_V) and close to a solid support (Q_S) are different. This assumption has a significant effect on the calculation of the surface properties of liquid crystals, so that a number of attempts have been made to determine the surface order parameter experimentally.

The first estimates of Q_S and Q_V for planar nematic textures[60,61] were made by multiple-wave interferometry.[62] It was assumed[60] that in the region of solid supports, surface forces produce layers with a surface order parameter Q_S (and corresponding refractive index n_S), which have a thickness of the order of the wavelength of light. The cell therefore forms a Fabry–Perot interferometer, but with a three-layer optical medium (n_S, n_V, n_S). The ratio of the intensities of the emergent and incident light beams is given by:[60]

$$\frac{I}{I_0} = \frac{8n_p^2 n_s^2}{(n_p^4 + 6n_p^2 n_s^2 + n_s^4) - (n_p^4 - 2n_p^2 n_s^2 + n_s^4)\cos^2\beta}$$

where $\beta = \pi \bar{n} d/\chi$, $\bar{n}$ is the average value of the refractive index in the volume of the specimen, and n_p the refractive index of the glass plate supports. Increase in temperature leads to changes in the values of both n_S and $\bar{n}$, so that the periodic change in (I/I_0) with increase in temperature makes it possible to determine the value of $\bar{n}$ from the phase, and of n_S from the amplitude of the graph.

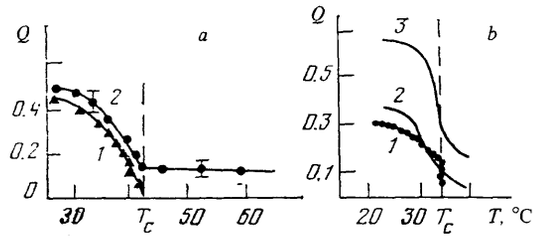


Figure 6. Temperature dependence of the bulk (curves *1*) and surface (curves *2* and *3*) parameters, measured for 7CB [60] (*a*) and 5CB [61] (*b*). Curves *2* were obtained for a support with a layer of SiO_2 deposited at an angle of 60°, and curve *3* for a profiled support with a rectangular lattice period of 0.5 μm.

The temperature dependence of Q_V and Q_S obtained by this method[60,61] is shown in Fig. 6. For a specimen of 7CB in a cell with a coating of SiO_2, applied at an angle of 60° to the normal, the value of Q_S is slightly greater than Q_V, but does not become zero after the phase transformation into the isotropic phase (where $Q_S \cong 0.1$).[60] A much higher value of Q_S compared with Q_V is observed for 5CB for a surface with a profile in the form of a grid with rectangular projections.[61] The authors themselves[61] mention the experimental difficulties associated with this type of interference method for determining Q_S. Measurements of the refractive indices $n_\perp$ in planar cells containing MBBA and 5CB have been carried out[63] by two methods: by total internal reflection and by multiple-wave interferometry, and the results obtained by the two methods agreed within the experimental error. This indicates an extremely small difference between Q_S and Q_V in these experiments or a small thickness of the boundary layer ($\xi \ll \lambda$).

A number of published papers[64–68] describe the birefringence in the isotropic phase of nematic compounds, produced by the influence of previously treated supports. To obtain planar orientation of the molecules, the glass plates were rubbed with paper, or covered with surface-active substances (for example polyvinyl alcohol) or with a layer of SiO_2. The phase difference δ of the ordinary and extraordinary waves was determined directly by measuring the intensity of the light passing through the cell, placed between two polaroids. The $\delta(T)$ relationships obtained for a number of specimens are shown in Fig. 7.

The values of the phase difference measured in this way make it possible to determine the briefringence Δn and then to calculate the parameter Q_S. For this purpose, the Landau–de Gennes approximation was used[65,66] to expand the free energy of the system in a series with respect to the order parameter Q:

$$F = F_0 + \frac{a}{2}(T - T^*)Q^2 - \frac{b}{3}Q^3 + \frac{c}{4}Q^4 + \frac{L}{2}|\nabla Q|^2$$

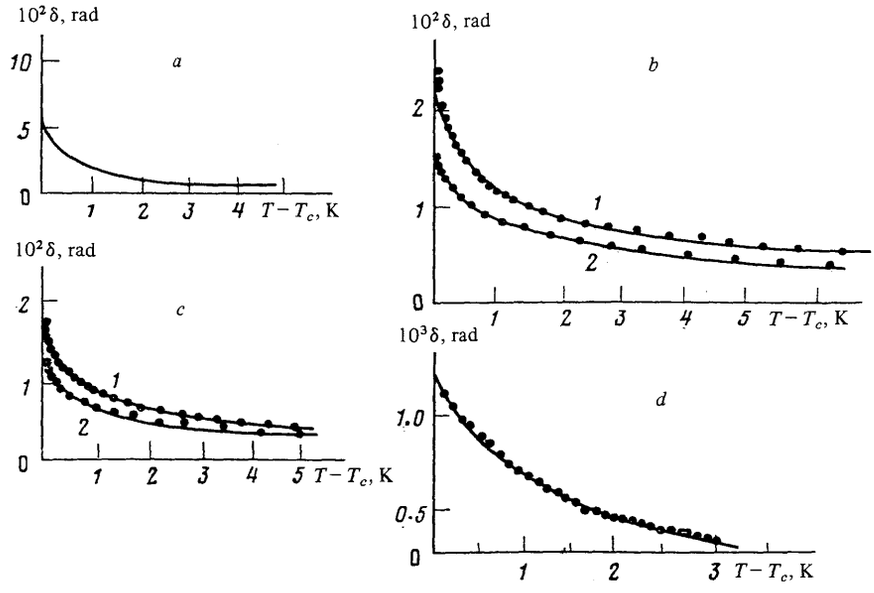


Figure 7. Experimental phase difference relationships $\delta(T)$ in specimens of isotropic nematogenic compounds: *a*) MBBA on glass covered with a rubbed layer of PVA;[66] *b*) 5CB on rubbed glass (*1*) and on a rubbed layer of MAP (*2*);[65] *c*) 5CB on glass covered with HTAB (*1*) and MOAP (*2*);[65] *d*) 7CB on rubbed glass (Pyrex)[67] (the notation for the SAS is explained in the notes to Table 3).

where the coefficients of the expansion a, b, c are the critical temperature of the virtual phase transformation of the second kind; T^* were estimated for the compounds studied.[67-69] It was assumed that the order parameter Q in the isotropic phase has a finite value at the boundary with the support $Q_{z=0} = Q_S$ and $Q_{z=\infty} = 0$. Minimisation of the free energy with respect to Q incorporating these boundary conditions gives an equation in $Q(z)$:

$$\frac{L}{aT^*}\left(\frac{dQ}{dz}\right)^2 = 2\left[\frac{a}{2}(T-T^*)Q^2 - \frac{b}{3}Q^3 + \frac{c}{4}Q^4\right]/dT^*$$

This equation is solved numerically for various known[67-69] values of a, b, c, and T^* and a reasonable value of L. The $Q(z)$ graph obtained is used to calculate Q_S. The area under the curve is equated to the value of the birefringence Δn induced by the support. The values of Δn calculated for different values of Q_S are compared with the experimental value to obtain the order parameter Q_S "next to the wall" for each experiment (see Table 3).

Table 3. Order parameter Q_S "next to the wall"[65,66] in an isotropic phase.

Method of treating the surface	MBBA	5CB
Cleaning	0	0
Cleaning and rubbing	0.052	0.22
Coating of HTAB	0.321	0.32
Coating of MAP and rubbing	0.063	0.18
Coating of DMOAP	0.054	0.17
Depositing SiO_2 at an angle of 60° to the normal	—	0
Coating of PVA and rubbing	0.364	0.172

Note. The following substances were used as surface-active substances for treating the surface of the glass support: for the normal orientation—hexadecyltrimethylammonium bromide and its 0.2% solution in chloroform (HTAB) and dimethyl-n-octadecyl-3-aminopropyltrimethoxysilane chloride (DMOAP); for the parallel orientation—N-methyl-3-aminopropyltrimethoxysilane (MAP), polyvinyl alcohol (PVA). Rubbing the surface already covered with SAS gave the planar orientation required to produce an axis of easy orientation in the plane of the support.

Experimental studies in the same direction were continued[67,68] by measuring $\delta(T - T_C)$ in 7CB (see Fig.7d). The values obtained were $Q_S = 0.1$ for rubbed glass, and $Q_S = 0$ for a layer of SiO_2 deposited at an angle of 60°. Without treatment of the glass, in the presence of a magnetic field H parallel to the glass surface, birefringence appears as a result of the orientation of the molecules of the isotropic phase by the magnetic field. When the magnetic field is switched off, the birefringence is preserved, that is the field plays the same role as rubbing; a direction of easy orientation is created in the plane of the support.

The birefringence induced by a support was measured[70] in the isotropic phase for a mixture of 5CB with the organic compound hexamethylbenzene (2.5 mole %) on supports covered with a rubbed film of PVA and a deposited layer of SiO_2. The surface order parameter Q_S had the values 0.27 and 0.005 respectively.[70] In those cases where the planar orientation of the nematic phase is induced by geometric factors (deposition of SiO_2), there is practically no birefringence in the isotropic phase close to the support.

Similarly, when the homeotropic texture of an NLC is produced by thorough cleaning of the glass, birefringence is not produced in the isotropic phase. Thus the birefringence (and hence the ordering) induced by the walls is apparently due to an anisotropic physicochemical interaction between the molecules of the nematogenic material and the support. The absence of ordering in the isotropic phase detected[65-68] when SiO_2 was deposited does not agree with other studies[60,61] in which a high value of Q_S on supports of this kind was reported.

Birefringence is also produced in strongly polar organic liquids close to the solid walls of the cell, and the optical axis is perpendicular to the surface of the glass supports. This birefringence is related to an order parameter Q_S, in spite of the fact that the liquids studied (nitrobenzene, etc.) do not have a liquid-crystal phase. It has been suggested that a layer of ordered liquid with properties similar to those of a nematic phase is produced close to the surface of the support.†

VI. ORIENTATION OF THE DIRECTOR ON THE FREE SURFACE OF A NEMATIC LIQUID CRYSTAL

Various optical methods have established that the director **n** on the free surface of an NLC is directed parallel to the surface in PAA,[6,7] and perpendicular to it in cyanobiphenyls,[8,9] and that the angle ψ between the director **n** and the normal **N** to the surface changes with change in temperature in MBBA and EBBA.[6,9] Thus the direction of the axis of easy orientation on the free surface depends on the nature of the liquid-crystal compound.

Accurate measurements of the angle ψ are possible only in uniform specimens: this is usually achieved by applying a magnetic field **H** at a small angle to the free surface. The axis of easy orientation then lies in a plane parallel to **H** and **N**. The magnitude of the relative coefficient of reflection of polarised light incident at small angles (~0.2°) to the normal has been determined experimentally:

$$R = (\rho_\parallel - \rho_\perp)/\rho_\perp$$

where $\rho_\parallel$ and $\rho_\perp$ are the reflection coefficients of light polarised parallel to and perpendicular to the plane of incidence of the light:[7]

$$\rho_\perp = \left(\frac{n_\perp - 1}{n_\perp + 1}\right)^2$$

$$\rho_\parallel = \left(\frac{n(\psi) - 1)}{n(\psi) + 1}\right)^2$$

ψ has been calculated[9] using the following expressions:

$$\rho_\parallel = \left[\frac{(n_\perp^2 \sin^2\psi + n_\parallel^2 \cos^2\psi)^{1/2} - n_\perp n_\parallel}{(n_\perp^2 \sin^2\psi + n_\parallel^2 \cos^2\psi)^{1/2} + n_\perp n_\parallel}\right]^2 \qquad (15)$$

$$\rho_\perp = \left[\frac{n_\perp - 1}{n_\perp + 1}\right]^2$$

It was found that throughout the entire range of existence of nematic PAA, the molecules are arranged so that their long axes are parallel to the free surface, to within 3%.[7] For MBBA and EBBA, Eqns.(15) were used to calculate the temperature dependence of the angle ψ (Fig.8). In a short temperature range close to the phase transformation (from T_C to T_C + 2 °C), the following relationship holds well:[9]

$$\psi = C(T_0 - T)^\beta$$

†See B.V.Deryagin, Yu.M.Popovskii, and B.A.Altoiz, J.Coll.Interface Sci., 1983, **96**, 492.

where for MBBA, $T_0 - T_C = -(0.9 \pm 0.3°)$, $\beta = 0.50 \pm 0.04$, $C = 14.5 \pm 0.6$ degree$^{-1/2}$; for EBBA, $T_0 - T_C = -(1.2 \pm 0.3)$ °C, $\beta = 0.51 \pm 0.1$, $C = 11.8 \pm 1.6$ degree$^{-1/2}$. Above the critical temperature T_0 (but below the point of the transition to the isotropic phase T_C), the angle $\psi = 0$.

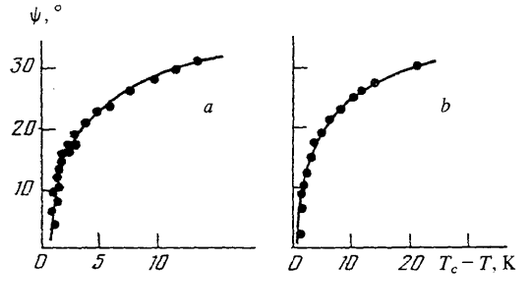


Figure 8. Temperature dependence of the polar angle ψ at the free surface of MBBA (*a*) and EBBA (*b*).[9]

Qualitatively similar results were obtained for free MBBA films[71] in the absence of a magnetic field. The angle of inclination ψ was measured from the conoscopic picture of individual uniform regions of the film; a convergent beam of laser radiation was passed through the specimen and the analyser. At a thickness $d > 70$ μm, the specimen was non-uniform; decrease in the thickness led to the production of a homeotropic texture, after which, at $d < 10$ μm, a schlieren texture typical of nematics with an oblique orientation of the director at the boundaries was produced. The angle ψ decreased with increase in temperature, becoming zero at T_0 slightly lower than T_C.

The temperature dependence of ψ can be explained using the equation proposed by Parsons[30,33,72] for the surface tension:

$$\gamma = \gamma_0 + \frac{1}{2}\gamma_Q (\mathbf{nN})^2 - \gamma_P \mathbf{nN}$$

where the second term describes the increase in the surface tension on the inclination of a director lying parallel to the surface, and the third term describes its simultaneous decrease as a result of the interaction of the dipole moments of the molecules close to the surface. Thus there exists an equilibrium state of the director, determined by the condition for a surface tension minimum:

$$\frac{d\gamma}{d\psi} = -\gamma_Q \sin\psi\cos\psi + \gamma_P \sin\psi = 0$$

from which

$$\cos\psi = \gamma_P/\gamma_Q \quad \text{for } \gamma_P < \gamma_Q$$
$$\cos\psi = 1 \quad \text{for } \gamma_P > \gamma_Q$$

Since γ_P and γ_Q, generally speaking, change in different ways with change in temperature, $\cos\psi$ is a function of temperature, and with the condition $\gamma_P = \gamma_Q$ the oblique texture is converted smoothly into a homeotropic structure. The temperature for this equality apparently corresponds to the experimental value of T_0.

In the direct proximity of T_0, the surface tension can be represented as a series with respect to powers of ψ:[9]

$$\gamma = \gamma_0 + {}^1/_2 A (T - T_0)\psi^2 + (B/4)\psi^4 \qquad (16)$$

For $T < T_0$, $A/B > 0$, and the minimisation of Eqn.(16) gives:

$$\psi = (A/B)^{1/2}(T_0 - T)^{1/2}$$

On the other hand, for $T_0 < T < T_C$, $\psi = 0$. These elementary estimates agree well with experimental data.[9]

The question of the orientation of the director on a free surface has been studied theoretically.[73,74] The specific energy of the oriented layer on the surface was written in a form analogous to that for the energy of an electric or magnetic field:

$$\Lambda_e = -\frac{1}{2}\Delta\pi\left[(\mathbf{nN})^2 - \frac{1}{3}\right]$$

where $\Delta\pi$ plays the role of the anchoring coefficient of the LC to the free surface. It was assumed[73,74] that $\Delta\pi = \Delta\beta Q$, where Q is the nematic order parameter, and $\Delta\beta$ was called the anisotropy of the ordering. High values of $\Delta\pi$ correspond to a strong orienting influence of the surface. The elastic orientational energy of the surface layer was then introduced, where the moduli of elasticity $\bar{K}_1$ and $\bar{K}_2$ differ from the bulk values K_{11} and K_{22}. The propagation of this deformation into the depth of the layer leads to an increase in the bulk elastic energy. From these considerations, the author cited[74] obtained an equation for the moments of the forces acting on the director on the free surface, and calculated the temperature dependence of the angle ψ (Fig.9).

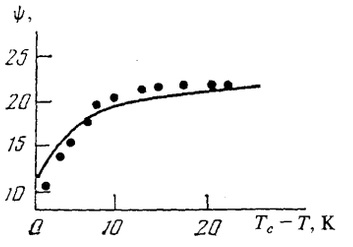


Figure 9. Temperature dependence of the angle between the director **n** and the free surface of MBBA: experiment[6] (points) and calculation (continuous curve).[74]

In all the above studies, ψ was assumed to be independent of the magnitude of H, which corresponds to "strong anchoring" of the LC on the free surface. At high values of H, however, and at a temperature close to T_0, the angle ψ increases with increase in the magnetic field strength.[75] For rotation through an angle $(\psi - \psi_0)$ relative to the original position ψ_0 it is necessary to expend the energy of the magnetic field corresponding to the sum of the energy of anchoring of the molecules to the free surface and the energy of elastic deformation in the volume of the NLC adjoining the surface. Thus the total free energy of the surface layer of the LC consists of three terms, and its minimisation with respect to variation of the polar angle $\theta(z)$ in the volume and ψ on the surface gives the equation:[75]

$$\psi \approx \psi_0 + (K_{33}\chi_a)^{1/2}\left(1 + \frac{(K_{11} - K_{33})\sin^2\psi}{K_{33}}\right)^{1/2}\frac{H\cos\psi}{2B_d} \qquad (17)$$

The quantity $\psi(H)$ is calculated from the coefficients of reflection of light $\rho_\parallel$ and $\rho_\perp$. If the temperature dependence of ψ, K_{ii}, and χ_a are known, it is possible to obtain from

Eqn.(17) the temperature dependence of the coefficient of adhesion B_σ of the NLC molecules to the free surface (Fig.10).

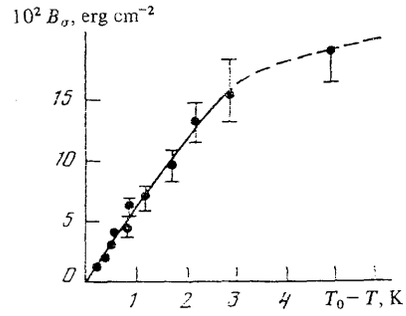


Figure 10. Temperature dependence of the coefficient of adhesion B_σ to the free surface of MBBA.[75]

VII. CRITERIA FOR DETERMINING THE NATURE OF THE ORIENTATION OF LIQUID CRYSTALS ON SUPPORTS

The relationship between the surface energy at the phase boundary and the molecular ordering of LC was first explained as follows.[68] For a sufficiently low surface energy of the support γ_S, the intermolecular forces within the LC are stronger than the forces acting at the phase boundary. As a result, the arrangement of the long axes of the NLC molecules perpendicular to the surface is energetically more favourable. When the surface energy of the solid support γ_S is high, the forces of inter-phase interaction predominate, and the NLC molecules are oriented parallel to the support.

Since it is difficult to determine the value γ_S, for crude estimates it is replaced by the value of the critical surface tension of the support γ_C, which can be determined by Zisman's method.[76] The procedure for determining γ_C by the published method[77] can be described. It is assumed that a drop of liquid with surface tension γ_L forms a drop with a contact angle α on a support with energy γ_S. In this case

$$\gamma_s - \gamma_{sL} = \gamma_L \cos\alpha$$

where γ_{SL} is the interfacial surface energy at the boundary between the liquid and the support. Zisman[76] showed experimentally that $\cos\alpha$ decreases linearly with increase in γ_L for homologous series of organic liquids. By selecting a series of different liquids with $\gamma_L > \gamma_S$, it is possible to construct the dependence of $\cos\alpha$ on γ_L for each support. By extrapolating $\alpha \to 0$ and $\cos\alpha \to 1$, the previous equation is transformed to

$$\gamma_s - \gamma_{sL} = \gamma_c$$

where γ_C is determined from the graph for $\cos\alpha = 1$.

The quantity γ_C has been called the critical surface tension of the support.

The simple assumption[36,78] that the homeotropic orientation is produced when $\gamma_L > \gamma_C$, and the planar orientation when $\gamma_L < \gamma_C$ gave satisfactory results for MBBA,[12] but was not confirmed for a large number of different NLC on supports covered with surface-active substances (SAS).[79] The molecular ordering was studied in LC of six types on five types of polymer support with γ_C in the range 22–40.5 erg cm^{-2}. It was found that the lower γ_C for the support, the greater the number of LC compounds that undergo homeotropic orientation. For very high values of γ_C, the planar texture of LC is observed most frequently.[77] For various types of LC and SAS, the ordering can be related to the value of the contact angle of the LC drop: a homeotropic texture is produced for $\alpha \geq 36°$, and a planar texture for $\alpha \leq 36°$.

The surface tension of liquid crystals γ_L has been measured at the same temperatures, and amounted to 34.4 erg cm^{-2} for 5CB, 34.2 erg cm^{-2} for MBBA, and 32.6 erg cm^{-2} for dibutyloxyazoxybenzene. Table 4 shows that the condition $\gamma_L > \gamma_C$ is not necessary for the production of a homeotropic texture. Other experiments, however, did not show any characteristic relationship between the ordering and the magnitude of the contact angle[79] (see Table 4).

Table 4. Critical surface tension of the support γ_C, the contact angles of wetting, and the orientations of the director in liquid crystals on glass supports treated with a solution of 0.5 mass % alkoxysilanes.[79]

Alkoxysilanes	γ_C, erg cm^{-2}	5CB		MBBA		Dibutyloxyazoxybenzene	
		α, °	orientation	α, °	orientation	α, °	orientation
GMS	38.5	0	∥	0	∥	0	∥
AAMS	36.0	0	∥	0	∥	0	∥
PHES	32.0	16	∥	15	∥	8	∥
MAP	29.0	16	⊥	15	∥	12	∥
DMOAP	23.0	55	⊥	56	⊥	46	⊥

Another method of introducing a criterion for the orientation of LC is by representing the surface energy as a function of the angle of orientation θ at the phase boundary.[13] The work of adhesion of the LC to the support is given by the expression

$$W_a(\theta) = \gamma_L(\theta) + \gamma_s - \gamma_{Ls}[\theta]$$

When there are dispersion forces between the LC and the support, the equation for the work of adhesion becomes:

$$W_a(\theta) = 2[\gamma_L(\theta)\gamma_s]^{1/2}$$

From this it follows that

$$\gamma_{Ls}(\theta) = \gamma_s + \gamma_L(\theta) - 2[\gamma_L(\theta)\gamma_s]^{1/2}$$

Assuming that the LC orientation produced corresponds to a minimum interfacial surface energy γ_{Ls} gives:

$$\frac{\partial\gamma_{Ls}(\theta)}{\partial\theta} = \frac{\partial\gamma_L(\theta)}{\partial\theta}\left[1 - \left(\frac{\gamma_s}{\gamma_L(\theta)}\right)^{1/2}\right] = 0$$

and the following typical cases[79] of homeotropic orientation on a support with $\gamma_S < \gamma_L(0)$, oblique on a support with

$$\gamma_L(0) < \gamma_s < \gamma_L(\pi/2)$$

and planar on a support with $\gamma_L(\pi/2) < \gamma_S$.

A systematic physicochemical interpretation of surface orientation has been proposed.[80] The values of the surface energy and the work of adhesion are written as the sum of dispersion and polar components:

$$\gamma_s = \gamma_s^d + \gamma_s^p$$
$$\gamma_L = \gamma_L^d + \gamma_L^p$$
$$W_a = W_a^d + W_a^p$$

where the indices d and p correspond to the dispersion and polar components of the interaction. W_a can be represented as:[81]

$$W_a^d = 2\,[\gamma_s^d \gamma_L^d(\theta)]^{1/2}$$

The total interfacial surface energy is then written as:[80]

$$\gamma_{Ls}(\theta) = \{(\gamma_s^d)^{1/2} - [\gamma_L^d(\theta)]^{1/2}\}^2 + \{(\gamma_s^p)^{1/2} - [\gamma_L^p(\theta)]^{1/2}\}^2$$

For the dispersion part of the surface tension it is possible to write[72]

$$\gamma_L^d(\theta) = (\gamma_L^d)_0 + \Delta\gamma_L^d \sin^2\theta$$

and for the polar part:[33]

$$\gamma_L^p(\theta) = (\gamma_L^p)_0 + \Delta\gamma_L^p \sin^2(\theta - \theta_p)$$

where the angle θ_p is introduced to take account of the spontaneous polarisation of the surface layer. If the characteristics of the support γ_s^d and γ_s^p and the characteristics of the LC $(\gamma_L^d)_0$, $\Delta\gamma_L^d$, $(\gamma_L^p)_0$, $\Delta\gamma_L^p$, and θ_p are known, the condition for a minimum $\theta_{Ls}(\theta)$ can be used to calculate the value of the angle θ between the director and the normal to the support. This method was used[80] to construct a diagram showing the orienting influence of supports of different kinds (Fig.11).

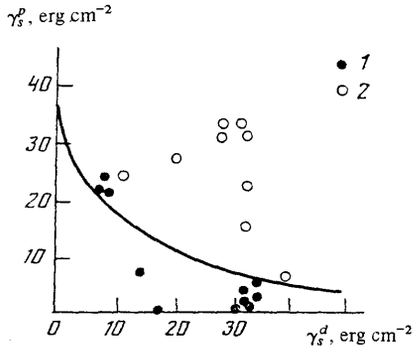


Figure 11. Diagram for determining the orientation of MBBA on supports (below the continuous theoretical curve, normal orientation of MBBA is assumed). The experimental points correspond to the known values of γ_s^p and γ_s^d for different supports; *1*) observed homeotropic orientation, *2*) oblique or planar.[80]

The polar and dispersion contributions to the surface energy have been determined[82] for two types of LC and supports treated with Chromolan solutions of different concentration. The polar γ_s^p and dispersion γ_s^d contributions to the surface energy of the supports were calculated by the least-squares method using the equation

$$1 + \cos\alpha = 2\,[(\gamma_s^d \gamma_L^d)^{1/2} + (\gamma_s^p \gamma_L^p)^{1/2}]/\gamma_L \qquad (18)$$

where α is the experimentally determined contact angle of wetting of the surface being studied by an isotropic liquid with known values of the polar γ_L^p and dispersion γ_L^d contributions to γ_L. The contact angles of wetting of these supports by the liquid-crystal material were then measured, and Eqn.(18) was used to determine γ_L^p and γ_L^d for the liquid crystal. Decrease in both the polar and the dispersion components of γ_S facilitates the homeotropic orientation of the LC.

VIII. INFLUENCE OF THE AZIMUTHAL ANISOTROPY OF THE SUPPORT ON SURFACE PHENOMENA

The characteristic features of the orientation of specific LC between two treated plates, and different methods of depositing coatings, have been described in detail.[29,36,37] The question of the extent to which the relief of the treated support and its anisotropy influence the orientation of the director and the contact angles of liquid-crystal droplets can be considered.

Rubbing a support always produces an axis of easy orientation in the plane of the support. This can be explained from purely geometric considerations.[1,47] Rubbed polymer films such as polyvinyl alcohol (PVA), polyamides, polyesters, polysiloxanes, etc. produce uniform ordering with a very small angle of inclination of the director to the plane of the support.[83] Rubbing glass with diamond paste produces well-formed grooves, along which the rod-shaped NLC molecules are arranged. Rubbing polymer coatings leads to local fusion of the polymers and orientation of the polymer chains along the direction of rubbing. Rubbing a glass plate with paper produces regions with a high temperature, leading to local fusion of the cellulose and subsequent orientation of the polymeric cellulose molecules along the direction of rubbing. Thus the orientation of NLC molecules is determined by the combined effect of the geometric (steric) factor and the anisotropic dispersion interaction between the oriented polymer and the NLC molecules.[83]

Coatings of pure metals, for example Al and Au,[84] facilitate planar orientation of LC. Depositing SiO_2 or metals on supports at different angles gives different angles of inclination of the director to the support.[10,36,83–88]

Experiments to determine the influence of the anisotropy of a support on the orientation of NLC have been carried out using the SAS hexadecyltrimethylammonium bromide (STAB).[20,89] The STAB molecules were adsorbed on the glass surface from solutions with different concentrations, so that monomolecular layers with different (parallel or perpendicular) orientations of the long axes of the STAB molecules were produced. In the first case, MBBA molecules are also oriented parallel to the surface of the support and the direction in which the plate was withdrawn from the STAB solution. In the second case, the homeotropic MBBA texture was produced. The role of rubbing in this experiment is played by the flow of the STAB solution along the glass plate, creating the required anisotropy of the support. Plates covered with STAB were used to measure the flow angles α_f and the wetting angles (established) α of droplets of nematic and isotropic MBBA at different temperatures (Fig.12). No break was observed for the angles α_f and α at the phase transformation from the nematic to the isotropic phase if the MBBA was oriented homeotropically on the support. On a support producing planar orientation, only the angle α_f changed smoothly, and on going to the nematic temperature range the NLC wet the support completely ($\alpha = 0$). The experimentally determined $\gamma_L(T)$ relationship did not show any unique features close to T_c. The measured values of the angles α were used to calculate the work of adhesion. The observations described above show that the orientation of the SAS molecules on the support has a significant influence on the orientation of NLC molecules.

Thus SAS which bring about the homeotropic orientation of NLC have their long molecular axes arranged at right angles to the surface, and the molecules of SAS which bring about planar orientation of NLC are usually arranged parallel to the surface of the support.[36,90,91] Two examples of the orientation of SAS on a support are shown in Fig. 13.

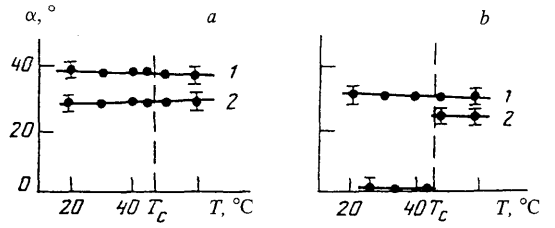


Figure 12. Temperature dependence of the angles of flow α_f (*1*) and the contact angles of wetting α (*2*) of drops of MBBA in the nematic and isotropic phases with homeotropic (*a*) and planar (*b*) orientation on STAB supports.[20]

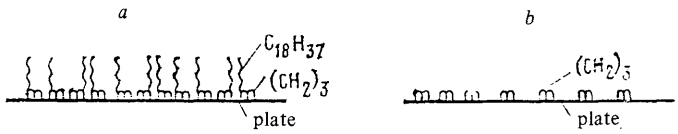


Figure 13. Diagram showing the arrangement of the molecules of the alkoxysilanes DMOAP (*a*) and MAP (*b*) on the surface of a support.[90]

Both thermodynamic considerations (minimisation of the inter-phase surface energy) and the steric factor (that is the surface relief) are used to explain the homeotropic texture. The orienting influence of the amphiphilic films studied[92,93] decreases with increase in the density of packing of the molecules. The contact wetting angles α decrease with increase in the area A corresponding to one molecule of the SAS layer (Fig. 14). At the same time the contact angles are independent of temperature in the range 25–50 °C when the angle is measured to within ±1°. The work of adhesion W_a increases smoothly with increase in A. These results were explained by the steric mechanism of orientation,[93] where the long NLC molecules are arranged in the depressions between the molecules of the amphiphilic monolayer, adopting the corresponding orientation, which is then propagated into the bulk of the NLC.

On anisotropic supports, the contact angles of wetting should depend on the azimuthal orientation of the cross-section of the drop, that is the measured angles α depend on the angle ϕ measured from the direction distinguished on the support. The anisotropy of the critical surface tension γ_c on a support with a deposited layer of SiO_2 for two mutually perpendicular directions on the support has been described. The value of $\gamma_c(\phi)$ was determined by Zisman's method, by measuring the contact angles of a series of organic liquids: the values obtained were $\gamma_c(0) \cong 37$ erg cm^{-2}, $\gamma_c(\pi/2) \cong 39$ erg cm^{-2}.[94]

The wetting angles of liquid-crystal drops on supports whose anisotropy was produced by rubbing have been measured.[95] It was assumed that the interaction of the LC with the support involves dispersion forces (index d) and hydrogen bonding (index h), so that the surface tension at the LC–support boundary is written as

$$\gamma_{Ls} = \gamma_s + \gamma_L - 2(\gamma_s^d \gamma_L^d)^{1/2} - 2(\gamma_s^h \gamma_L^h)^{1/2} \qquad (19)$$

and the wetting angle is given by the expression

$$1 + \cos\alpha = 2[(\gamma_L^d \gamma_s^d)^{1/2} + (\gamma_L^h \gamma_s^h)^{1/2}]/(\gamma_L^d + \gamma_L^h) \qquad (20)$$

in which all the parameters depend on the azimuthal orientation of the cross-section of the drop. The wetting angles of an ethanol–water mixture with known values of γ_L^d and γ_L^h were first measured, and used to determine the parameters γ_s^d and γ_s^h for different supports; these parameters and the measured wetting angles of nematic 7CB were then used to calculate the surface tension of the latter.[95]

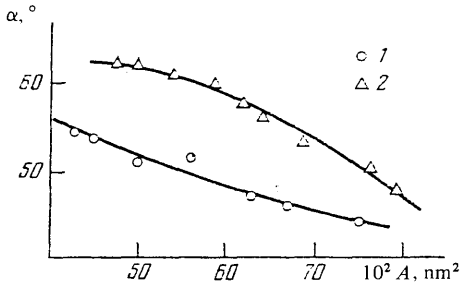


Figure 14. Dependence of the wetting angles α of drops of MBBA on supports covered with a layer of *DL*-γ-palmitoyl-isolecithin (*1*) and *DL*-β,γ-dilauroyl-α-lecithin (*2*) on the area A at 35 °C.[92]

The contact angles were measured in two vertical cross-sections of the drop: one section was parallel to the orientation of the director on glass with a deposited layer of SiO_2 ($\alpha_\parallel$), and the other perpendicular to the axis of easy orientation ($\alpha_\perp$). The corresponding values of $\gamma_{s_\parallel}$, $\gamma_{s_\perp}$, $\gamma_{L_\parallel}$, and $\gamma_{L_\perp}$ were calculated using Eqns. (19) and (20).

---o0o---

Thus available experimental data on the surface tension of the nematic and isotropic phases of nematogenic compounds are often contradictory, and are clearly inadequate for developing a general model of the surface tension of liquid-crystal compounds. Existing theories have proved to be applicable only for individual substances (Okano and Murakami,[25] Gannon and Faber[8]), or to explain experimental phenomena at a qualitative level (Parsons,[30] Croxton[34]).

The anchoring of liquid crystals to a support has been studied in more detail, undoubtedly because of the interest in the practical applications of liquid crystals. The surface energy of adhesion is introduced in a form convenient for calculation, and makes possible a satisfactory description of the experimental results, but the physical nature of the energy of adhesion has not yet been sufficiently fully studied.

Studies of texture transformations induced by a surface have been published comparatively recently, and are predominantly theoretical. In spite of some contradictions, a number of serious experimental studies have proved the existence of a nematic order parameter induced by the support in the isotropic phase of an LC. The theoretical interpretation of these phenomena, however, is restricted to the Landau–de Gennes phenomenological explanation.

The experimental temperature dependence of the angle of inclination of the director to the free surface gives sufficient material for the development of a theoretical model. Neither the simplest thermodynamic considerations (Faetti and Fronzoni[9]), nor the extensive assumptions of the calculation of the moments of the forces on the surface (Mada[73,74]) are satisfactory, however.

The calculation of the dispersion and polar components of the surface energy, and attempts to introduce the orientation of the director into the calculations, are necessary steps in the development of theories of the mechanism of the orientation of LC. Nevertheless, up to the present these calculations have been based on phenomenological arguments and have not been related to models of the anisotropic interaction potential.

Practical requirements (the production of displays, radiant energy indicators, etc.) are making it necessary for research workers to learn to predict the characteristics of developed liquid-crystal elements. The large number of studies describing practical methods for producing stable LC textures show clearly the variety of orienting factors, including physicochemical interaction and the three-dimensional structure of the support and the oriented LC layer. The attempts which have been made, however, to formulate the conditions which would make it possible to predict the orientation of the director from the physicochemical characteristics of a liquid crystal and a support have not yet led to the development of criteria suitable for all LC–support pairs studied. Success will probably be achieved by a combined study of the physicochemical parameters of the surface of the support, the surface of the liquid crystal, and various phenomena associated with the interaction of the LC with the support.

REFERENCES

1. P.G.De Gennes, "The Physics of Liquid Crystals" (Translated into Russian), Izd.Mir, Moscow, 1977.
2. S.Chandrasekhar, "Liquid Crystals" (Translated into Russian), Izd.Mir, Moscow, 1980.
3. L.M.Blinov, "Elektro- i Magnitooptika Zhidkikh Kristallov" (The Electro- and Magneto-optics of Liquid Crystals), Izd.Nauka, Moscow, 1978.
4. P.G.De Gennes, "The Physics of Liquid-Crystals" (Translated into Russian), Izd.Mir, Moscow, 1983.
5. Yu.B.Amerik and B.A.Krentsel', "Khimiya Zhidkikh Kristallov i Mezomorfnykh Polimernykh Sistem" (The Chemistry of Liquid Crystals and Mesomorphic Polymeric Systems), Izd.Nauka, Moscow, 1981.
6. M.A.Bouchiat and D.Langevin-Cruchon, Phys. Letters, 1971, **34A**(6), 33.
7. P.Chiarelli, S.Faetti, and L.Fronzoni, Letters Nuovo Cimento, 1983, **36**(3), 60.
8. M.G.J.Gannon and T.E.Faber, Phil.Mag., 1978, **37**(1), 117.
9. P.Chiarelli, S.Faetti, and L.Fronzoni, J.Phys. (France), 1983, **44**, 1061.
10. J.Cognard, Mol.Cryst.Liquid Cryst.(Letters), 1981, **69**, 331.
11. J.E.Proust and L.Ter Minassian-Saraga, J.Phys. (France), 1975, **36**, 61.
12. I.Haller,Appl.Phys.Letters, 1974, **24**, 349.
13. G.Porte, J.Phys.(France), 1976, **37**, 1245.
14. S.Krishnaswamy and R.Shashidhar, Mol.Cryst.Liquid Cryst., 1976, **35**, 253.
15. A.Ferguson and S.J.Kennedy, Phil.Mag., 1938, **26**, 4.
16. W.M.Schwartz and H.W.Moseley, J.Phys.Colloid.Chem., 1947, **51**, 826.
17. N.I.Kalinnikova, P.P.Pugachevich, I.G.Chistyakov, and I.V.Sushkin, Uch.Zap.Ivanov.Gos.Ped.Inst., 1967, **62**, 176.
18. S.Krishnaswamy and R.Shashidhar, Mol.Cryst. Liquid Cryst., 1977, **38**, 711.
19. N.I.Kalinnikova, "IV Mezhdunarodnaya Konferentsiya Sotsialisticheskikh Stran po Zhidkim Kristallam" (Fourth International Conference of Socialist Contries on Liquid Crystals), Tbilisi, 1981, p.342.
20. J.E.Proust and L.Ter Minassian-Saraga, Coll. Polymer Sci., 1976, **254**, 492.
21. D.Langevin, J.Phys.(France), 1972, **33**, 237.
22. C.H.Sohl, K.Miyano, J.B.Ketterson, and G.Wong, Phys.Rev., 1980, **A22**, 1256.
23. D.Langevin,J.Phys.(France), 1975, **36**, 745.
24. L.B.Shih, J.A.Mann, and G.H.Brown, Mol.Cryst. Liquid Cryst., 1983, **98**, 47.
25. K.Okano and J.Murakami, J.Phys.(France), 1979, **40**, 525.
26. D.J.Mitchell and P.Richmond, Chem.Phys.Letters, 1973, **21**, 113.
27. J.N.Israelachvili, J.Chem.Soc., Faraday Trans.II, 1973, **69**, 1729.
28. P.Richmond and L.R.White, Mol.Cryst.Liquid Cryst., 1974, **27**, 217.
29. L.A.Goodman, RCA Review, 1974, **35**, 447.
30. J.D.Parsons, J.Phys.(France), 1976, **37**, 1187.
31. H.T.Davis, J.Chem.Phys., 1975, **62**, 3412.
32. W.Maier and A.Saupe, Z.Naturforsch., 1959, **14a**, 882; 1960, **15a**, 287.
33. J.D.Parsons, Mol.Cryst.Liquid Cryst., 1975, **31**, 79.
34. C.A.Croxton, Mol.Cryst.Liquid Cryst., 1980, **59**, 219.
35. Y.Poggi, J.C.Fillipini, and R.Aleonard, Phys. Letters, 1976, **A57**, 53.
36. F.J.Kahn, G.N.Taylor, and H.Schonhorn, Proc. IEEE, 1973, **61**, 823.
37. J.Cognard, Mol.Cryst.Liquid Cryst.Suppl., 1982, 1, 1.
38. S.Naemura, J.Phys.(France), Coll., 1979, **40**, C–3–514.
39. A.Rapini and M.Papoular, J.Phys.(France), 1969, **30**, 4.
40. E.Guyon, J.Vac.Sci.Technolog., 1973, **10**, 681.
41. S.Naemura, Appl.Phys.Letters, 1978, **33**(1), 1.
42. J.Nehring, A.R.Kmetz, and T.J.Scheffer, J.Appl. Phys., 1975, **47**, 850.
43. L.M.Blinov and A.A.Sonin, Zhur.Eksp.Teor.Fiz., 1984, **87**, 476.
44. K.H.Yang and Ch.Rosenblatt, Appl.Phys.Letters, 1983, **43**, 62.
45. K.H.Yang, J.Appl.Phys., 1983, **54**, 6864.
46. M.I.Barnik, L.M.Blinov, T.V.Korkishko, B.A.Umanskii, and V.G.Chigrinov, Zhur.Eksp.Teor. Fiz., 1983, **85**, 176.
47. D.W.Berreman, Phys.Rev.Letters, 1972, **28**, 1683.
48. A.Derzhanski, A.G.Petrov, and M.D.Mitov, J.Phys.(France), 1978, **39**, 273.
49. A.S.Vasilevskaya, A.V.Kaznacheev, and A.S.Sonin, Zhur.Eksp.Teor.Fiz., 1983, **85**, 943.

50. D.Schmidt, M.Schadt, and W.Helfrich, Z.Naturforsch., 1972, 27a, 277.
51. B.A.Umanskii, L.M.Blinov, and M.I.Barnik, Kristallografiya, 1982, **27**, 729.
52. A.N.Chuvyrov, Kristallografiya, 1980, **25**, 326.
53. A.V.Kaznacheev and A.S.Sonin, Fiz.Tverd.Tela, 1983, **25**, 917.
54. A.A.Sonin and A.V.Kaznacheev, Fiz.Tverd.Tela, 1984, **26**, 807.
55. E.I.Kats, Zhur.Eksp.Teor.Fiz., 1976, **70**, 1394.
56. A.A.Sonin, Fiz.Tverd.Tela, 1984, **26**, 310.
57. E.Dubois-Violette and P.G.de Gennes, J.Phys. (France), Letters, 1975, 36, L–255.
58. E.Dubois-Violette and P.G.de Gennes, J.Coll.Interface Sci., 1976, **57**, 403.
59. L.M.Blinov, N.N.Davydova, A.A.Sonin, and S.G.Yudin, Kristallografiya, 1984, **29**, 537.
60. H.Mada and S.Kobayashi, Appl.Phys.Letters, 1979, 35, 4.
61. A.Sugimura, N.Yamamoto, and K.Kawamura, Japan.J.Appl.Phys., 1981, **20**, 1343.
62. H.Mada and S.Kobayshi, Mol.Cryst.Liquid Cryst., 1976, **33**, 47.
63. T.Akahane and T.Tako, Japan.J.Appl.Phys., 1979, **18**, 19.
64. K.Miyano, Phys.Rev.Letters, 1979, **43**, 51.
65. K.Miyano, J.Chem.Phys., 1979, **71**, 4108.
66. J.C.Tarczon and K.Miyano, J.Chem.Phys., 1980, 73, 1994.
67. H.A.Van Sprang, Mol.Cryst.Liquid Cryst., 1983, **97**, 255.
68. H.A.Van Sprang, J.Phys.(France), 1983, **44**, 421.
69. H.J.Coles, Mol.Cryst.Liquid Cryst., 1978, **49**, 67.
70. H.Yokoyama, S.Kobayashi, and H.Kamei, Appl.Phys. Letters, 1982, **41**, 438.
71. S.Faetti and L.Fronzoni, Solid State Communs., 1978, **25**, 1087.
72. J.D.Parsons, Phys.Rev.Letters, 1978, **41**, 877.
73. H.Mada, Mol.Cryst.Liquid Cryst., 1979, **51**, 43.
74. H.Mada, Mol.Cryst.Liquid Cryst., 1979, **53**, 127.
75. P.Chiarelli, S.Faetti, and L.Fronzoni, Phys.Letters, 1984, **101A**, 31.
76. W.A.Zisman, Adv.Chem.Ser., 1964, **43**, 1.
77. J.C.Dubois, M.Gazard, and A.Zann, Appl.Phys., 1976, **47**, 1270.
78. L.T.Creach and A.R.Kmetz, Mol.Cryst.Liquid Cryst., 1973, 24, 59.
79. T.Uchida, K.Ishikava, and M.Wada, Mol.Cryst. Liquid Cryst., 1980, **60**, 37.
80. S.Naemura, Mol.Cryst.Liquid Cryst., 1981, **68**, 183.
81. F.M.Fowkes, Adv.Chem.Ser., 1964, **43**, 99.
82. E.S.Luk'yanenko, V.A.Kozunov, V.I.Grigos, and B.G.Gribov, Poverkhnost', 1983(10), 124.
83. J.A.Castellano, Mol.Cryst.Liquid Cryst., 1983, **94**, 33.
84. G.J.Sprokel, Mol.Cryst.Liquid Cryst., 1973, 22, 249.
85. D.W.Berreman, Mol.Cryst.Liquid Cryst., 1973, 23, 215.
86. W.Urbach, M.Boix, and E.Guyon, Appl.Phys.Letters, 1974, 25, 479.
87. M.Nakamura, J.Appl.Phys., 1981, **52**, 4561.
88. O.B.Gorbunov, Izv.Akad.Nauk SSSR, Neorg. Materialy, 1983, **19**(3), 467.
89. J.E.Proust, L.Ter Minassian-Saraga, and E.Guyon, Solid State Communs., 1972, **11**, 1227.
90. F.J.Kahn, Appl.Phys.Letters, 1973, 22, 386.
91. S.Matsumoto, M.Kawamoto, and N.Kaneko, Appl. Phys.Letters, 1975, **27**, 268.
92. K.Hiltrop and H.Stegemeyer, Mol.Cryst.Liquid Cryst. Letters, 1978, **49**, 61.
93. K.Hiltrop and H.Stegemeyer, Ber.Bunsenges.phys. Chem., 1981, **85**, 582.
94. S.Hirano, H.Mada, and S.Kobayashi, Japan.J. Appl.Phys., 1979, **18**, 1413.
95. H.Mada, J.Chem.Phys., 1981, **75**, 372.

Lomonosov Moscow State
University