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The Orientation of Nematic Liquid Crystals

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The methods for the homeotropic, filted, and homogeneous alignment of nematic liquid crystals on solid supports are examined. A systematic account is given of the literature on chemical orientation agents and methods for the formation of anisotropic orienting surfaces. The physicochemical and anisotropic-elastic mechanisms of the alignment of liquid crystals on solid supports are discussed.
The bibliography includes 225 references.

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I. INTRODUCTION

The studies of Frederiks and Tsbetkov,[1,2] carried out in our country during the 1930's, attracted the attention of investigators to the liquid crystal state of matter and recent advances in microelectronics have made it possible to employ the unique properties of liquid crystals in practice. Fields associated with the investigation and development of information-reproducing devices employing electro-optical effects in nematic liquid crystals (NLC) are developing particularly vigorously.

The study of the alignment (orientation) of the NLC on solid surfaces is of great interest for both theoretical research into the physical chemistry of surfaces and for the application of electro-optical effects in the technology of the preparation of liquid crystal displays. The orientation methods depended for a long time on the experimenter's art and skill and only recently have become available for industrial use as a consequence of intense investigations, which have been described in a number of reviews.[3-7]

In recent years the number of studies devoted to this problem has continued to grow. Research is being prosecuted in the following main fields: the development of new technological procedures and chemical agents for the alignment of NLC; the study of the mechanism of the orienting effect of the surface; the optimisation of the orientation parameters in liquid crystal devices. An attempt has therefore been made in the present review to give an up-to-date description of the methods and mechanisms of orientation with allowance for the influence of the latter on the electro-optical characteristics of NLC.

II. CHARACTERISTICS OF THE ALIGNMENT OF NEMATIC LIQUID CRYSTALS

(a) The NLC Director

The macroscopic state of NLC is characterised by the direction of the preferential orientation of the long molecular "axis" which is called the director. The intermolecular interaction of the liquid crystal material with the solid surface can lead to different positions of the director relative to the support. Depending on the angle ϕ between the director and the normal to the surface (Fig.1), the following types of alignment are distinguished: homeotropic ($\phi = 0$), tilted ($0 < \phi < \pi/2$), and planar ($\phi = \pi/2$). The homogeneous (planar or tilted) alignment, where the NLC molecules are arranged almost parallel to a specific direction, i.e. have a constant azimuthal angle α,† is a special case of the alignment of NLC most frequently used in indicator devices.

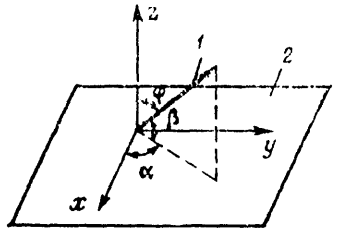


Figure 1. Alignment of the NLC director (line *1*) relative to the plane of the support (line *2*).

(b) The Energy of the Anchoring of NLC to the Support

An important characteristic of the interaction of NLC molecules with the surface is the energy of anchoring to the surface, defined as the energy which must be consumed to rotate the director from the equilibrium position by a certain angle. Two quantities are distinguished, one of which (W_1), corresponds to the rotation of the director by an angle $\Delta\phi$ in a plane perpendicular to that of the support and the other (W_2) corresponds to the rotation by an angle $\Delta\alpha$ in the azimuthal plane xy. The dependence of the anchoring energy on the angle of rotation of the director is represented by the phenomenological formulae[6] $W_1 = W_\phi \sin^2 \Delta\phi$ and

† Henceforth we shall assume throughout that this direction coincides with that of the x axis, i.e. $\alpha = 0$.

$W_2 = W_\alpha \sin^2 \Delta\alpha$, where W_ϕ and W_α are the polar and azimuthal anchoring energies corresponding to the rotation of the director from the initial position by angles $\phi = \pi/2$ and $\alpha = \pi/2$ respectively.

In the terminology of physical chemistry of surfaces, the anchoring energy W_ϕ can be represented as the difference between the energies of the interfacial NLC–solid support interaction γ_{LS} for the planar and homeotropic alignments: $W_\phi = \gamma_{LS}(\pi/2) - \gamma_{LS}(0)$. The interfacial energy can be expressed in its turn in terms of the surface energies of both phases at the interface with a vacuum (γ_L and γ_S):[8]

$$\gamma_{LS} = \gamma_S + \gamma_L - W_a, \quad (1)$$

where W_a is the energy of adhesion of the NLC to the support.

If the energy of the interaction of the NLC molecule with the surface of the support is sufficiently large and determines a particular direction of the director relative to the surface which does not change under the influence of external fields (i.e. the energies W_ϕ, $W_\alpha \to \infty$), then such a case is referred to as strong anchoring. On the other hand, if an electric or magnetic field can break down the order on the surface (W_ϕ and W_α are finite), then the anchoring is regarded as weak.[9]

III. CHEMICAL ORIENTING AGENTS

In the formation of homogeneously aligned NLC specimens, it is necessary to take into account the chemical nature of both the liquid crystal material and of the solid surface. In research and technological developments NLC belonging to the classes of Schiff bases, azobenzenes, azoxybenzenes, phenyl benzoates, cyanobiphenyls, phenylcyclohexanes, and their derivatives are used most frequently.[10] The surface of the supports used in liquid crystal devices is as a rule inhomogeneous and contains sections consisting of glass and a conducting film (usually indium or tin oxide). The chemical structure of the support can be modified in various ways in order to impart to it the required surface properties: as a result of the influence of external factors (temperature, chemical medium); by the adsorption of a monolayer of a surfactant; by depositing a special orienting layer with the required surface structure.

1. The Alignment of NLC on Glass and Oxide Films

The majority of clean oxide surfaces promote the planar alignment of NLC.[7,11–14] The homeotropic alignment observed on freshly sputtered In_2O_3, SnO_2, ZrO_2, Al_2O_3, and MgO films[13–18] for Schiff base and cyanobiphenyl NLC can be accounted for by the effect of amphiphilic impurities present in them as a result of the partial degradation of the NLC.[13]

The influence of external factors on the chemical structure and orienting properties of the surface can be traced in relation to a glass support. The glass surface contains mainly the siloxane $\geqslant$Si–O–Si$\leqslant$ and silanol $\geqslant$Si–OH groups, whose number is determined by the previous history of the glass. The cleaning of supports by etching in acid and peroxide solutions converts the siloxane groups into silanol group and promotes the homeotropic alignment of the NLC molecules with polar end groups.[18–21] On the other hand, etching of the supports in alkalis or annealing at an elevated temperature, particularly *in vacuo*, entails the conversion of the silanol groups into siloxane groups and homeotropic alignment is not observed even for NLC with polar groups at either end of the molecule.[21]

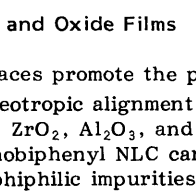
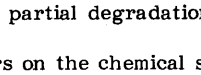
Chemical cleaning of the surface proved to be one of the first methods for the preparation of homogeneously aligned specimens,[17–21] but, as a result of the marked dependence of the type of alignment on the nature of the NLC[13,14] and poor reproducibility, it is hardly used nowadays.

2. The Orienting Effect of Surfactants

(a) Surfactant Additives in a Liquid Crystal Material

After the observation of the homeotropic alignment of *p*-methoxybenzylidene-*p'*-n-butylaniline (MBBA—one of the classical objects in studies on NLC) following the addition to the latter of small amounts (0.5 wt.%) of a polyamide resin,[22,23] a large number of additives with an analogous effect also on other types of NLC were proposed (Table 1). Many fewer additives have been proposed for the attainment of the planar alignment of NLC; these include dicarboxylic acids,[37] diazopolyoxycycloalkanes, diazopolyoxydicycloalkanes,[57] and aromatic ethers with an NLC structure.[58]

Table 1. The surfactants used for the homeotropic alignment of NLC.

Surfactant	NLC*	References
Polyamide resins and cellulose esters	SB	22–24
Lecithins	MBBA, CBP, PB, AOB	7, 25–32
Aliphatic amines $C_nH_{2n+1}NH_2$, $n \geqslant 12$	SB	31–34
Nitriles $C_nH_{2n+1}CN$, $n \geqslant 7$	SB, AB, AOB, PB	34
Esters $C_nH_{2n+1}COOC_mH_{2m+1}$, $n = 11$, $m = 6$; $n = 1$, $m = 1$–18	SB, AB, AOB, PB	34, 35
Alcohols $C_nH_{2n+1}OH$, $n = 1$–20	SB	36, 37
Aromatic amines and phenols: *N*-isopropyl-*N*-phenyl-*p*-phenylenediamine, β-naphthylphenylamine, *p*-hydroxyphenyl-β-naphthylamine, 2,6-di(t-butyl)-4-methylphenol, hydroquinone, 4-t-butylcatechol, 2-t-butoxyanisole	SB	38
Tetracyanodiphenodimethane, tetracyanonaphthoquinodimethane, and their derivatives	NLC with $\Delta\epsilon^{**} < 0$	39, 40
Alkylammonium salts $(C_{16}H_{37})_2(CH_3)_2\overset{+}{N}B(C_6H_5)_4^-$; $[C_nH_{2n+1}N(CH_3)_3]^+X^-$, $n = 1$–16, X = Hal; $(C_nH_{2n+1})_4N^+X^-$, $n = 1, 4, 6$, X = Hal	SB, AOB, PB, PCH	23, 30–32, 41–48
N-Alkylpyridinium salts: $n = 12, 14, 16$; X = Cl, Br, I	SB, PB	46, 47
Carboxylic acids: $C_nH_{2n+1}COOH$, $n > 10$; $C_{18}H_{37}CH{=}CH(CH_2)_7COOH$; 	SB, PB, AB, AOB, CBP	34, 35, 49
Carboxylatochromium complexes:  X = Hal, NO_3	SB, CBP, AOB	50, 54
Tributyltin oxide and chloride	SB	53, 54
Fluorine-containing surfactants: $C_6F_{11}SO_3K$; $C_nF_{2n+1}Si(OR)_3$, $n = 4$–8, $R = CH_3$, C_2H_5; $C_nF_{2n+1}SO_2NRC_2H_4N^+(R^1)_2X^-$; $C_nF_{2n+1}SO_2NRC_2H_4N(R^1)_2 \cdot HX$; $C_nF_{2n+1}CONR(CH_2)_lN^+(R^1)_3X^-$; $C_nF_{2n+1}CONR(CH_2)_lN(R^1)_2 \cdot HX$, $n = 5$–10, $l = 1$–5; X = acid group, R, R^1 = lower alkyls	SB, PB	31, 32, 55, 56

*Here and henceforth SB = Schiff bases, CPB = cyanobiphenyls, PB = phenyl benzoates, AOB = azoxybenzenes, AB = azobenzenes, PCH = phenylcyclohexanes.

**The anisotropy of the dielectric constant of the NLC.

The mechanism of this type of alignment is based on the fact that the surfactant molecules present in the liquid crystal material as additives are adsorbed on the surface of the support after coming into contact with it and alter the energy of the interface, promoting a specific type of alignment of the NLC.

The concentration of the additive selected is usually in the range 0.1–2 wt.%. A smaller amount may not have a sufficient orienting effect, a larger amount reduces the temperature range for the existance of the mesophase, while ionic surfactants cause in addition an appreciable increase of the conductivity of the NLC, which is undesirable for NLC indicators based on field effects. A disadvantage of this method of aligning NLC is a decrease of the concentration of the adsorbed surfactant molecules going from the filling orifice of the indicator to its periphery, which leads to a non-uniformity of the alignment of the NLC. Account must be taken of the fact that the surfactants entering the NLC from adhesives and substances used to make a hermetic seal[59] or the impurities in the NLC and its decomposition products[13,14] may exert an undesirable orienting influence in the preparation of liquid crystal indicators.

(b) Deposition of a Surfactant Film on the Support

The majority of the surfactants described above can be deposited directly on the support by adsorption from solutions or by the Langmuir–Blodgett method. The structure of the surfactant monolayers and the alignment of the NLC on the latter depend on the density of the molecules adsorbed on the surface.[7,27] Thus, when hexadecyltrimethylammonium bromide is used, an increase of its molecular density on glass results in the replacement of the planar alignment of MBBA by its homeotropic alignment;[44,45] the homeotropic alignment of cyanobiphenyls and azoxybenzenes is achieved only at a specific concentration of stearatochromium chloride, used to treat the support;[60] on the other hand, the orienting influence of lecithin is impaired by increased packing density of its molecules on the surface.[27,28]

Surfactants containing long alkyl groups, for example, barium stearate,[42] the aliphatic monoamines $C_nH_{2n+1}NH_2$ (n = 12 to 16),[31–33] and fluoro-derivatives of various types with a C_nF_{2n+1} (n = 5–10) end group[55,66] are used as a rule to achieve the homeotropic alignment of NLC. The length of the hydrocarbon group affects the surface energy of the surfactant film and hence the alignment of the NLC. Thus, when the number of carbon atoms is changed from 10 to 6 in aliphatic monoamines, the angle of tilt of the MBBA director to the surface β (see Fig. 1) diminishes from 78° to 30°.[33] The molecules of surfactants proposed for the attainment of a planar alignment frequently contain not less than two polar end groups capable of being adsorbed on the surface.[37,61,62]

Orienting surfactants are usually deposited on the support from organic or aqueous solutions, but other methods can also be employed. For example, on films deposited from a gas discharge in metal alkoxide vapours, a homeotropic alignment of NLC has been observed for quadrivalent metals and a planar alignment for tervalent metals.[63]

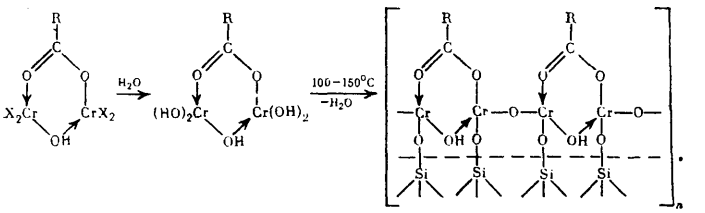
The structure of the NLC molecules themselves also plays a major role. In contrast to the majority of other classes of compounds, azoxybenzenes are not aligned homeotropically on surfaces covered by lecithin,[28] while cyanobiphenyls are not aligned in a planar manner on films of dicarboxylatochromium complexes.[64]

The surfactant monolayers physically adsorbed on the surface are unstable with time: the interaction of the polar groups of the NLC or impurities with surfactant molecules can alter the structure of the orienting layer and lead to breakdown of orientation.

(c) The C emisorption of Surfactants by the Surface of the Support

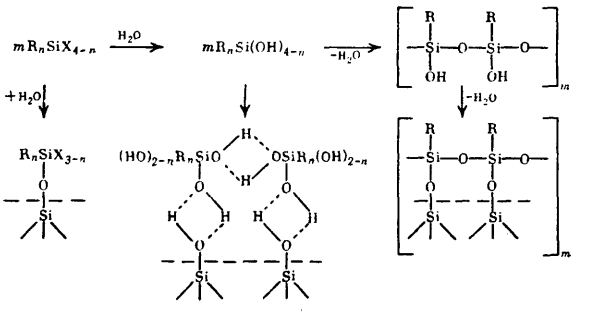
In order to improve the stability of the alignment of NLC, it has been suggested that one use surfactants which bind chemically to the support as a result of the interaction with the surface hydroxy-groups. It has been reported that the replacement of the silanol groups on the surface of silica by alkoxy-groups at elevated temperatures when amines are used as catalysts makes it possible to obtain a stable homeotropic alignment of many NLC.[36,37] However, this method is apparently very sensitive to the number of silanol groups, because it was impossible to reproduce these results in another study.[7]

A stable homeotropic alignment of not only nematic but also cholesteric and smectic liquid crystals is achieved on supports treated with carboxylatochromium complexes, which form hydrogen and siloxane bonds with the atoms in the surface layer of the support:



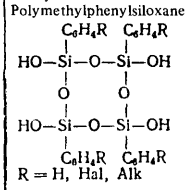
Here R is an aliphatic[50,51] or *o*-phenyl group[52] and X is an anion. On the other hand, organochromium complexes with dicarboxylate ligands are used to achieve a planar alignment.[64]

Alkoxy- and chloro-silanes have been widely investigated and used as orienting surfactants.[3,7,65–67] The increased interest in these substances is due to the effective adhesion and stability of organosilicon films on hydrophilic supports as a result of chemical interaction with the silanol surface groups. The hydrolytic and polycondensation processes occurring both in the solution of R_nSiX_{4-n} and on the surface of the support lead to the formation of a polysiloxane layer:[68]



Silanes can therefore be regarded as both surfactants and as the starting compounds for the deposition of polymer films (see Table 2 below). The supports are usually treated with silanes by immersion, centrifugation, and boiling in aqueous or organic solutions (1–5 wt.%) or in the vapour phase (in the case of volatile silanes).

Table 2. Polymeric materials of the orienting films.

Material of orienting film	Method of deposition	Starting materials	References
	Homeotropic alignment of NLC		
Polysiloxanes	Polymerisation in glow discharge	Hexamethyldisiloxane, trimethylvinylsilane	75, 76
"	Cathodic sputtering	Tetraethoxysilane	63
"	From organic solutions	Silicone liquids	77, 78
Compositions based on organosilicon and organotitanium cpds.	From organic solutions	$C_nH_{2n+1}Si(OC_2H_5)_3$ + $Ti(OC_4H_9)_4$, n = 16–18	71, 72
Fluorinated polymers	Cathodic sputtering	Polytetrafluoroethylene	76
Ditto	Polymerisation in plasma	Tetrafluoroethylene, perfluorocyclohexene, perfluorodimethylcyclobutane, perfluoro-1,3-dimethylcyclohexane	79–83
	Homogeneous alignment of NLC		
Polyisobutene	Polymerisation in plasma	Isobutene	76
Polybutadiene	From polymer solution	Butadiene	7
Polystyrene, copolymers with divinylbenzene	From polymer solution	Polystyrene, polystyrene plus divinylbenzene	84
Poly-*p*-xylylene and its derivatives	Pyrolysis with subsequent condensation on a support	CH_2–C_6H_4–CH_2 | | CH_2–C_6H_4–CH_2	37, 84, 85
Poly(vinyl alcohol) (PVA) and its derivatives	From aqueous solutions	Poly(vinyl alcohol)	86–88
Polyoxyethylenes	—	$CH_3(CH_2)_{15}(OC_2H_4)_{20}OH$	37, 86
Polyacrylates	From polymer solution	Polyacrylate, polycyanoacrylate, polyacrylonitrile plus PVA	7, 89, 90
"	Polymerisation in plasma	Methyl methacrylate	84
Polyesters, polyurethanes, polysulphones	From polymer solution	Polyesters, polyurethanes, polysulphones	7, 87
Cellulose resins	From organic solutions	Methylcellulose, nitrocellulose acetylcellulose, cellulose acetate butyrate	91–93
Polyoxazole, polythiazole, polyoxazinol, polyoxazinediol, polydiquinoxaline	From organic solutions	Isophthaloyl chloride plus 3,3'-dihydroxybenzidine in *N*-methylpyrrolidinone	94
Polyimides and their copolymers with epoxide and organosilicon resins	From organic solutions of polyamidoacids with subsequent imidisation	Polyamidoacids	95–111
Polysiloxanes and compositions containing them together with Ti, Al, Sn, Ce, etc compounds	From solutions of hydrolysable compounds	$Si(OR)_4$, $R^1Si(OR)_3$, R = CH_3, C_2H_5; R^1 = C_6H_5; CH_2 = CH; $Ti(OC_4H_9)_4$; $AlCl_3$	69, 73, 74, 76, 112–120
Ditto	Polymerisation in plasma	Methylsiloxane	84
"	From polymer solution	Polymethylphenylsiloxane	7
Silsesquioxanes	From organic solutions, sputtering	 R = H, Hal, Alk	121
Fluorinated polymers	Vacuum sputtering	Polytetrafluoroethylene	87
Ditto	Sliding contact	Poly(vinyl fluoride)	24, 42
Poly (vinylpyridinium bromides)	From aqueous solution	Poly(2-methyl-5-vinylpyridylbutyl bromide)	46
Poly-γ-methyl-*L*-glutamate	—	—	122

In order to achieve a homeotropic alignment, alkoxy- and chloro-silanes with long alkyl or fluoroalkyl chains are used, for example $[C_nH_{2n+1}(CH_3)_2N(CH_2)_3Si(OCH_3)_3]^+Cl$ with n = 12–18,[3,31,32,65] $C_{18}H_{37}SiCl_3$,[7,42] and $C_nF_{2n+1}Si(OR)_3$ with n = 4–8.[56] Organosilicon compounds which promote a planar alignment of NLC contain as a rule a group with a ring structure (phenyl, biphenyl, or cyclohexyl groups)[7,66,69] or a hydrocarbon chain capable of binding via several groups to the support, for example, $CH_3OOCCH_2NHNH(CH_2)_nNH.(CH_2)_mSi(OC_2H_5)_3$ with n = 2, 3 and m = 2–5[70] or $CH_3NH.(CH_2)_3Si(OCH_3)_3$.[3,65]

One must note that, owing to the marked dependence of the quality of the orienting surfactant film on the preparation of the surface, an inhomogeneity in the orientation of the NLC may be observed on plates with an electrode pattern. This disadvantage is eliminated by introducing surfactants into film-forming solutions based on hydrolysable compounds, such as, for example, $Si(OC_2H_5)_4$, $Ti(OC_4H_9)_4$, or $AlCl_3$.[71–74] The polymer coatings formed adhere strongly to both the glass and to the electrode film, playing at the same time the role of a protective dielectric layer.

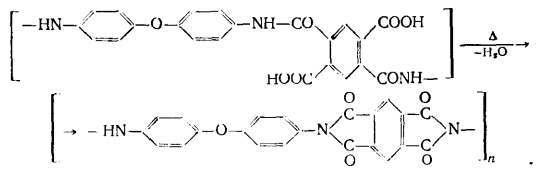
Orienting surfactants forming chemical bonds with the support are nowadays widely used in the technology of the manufacture of liquid crystal devices, particularly with an initial homeotropic alignment. However, their use is not always compatible with the formation of a hermetic seal for the indicators by means of a glass frit because the thermal stability of surfactant films is comparatively low (usually up to not more than 200 °C).

3. Orienting Polymer Coatings

In order to create surfaces with specific physicochemical properties, polymer films obtained by a wide variety of methods are frequently used. With the exception of certain polymers, proposed to achieve a homeotropic alignment of NLC, most of them orient NLC homogeneously after mechanical rubbing (Table 2). The conditions in the deposition of the polymer have a considerable influence on its orienting properties. For example, the homeotropic and planar alignments of MBBA on polytetrafluoroethylene films, deposited respectively by cathodic sputtering[76] and by means of a sliding contact,[42] have been reported. The method involving deposition from solutions of compounds which undergo hydrolysis and polycondensation has interesting possibilities in this connection. The wide-scale application of this procedure (see, for example, the relevant patents[71–74,112–120]) can be explained by the fact that, by selecting the heat treatment temperature and by mixing in various proportions silicon, titanium, aluminium, tin, cerium, zinc, etc. compounds, it is possible to alter the chemical structure of the surface, achieving thereby a homeotropic or planar alignment of the NLC and at the same time one can regulate the optical and dielectric properties of the orienting films.

Among the multiplicity of materials listed in Table 2, poly(vinyl alcohol) (PVA) layers and polyimide films are most widely employed. The ready availability of PVA films, the simplicity of their deposition, and their effective adhesion to glass and oxide surfaces have led to their extensive application in laboratory practice. However, their unsatisfactory dielectric characteristics, low thermal stability (up to not above 180 °C), and the loss of their orienting capacity under the influence of moisture frequently prevent their application in industrial technology.

Polyimide films have a high breakdown potential and a very high thermal stability (up to 450 °C), which makes it possible, in particular, to achieve a hermetic seal for indicators with the aid of readily fusible glass. Polyimide films are obtained by the thermal dehydrocyclisation of polyamidoacids, which are deposited on the support by centrifugation or by immersion in an organic solution; a 5–10 wt.% solution of polypyromellitamido-acid in dimethylformamide (DMF) is used as a rule.[103] The heat treatment of the films must be carried out in at least two stages: at 80–100 °C the solvent is removed from the layer and at 300° to 400 °C the imidisation process proper takes place:



The main disadvantage of polyimide films is the reduction of the effectiveness of adhesion under the influence of moisture. In order to improve the adhesion of the orienting coating to glass, it has been suggested that the surface of the support be modified with organosilicon compounds having the formula R_nSix_{4-n} [104] or that a sublayer of an inorganic material[123,124] or an epoxide resin[125] be deposited. An increased resistance of polyimides to moisture can also be attained by copolymerising them with organosilicon[107,111] and epoxide compounds.[108,109]

A new promising trend in the formation of liquid crystal devices, involving the employment of plastic supports instead of glass supports, has been established in recent years.[126,127] In this connection publications devoted to the selection of chemical orientation agents for such surfaces have appeared. Thus it has been suggested that an orienting PVA film[127] or mixed alkylalkoxy-derivatives of titanium and aluminium[128,129] be deposited on a poly(ethylene terephthalate) support.

4. The Polar Energy of the Achoring of the NLC to the Support

The structure of the surface determines not only the direction of alignment of NLC molecules but also the energy of their anchoring to the support. This quantity has a significant influence on the behaviour of the NLC layer in electric and magnetic fields[9] and information about its estimation and about the possibility of its regulation is therefore important. It has been suggested that the bonding energy with the surface in the case of weak anchoring be determined qualitatively from the dimensions of different alignment defects,[33] from the critical field in the deformation of the NLC layer by magnetic[31,32] or electric[29,132,133] fields, or from the extent of double refraction.[134,135] It must be emphasised that reliable methods for the measurement of the anchoring energy are so far lacking and the values quoted in the literature are merely estimates.

The influence of chemical orienting agents on the polar energy of the anchoring of the NLC to a solid surface W_ϕ is illustrated in Table 3, which lists the few experimental and theoretical estimates available in the literature. The dependence of W_ϕ on the length of the hydrocarbon group, the type of the polar group in the surfactant molecules, and the nature of the support has been investigated.[31,32] It has been shown that, with increase of the length of the alkyl group of the orienting surfactant, the anchoring energy initially increases and then falls; in the homologous series $[C_nH_{2n+1}(CH_3)_2N(CH_2)_3Si(OCH_3)_3]^+Cl^-$ the maximum value of W_ϕ is attained for n = 14–16. It has also been noted that the use of cationic surfactants leads to a higher value of W_ϕ than in the case of non-ionic alkylamines and amphoteric lecithin, the energy of anchoring the NLC to glass being almost a factor of two smaller for the same surfactant than the energy of anchoring to indium oxide. Thus the polar energy of anchoring the NLC to a solid surface is evidently determined by steric, dispersion, and polar factors.

IV. ANISOTROPIC ORIENTING COATINGS

In order to produce liquid crystal specimens with a homogeneous (planar or tilted) alignment, it is insufficient to ensure the distribution of NLC molecules at a specific angle relative to the surface of the support; it is also necessary to impart anisotropic properties to the surface, so that, on interaction with the latter, the NLC molecules are "built in" along one specified direction. For this purpose, one usually employs supports with a definite surface relief (as a rule in the form of grooves and humps) and also films with an ordered molecular structure.

Table 3. The polar energies of the anchoring of NLC to orienting surfaces.

Orienting surface	NLC	φ, °	W_ψ, mJ m^{-2}	References
Glass	PAA†	90	0.36*	[136]
Heated paper decomposition products	MBBA	0	10^{-4}	[130]
Lecithin	MBBA	0	$(1-3)\cdot10^{-3}$	[25, 31, 32]
Lecithin on rubbed surface	AOB + PB	6	$9\cdot10^{-3}$	[29]
Aliphatic acid derivatives on polished glass	MBBA	$\geqslant 0$	10^{-1}	[133]
$C_{16}H_{33}OH$	MBBA	0	$2.4\cdot10^{-3}$	[32]
$C_nH_{2n+1}NH_2$, n = 14–18	MBBA	0	$(1.2-2.0)\cdot10^{-3}$	[31]
$C_nH_{2n+1}NH_2$, n = 6–12	MBBA	3–24	10^{-4}–10^{-3}	[33]
$C_nH_{2n+1}NH_2$, n = 7	MBBA	35	$(1-5)\cdot10^{-3}$	[31]
$[C_nH_{2n+1}N(CH_3)_3]^+X^-$, X = Cl, n = 10–18	MBBA	0	$(1.0-3.8)\cdot10^{-3}$	[31]
Ditto, X = Br, n = 16–14	MBBA	0	$(2.2-4.5)\cdot10^{-3}$	[31]
Ditto, X = Br, n = 6–8	MBBA	75	10^{-3}	[31]
$C_nH_{2n+1}N^+(CH_3)_2(CH_2)_3Si(OCH_3)_3Cl^-$, n = 10–18	MBBA	0	$(0.3-1.3)\cdot10^{-2}$	[31, 137, 138]
$C_8F_{17}SO_2NH(CH_2)_3N^+(CH_3)_3I^-$	MBBA	0	$(1.0-2.7)\cdot10^{-2}$**	[138]
Ditto	MBBA	0	$(3.0-5.0)\cdot10^{-3}$	[1, 137, 138]
SnO_2	MBBA	0	$2\cdot10^{-3}$	[132]
SiO_x**	MBBA	60	10^{-4}	[131]
SiO_x***	CBP	60	$2.1\cdot10^{-3}$	[134]
Free NC surface	MBBA	15	$4.5\cdot10^{-2}$*	[32]
Ditto	CBP	0	$5\cdot10^{-3}$	[32]

*Calculated values.
**Oblique spluttering; the angle between the beam and the surface of the support $\psi < 5°$.
***Double oblique sputtering, initially with $\psi = 30°$ and then with $\psi = 5°$.
† *p*-Azoxyanisole (Ed.of Translation).

The methods used to impart anisotropy to the surface properties of the support in order to achieve various angles of tilt of the director relative to the surface (the angle β, see Fig.1) are given in Table 4. A homogeneous alignment of the NLC parallel to the surface (β = 0) is observed on inorganic films obtained by "oblique" sputtering at angles ψ between the direction of the stream of particles and the support in the range 15° < ψ < 45 °C, on surfactant films with an ordered molecular structure, and on photolithographic gratings. Low tilt angles of the director (0° < β < 5 °) are realised on rubbing the surface, on double oblique sputtering, and on ionic etching of the support; intermediate values of β are achieved on oblique sputtering of silicon or germanium oxide at low angles relative to the surface of the support. Finally, angles β close to 90° are obtained when films which have been rubbed or sputtered on are treated with surfactants used for homeotropic alignment and also as a result of oblique sputtering of Al_2O_3 or CaF_2 on fluorocarbon films polymerised in a plasma and on surfaces treated with surfactants having short alkyl chains.

Table 4. The tilt angles of the NLC director on various orienting surfaces.

Chemical orienting agent	Method of generation of surface anisotropy	NLC	β, °	Method of measurement of β*	Refs.
SiO_x, Au	Sputtering, $\psi = 15-50°$	SB, CBP	0	1, 2, 3	[138–144]
GeO	Sputtering, $\psi = 40-60°$	CBP	0	4	[145]
Bis(*N*-methylamino)-dimethyl silane	Polymerisation in plasma stream, $\psi = 15-70°$	CBP	0±0.5	3,4	[146, 147]
PVA	Transfer of oriented monolayer from surface of water	AOB	0±0.2	5	[148]
SiO_2	Polishing with diamond paste	PB	0.05	1	[149]
Glass	Rubbing	SB	0.5–5	3	[142]
$In_2O_3 + SnO_2$	Rubbing with fabric	PCH	1–4		[151]
In_2O_3	Rubbing	CBP	2.15	1	[150]
SiO_2+$CH_3NH(CH_2)_3Si(OCH_3)_3$	Rubbing with fabric	PB	0.3	1	149
In_2O_3+ polyamideimide	Rubbing with emery paper	PB	0.95	1	[149]
Polyimides	Rubbing	PB	0.11	2	[152]
ditto	Ditto	CPB	0.24	2	[152]
»	»	AOB	0.44	2	[152]
»	»	PCH	0.29–1.20	2	[152]
Polymides	»	PCH	0.35	2	[153]
»	Rubbing on with brushes	AOB	1.0–1.2	5	[148]
PVA	Ditto	AOB	1.1–1.4	5	[148]
SiO_2	Etching with a stream of ions $\psi = 10-30°$	CPB	4	1	[154]
SiO_x	Double sputtering, $\psi_1 = 30°, \psi_2 = 5°$	PB, CBP	0–45	1,4	[155–159]
»	Ditto, $\psi_1 = 5°, \psi_2 = 30°$	SB, CBP	0–30	4	[159]
»	Sputtering, $\psi = 0-20°$	MBBA	15–35	1	[139, 140]
»	» , $\psi = 6-13°$	SB	30–45	3,2	[142, 143]
»	» , $\psi = 5-16°$	CBP	28–41	4	[160]
»	» , $\psi = 5°$	CBP	45		[141]
»	» , $\psi = 5-8°$	CBP	24–29	1,2,6	[7, 161, 143]
»	» , $\psi = 8°$	SB	15–22	1,2	[7, 143]
»	» , $\psi = 4-23°$	MBBA	3–28	—	[162]
GeO	» , $\psi = 5-25°$	CBP	25–28	4	[145, 163]
ditto	Ditto	AOB	28–35	4	[164]
Polytetrafluoroethylene	Polymerisation in plasma on SiO_x films sputtered at an angle $\psi = 30°$	MBBA	87–90	4,5	[83]
ditto	Ditto, $\psi = 5°$	CBP	64	4	[165]
Au	Sputtering on rubbed glass $\psi = 30-45°$	PCH + surfactant	90	5	[166]
$[C_{18}H_{37}N(CH_3)_2(CH_2)_3Si(OCH_3)_3]^+Cl^-$	Treatment in aqueous solution of SiO_x films sputtered at an angle $\psi = 5°$	CBP	74–64	4	[165]
ditto	Ditto	CBP	88–71	4	[167]
»	»	AOB	70–55	4	[165]
»	» , $\psi = 0-30°$	SB, CBP	60–90	1,4	[168]
Lecithin, $RSiX_3$	Treatment in solution of SiO_2, Al_2O_3, and Ti films after ionic etching at an angle of 20–90°	SB	60–90	—	[169]
$RSiX_3$	Treatment in solution of rubbed on In_2O_3 and SiO_2 films	SB	60–90	—	[170, 171]
$C_nH_{2n+1}NH_2$, $n = 6–12$	Treatment in aqueous solutions	MBBA	30–90	4	[33]
	Addition of surfactants to NLC (0.1–0.5%)	MBBA	≤90	—	[38]
$C_nH_{2n+1}OH$, $n = 7–22$	Treatment in surfactant solutions of SiO_2 films after etching with an ionic beam at $\psi = 20°-30°$	SB, PB	75–90	5	[36]
Al_2O_3	Sputtering, $\psi = 0-40°$	CBP, PB	60–90	4	[172]
ditto	» , $\psi = 40-60°$	CBP, PB	≤90	4	[172]
»	» , $\psi = 60-90°$	CBP, PB	90	4	[172]
CaF_2	» , $\psi = 35°$	CBP	15	4	[173]
ditto	» , $\psi = 85°$	CBP	60	4	[173]
»	» , $\psi = 90°$	CBP	90	4	[173]

Methods of measurement of the angle β: 1) magneto-capacitive;[149,150] 2) magnetic with optical recording;[143] 3) capacitive;[158] 4) from conoscopic figures;[160] 5) from extremum phase shift;[174,175] 6) from double refraction.[161]

1. Surfaces with an Orienting Microrelief

One of the commonest methods for the achievement of a homogeneous orientation of NLC involves rubbing the support with a soft fabric, paper, and brushes.[176,177] This method has been modified in a study[178] whose authors suggest that the support be lapped in one direction with diamond paste. The study of the surface by electron microscopy showed that this results in the formation of a system of parallel humps and grooves ~1 μm wide. However, rubbing a chemically inhomogeneous surface can lead to the inhomogeneity of the orientation on different sections of the support with an electrode pattern and to low thermal stability and moisture resistance of the orienting coating. Lapping the protective SiO_2 layer deposited on top of the electrodes makes it possible to obtain a more homogeneous alignment of the NLC with a tilt angle of the director $\beta \approx 0.05°$.[149]

A highly ordered homogeneous alignment on large areas can be achieved by rubbing organic coatings whose surface properties promote a planar alignment of the NLC (see Table 2). The tilt angle of the director achieved on rubbed surfaces depends on the type of NLC, the material of the orienting layer, and the pressure of the rubbing device, varying from 0.2–0.3°[149] to 3–4°.[151]

A multiplicity of other methods have also been proposed recently for the creation of an orienting surface microrelief, for example ionic etching of a dielectric film,[154] scanning with an electron or laser beam,[179] and the use of lithographic procedures.[180–182] However, all these methods are fairly complex for industrial use and, by virtue of its simplicity high productivity and low cost, the rubbing of polymer films therefore remains the most suitable technological method for the attainment of a homogeneous alignment of NLC.

2. Sputtered Inorganic Films

The vacuum sputtering of metals and their oxides and fluorides at low angles relative to the surface of the support results in the formation of a thin film with an anisotropic structure. The suggestion that such films be used for the homogeneous alignment of NLC [183] gave rise to a large number of studies of their orienting capacity.[139–145,155–164,184–190] For example, Au, SiO, GeO, Al_2O_3, MgF_2, CaF_2, as well as other metals, oxides, and fluorides have been tested as materials for the formation of sputtered films; the majority of these orient the NLC molecules in a planar manner with an arbitrary azimuth under the conditions of normal sputtering (sputtering at right angles to the surface?).

The dependence of the surface structure of the sputtered films and of their orienting properties on the angle between the beam and the support during sputtering has been examined in detail in a number of studies.[140,187–190] When the sputtered particles are incident at angles in the range $15° < \psi < 45°$ relative to the support, its surface consists of a system of islands which are extended in the direction at right angles to the plane containing the normal to the surface and the direction of sputtering.[140] Such a surface orients NLC homogeneously, so that $\beta = 0$ and the director coincides with the direction of the long axis of the islands. For $\psi < 15$ °C, the surface relief of the orienting film consists of closely adjacent small asymmetric columns, whose shape and dimensions depend on the material of the film and its thickness; on supports of this kind, NLC molecules are aligned at an angle $\beta = 20–30°$ relative to the plane of incidence of the sputtered particles.[163,187,188]

In order to achieve low tilt angles of the NLC director relative to the surface, it has been suggested that the sputtering process be carried out in two stages: initially at an angle $\psi = 30°$ and then at a very low angle (≤5°) at right angles to the direction of the first sputtering (or in the reverse order).[155–159] Under these conditions, β depends on the thickness of the second layer, which should be very small (~4 Å), since it has been suggested that, in order to

introduce asymmetry along the grooves formed in the first sputtering, it is necessary to deposit individual asymmetric islands and not a continuous film.[156]

It is noteworthy that, in contrast to other fluoride and oxide films, the sputtered CaF_2 [173] and Al_2O_3 [172] films align NLC almost homeotropically with different deviations from $\phi = 0$, depending on the angle of sputtering.

High-frequency plasma reactors can also be used to deposit thin anisotropic films.[79,80,146,147] The homogeneous alignment of NLC with $\beta = 0$ is observed on supports treated at an angle of 50–70° with a stream of plasma containing argon, oxygen, and organosilicon free-radical species.

The principal disadvantage of the vacuum method is the inhomogeneity of the alignment of NLC on supports of comparatively large size owing to the differences between the angles of sputtering for different sections of the plate. In view of the difficulty of achieving low tilt angles of the director, the method of oblique sputtering is used most frequently only in the preparation of indicator devices of small size working under static conditions in those cases where a high thermal stability and moisture resistance of the orienting layers is required.

3. Surfactant Films with an Ordered Molecular Structure

The surfactant films formed on withdrawing the supports from solutions by the Langmuir–Blodgett method can have anisotropic surface properties as a result of an ordered molecular structure and can align NLC homogeneously with the angle of tilt of the director $\beta = 0$. Polymer molecules of extended shape, capable of binding chemically to the support, have been reported to be surfactants of this type: PVA,[191] polymethylsiloxane,[84] and poly(2-methyl-5-vinylpyridiniabutyl) bromide.[46]

In the presence of a dichroic dye, the layers of organic polymers with molecules arranged in such a way that their long axes are almost parallel to one another, possess not only orienting but also polarising properties and can be used as internal polaroids in liquid crystal indicators. Thus the anisotropy of the surface and optical properties of PVA layers with a dye is achieved by directional withdrawal from solution or by shear deformation with the aid of a scraper.[192,193] An orienting polarising film is also formed when a gel of a dichroic dye is deposited with subsequent centrifugation or mechanical deformation of the layer parallel to the surface of the support with the aid of an auxillary plate.[194] The use of internal polaroids does not as yet allow the attainment of a high degree of polarisation of light and a homogeneous alignment of the NLC on supports of a large area but nevertheless it leads to the possibility of simplifying the design of the display and the protection of the polaroids against the unfavourable effect of the external medium.

Thus all the methods described for the formation of anisotropic coatings permit the achievement of any homogeneous tilted alignment of NLC.

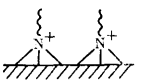
V. THE MECHANISMS OF THE ORIENTING EFFECT OF THE SURFACE

In the first studies undertaken to produce homogeneously aligned specimens it was already suggested that physicochemical forces play a decisive role in the mechanism of the alignment of NLC on a solid surface. On the basis of experimental observations, Friedel[20] concluded as early as 1922 that the NLC is aligned homeotropically on the support, provided that its molecules do not interact with the solid surface and in a planar manner in the presence of any kind of physicochemical interaction. The homogeneous alignment of NLC on supports rubbed with leather, paper, or fabric has been explained[177] by the dipole interaction of the liquid crystal molecules with the organic impurities transferred on to the surface during rubbing. The subsequent studies made it possible to refine these conclusions, but a complete understanding of the orienting effect of the support has not as yet been achieved. This is associated both with the inadequate theoretical development of the physical chemistry of surfaces and with the experimental difficulties due to the indefinite structure of the support and the lack of reliable methods for the measurement of the surface energy and the energy of the anchoring of the NLC to the support, the contamination of the liquid crystal material by decomposition products, and other causes.

Nematic liquid crystals usually consist of extended molecules ~20 Å long containing alkyl chains and alkoxy-, cyano-, azoxy-, and other polar groups and for this reason the intermolecular interaction with a solid surface can take place via both dispersion and polar forces (interactions of the dipole–dipole and dipole–induced dipole types) and hydrogen and other bonds. Account must also be taken of steric factors and, when a specific relief is created on the surface of the support, the anisotropic-elastic forces also play a significant role.

1. The Steric Model

Investigations of the intermolecular interaction of NLC with a solid surface have been stimulated by reports of the orienting influence of surfactants adsorbed on the support.[22–25] One of the first models[27,43] considered only steric factors on the assumption that surfactant molecules with long alkyl chains are arranged at right angles to the surface owing to the electrostatic interaction with the polar surface of the support, as happens for example, in the case of hexadecyltrimethylammonium bromide $C_{16}H_{33}N^+(CH_3)_3Br^-$ (HMAB):



Steric factors then favour the incorporation of the long NLC molecules parallel to the alkyl chains, i.e. the homeotropic alignment. Evidently this approach is important only in special cases.

2. The Criterion of Creagh and Kmetz

The first attempt at a thermodynamic explanation of the alignment of NLC on a solid surface was undertaken by Creagh and Kmetz,[15] who proposed that the difference between the surface energies of the support and the liquid crystal ($\gamma_S - \gamma_L$) be used as a measure of the free energy which determines the relative probability of the homeotropic alignment relative to the planar orientation. When $\gamma_S < \gamma_L$, the intermolecular forces within the NLC prove to be greater than the surface interaction forces, the liquid crystal does not wet the support and is aligned homeotropically. When $\gamma_S > \gamma_L$, the forces governing the anchoring to the surface predominate, the NLC wets the support, and is aligned in a planar manner.

The theoretical principles of this approach have been formulated by Porte.[33] If only dispersion forces operate between the NLC and the support, then the adhesion energy

W_a can be described by the Fowkes relation:[195]

$$W_a = 2(\gamma_L\gamma_S)^{1/2} \quad (2)$$

The equilibrium angle ϕ between the director and the normal to the surface corresponds to the condition for a minimum in the interfacial tension expressed in the form $\gamma_{SL}(\phi) = \phi_S + \gamma_L(\phi) - 2[\gamma_L(\phi)\gamma_S]^{1/2}$. The simplest calculation shows that the homeotropic alignment obtains when $\gamma_S < \gamma_L(0)$, the tilted alignment obtains when $\gamma_L(0) < \gamma_S < \gamma_L(\pi/2)$, and the planar alignment obtains when $\gamma_S > \gamma_L(\pi/2)$, which is consistent with the criterion of Creagh and Kmetz.

In view of the difficulty of the experimental determination of the surface energy of the support γ_S, it has been suggested that the critical surface energy γ_{cr} be used as the characteristic of the energy state of the orienting surface.[3]. The quantity γ_{cr} is found by extrapolating the results of measurement of the wetting angles θ for non-polar liquids with known values of $\gamma_L > \gamma_{cr}$ to $\theta = 0°$.[196] This empirical criterion has come to be widely used and was subsequently repeatedly tested.[28,42–45,76,197] However, the quantity γ_{cr} is not a fundamental property of the solid and depends on the nature of the liquids and the presence of adsorbed layers on the surface and the relative humidity. It has been shown that the critical surface energy is determined by the dispersion contribution to the surface energy of the support ($\gamma_{cr} = \gamma_S^d$) and can be used to characterise only non-polar surfaces.[198] The experimentally observed types of alignment are therefore by no means always consistent with the rule of Creagh and Kmetz.[7,28,42–45] Subsequent studies showed that this model constitutes only a special case of a more general mechanism of alignment.

3. The NLC–Support Polar Interaction

The polar interaction of NLC molecules with a charged solid surface is more difficult to describe theoretically than the dispersion interaction but it must be taken into account in considering the alignment mechanisms. The importance of allowing for polar forces has been demonstrated in a number of studies,[43–45] whose authors investigated systematically the alignment of MBBA on surfaces with different surface densities of adsorbed HMAB molecules. On a clean glass support, MBBA molecules are arranged parallel to the surface as a result of a dipole interaction. With increase in the density of the molecules of the orienting agent adsorbed on the glass the electrostatic field of the support is shielded. Finally, for the maximum density of HMAB molecules, only the dispersion component of the adhesion energy of MBBA remains and its molecules are oriented at right angles to the surface.

Thus, in describing the surface interaction of two phases with the aid of Eqn.(1), one must bear in mind that all the terms of this equation consist of dispersion and polar components: $W_a = W_a^d + W_a^p$; $\gamma_i = \gamma_i^d + \gamma_i^p$; $d_i + p_i = 1$, where $d_i = \gamma_i^d/\gamma_i$ and $p_i = \gamma_i^p/\gamma_i$ are the relative contributions of the dispersion and polar component of the surface energy, while i = L or S. The quantity γ_i^p can be made up in its turn of the following principal components: $\gamma_i^p = \gamma_i^{pp} + \gamma_i^{pi} + \gamma_i^h$, where γ_i^{pp} takes into account the dipole–dipole interaction, γ_i^{pi} the interaction of the dipole–induced dipole type, and γ_i^h the hydrogen and other bonds on the surface.

The total adhesion energy can be formulated as the sum of the dispersion component of the type defined by Eqn.(2) [$W_a^d = 2(\gamma_L^d\gamma_S^d)^{1/2}$] and the polar component, for which different expressions have been proposed. Thus Perez et al.[46] use an expression for W^p in terms of the electrostatic field of the support E: $W_a^p = E\delta\mu$, where δ is the number of NLC molecules per unit surface and μ the effective dipole moment of the NLC molecules, which depends on their alignment. Another expression for the total adhesion energy with allowance for polar factors has been proposed by Girifalco and Good:[199] $W_a = 2\Phi(\gamma_S\gamma_L)^{1/2}$, where Φ is the interaction parameter. When there are no polar forces, $\Phi = 1$ and this expression becomes identical with the Fowkes equation [Eqn.(2)] and the criterion of Creagh and Kmetz can be used to estimate the degree of alignment of the NLC on a solid surface. If the dipole–dipole interaction predominates among all types of polar interaction between the NLC molecules and the support, then the parameter Φ can be expressed in terms of the geometrical mean of the corresponding components of the surface energy:[200]

$$\Phi = (p_S p_L)^{1/2} + (d_S d_L)^{1/2}, \quad (3)$$

whereupon $W_a^p = 2(\gamma_S^p\gamma_L^p)^{1/2}$. It has been shown empirically that in many cases the harmonic approximation[46,200] can also be used to calculate W^p, which leads to the expression $W_a^p = 4\gamma_S^p\gamma_L^p/(\gamma_S^p + \gamma_L^p)$.

4. The Models of Alignment Based on the Girifalco–Good–Fowkes Equation

A whole series of studies[60,137,138,201–203] have considered models of the alignment of NLC on a solid surface employing the Girifalco–Good–Fowkes equation:[199] $\gamma_{SL} = \gamma_S + \gamma_L - 2\Phi(\gamma_L\gamma_S)^{1/2}$ or, after substituting Eqn.(3) for the parameter Φ:

$$\gamma_{SL}(\varphi) = \{[\gamma_L^d(\varphi)]^{1/2} - (\gamma_S^d)^{1/2}\}^2 + \{[\gamma_L^p(\varphi)]^{1/2} - (\gamma_S^p)^{1/2}\}^2. \quad (4)$$

Here the dependence of γ_L on the angle of alignment of the NLC ϕ is written in the form proposed by Parson:[204]

$$\gamma_L^d(\varphi) = \gamma_L^d(0) + \Delta\gamma_L^d \sin^2\varphi \ ;$$
$$\gamma_L^p(\varphi) = \gamma_L^p(0) + \Delta\gamma_L^p \sin^2(\varphi + \theta_p) \ . \quad (5)$$

The analogous relations for $\gamma_L(\phi)$ and $p_L(\phi)$ are also used.[201] Here $\Delta\gamma_L^{d,p} = \gamma_L^{d,p}(\pi/2) - \gamma_L^{d,p}(0)$ are the anisotropies of the dispersion and polar contributions to the surface energy of the NLC at the interface with a vacuum and the parameter θ_p takes into account the possible discrepancy between the directions of the dipole moment of the NLC molecules and the director.

The polar anchoring energy $W_\phi = \gamma_{SL}(\pi/2) - \gamma_{SL}(0)$, calculated by Eqns.(4) and (5) for MBBA [$\gamma_L^d(0) = 29$ mJ m^{-2}, $\gamma_L^p(0) = 9$ mJ m^{-2},[205] and $\Delta\gamma_L^d = \Delta\gamma_L^p = 4.5 \times 10^{-2}$ mJ m^{-2} [32]] on surfaces treated with organosilicon surfactants, is 20–54 mJ m^{-2},[138] which agrees with the measured values (Table 4). The experimental determination of the azimuthal anchoring energy $W_\alpha = \gamma_{SL}(\pi/2) - \gamma_{SL}(0)$ in terms of Eqn.(4) for heptylcyanobiphenyl on rubbed surfaces leads to values in the range 4×10^{-3}–5×10^{-2} mJ m^{-2}, while on SiO_x films sputtered at an angle $\psi = 30$ °C it leads to 8.8×10^{-2} mJ m^{-2} [206] (see Table 5 above).

The equilibrium angle ϕ can be calculated from the condition for a minimum in the interfacial energy: $\partial\gamma_{SL}/\partial\phi = 0$.

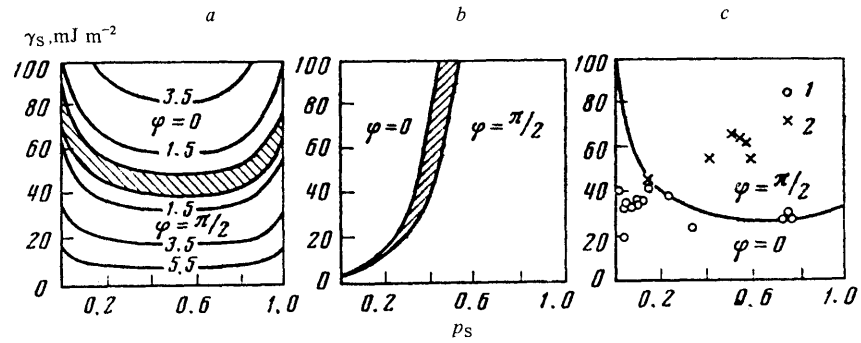


Figure 2. Alignment diagrams for the angle ϕ: *a*) for model NLC with the parameters $\gamma_L(\pi/2) = 40$ mJ m^{-2}, $\gamma_L(0) = 50$ mJ m^{-2}, $p_L(0) = p_L(\pi/2) = 0.5$; *b*) for MBBA according to Köhler's data:[201] $\gamma_L(\pi/2) = 29.1$ mJ m^{-2}, $\gamma_L(0) = 28.1$ mJ m^{-2}, $p_L(\pi/2) = 0.29$, $p_L(0) = 0.34$; c) for MBBA according to Naemura's data:[138] $\gamma_L^d(0) =$ 29 mJ m^{-2}, $\gamma_L^p(0) = 9$ mJ m^{-2}, $\Delta\gamma_L^d = \Delta\gamma_L^p = 0.045$ mJ m^{-2} [$\gamma_L(0) = \gamma_L(\pi/2) = 38$ mJ m^{-2}, $p_L(\pi/2) = p_L(0) = 0.24$]. The numerals opposite the curves indicate the values of W_ϕ (mJ m^{-2}); the transition region with $0 < \phi < \pi/2$ is shaded. Experimental points according to Naemura's data:[138] 1) for $\phi = 0$; 2) for $\phi = \pi/2$.

It has been suggested that the results of the calculation be represented in terms of the so-called alignment diagrams. where each point corresponds to a support with specific values of γ_S and p_S.[201] The alignment of the NLC molecules on such a surface is characterised by the position of this point relative to the boundary lines calculated by Eqns.(4) and (5) for $\phi = 0$ and $\phi = \pi/2$ (Fig.2*a*).

Table 5. Azimuthal energies of anchoring of NLC to various anisotropic surfaces.

Material of surface of support	Method of generation of surface anisotropy	Characteristics of surface relief		W_α, mJ m^{-2}		NLC	Refs.
		A, Å	λ, Å	calc.	expt.		
Glass	Rubbing	—	—	—	$7\cdot10^{-2}$	MBBA	[215]
ditto	ditto	—	—	—	$4\cdot10^{-2}$	CBP	[206]
SiO_2	»	—	—	—	$1\cdot10^{-2}$	CBP	[206]
PVA	»	—	—	—	$5\cdot10^{-2}$	CBP	[206]
Glass	Lapping with diamond paste	10	200	$8\cdot10^{-2}$*	—	—	[214]
ditto	Oblique sputtering of SiO_x	100	200	1.0*	$6\cdot10^{-1}$	MBBA	[140]
»	Ditto	—	—	—	$8.8\cdot10^{-2}$	MBBA	[206]
»	Diffraction gratings	250	3200	$1.2\cdot10^{-4}$*	—	—	[180]
»	Ditto	1700—2500	3300—8300	10^{-4}—10^{-5}*	—	—	[11]
»	Withdrawal from solution of $C_7H_{15}NH_2$	—	—	—	$5\cdot10^{-2}$	MBBA	[33]
»	Treatment with $(CH_3)_3SiCl$	—	—	—	$5\cdot10^{-3}$	MBBA	[216]
»	Without special treatment	—	—	—	$5\cdot10^{-3}$	MBBA	[217]
Quartz	Ditto	—	—	10^{-2}	—	CBP	[218]
ditto	»	—	—	$3\cdot10^{-2}$	—	PAA	[218]

*Calculation by Eqn.6.

The form of the alignment diagram depends on the parameters of the NLC: $\gamma_L^p(0)$, $\gamma_L^d(0)$, $\Delta\gamma_L^p$, and $\Delta\gamma_L^d$. Thus Figs.2*b* and 2*c* present the alignment diagrams for MBBA calculated from Köhler's results[201] and Naemura's results.[137] The significant difference between the accuracies of the predictions of the type of alignment can be accounted for by the difference between the accuracies of the estimates of the molecular parameters of MBBA and primarily the sign of $\Delta\gamma_L^p$. The experimental observations of the alignment of MBBA on various supports carried out by Naemura[137,138] agree best with the alignment diagram shown in Fig.2*c*.

The example described clearly demonstrates the difficulty of using alignment diagrams associated with the lack of reliable methods for the measurement of the components of the surface energies for both the NLC and the solid surface. Even the measurement of the surface energy of the NLC by familiar procedures, such as the Wilhemy plate, sessile drop, and capillary rise methods, leads to a scatter of the values of γ_L for the same material up to 30%. This can be caused both by the non-equilibrium conditions in the measurements and by the presence of impurities in the NLC. The values of γ_L for different NLC range from 25 to 40 mJ m^{-2}.[7,207–211]

The experimental determinations of the anisotropy of the surface tension $\Delta\gamma_L$ are available in the literature for only two NLC: 4.5×10^{-2} mJ m^{-2} for MBBA [32] and 5×10^{-3} mJ m^{-2} for cyanopentylbiphenyl.[134] It is noteworthy that such a low value of $\Delta\gamma_L$ corresponds to the virtual absence of a transitional region with $0 < \phi < \pi/2$ from the alignment diagram.

The determination of the surface energy of the solid surface presents even greater difficulties, since it cannot be measured directly. Furthermore, the structure of the surface of the support is as a rule undetermined and depends on the conditions of preparation, heat treatment, and purification of the supports. For example, the undetermined adsorption of the vapour of the liquid diminishes the interfacial free energy at the solid surface–vacuum interface by an amount $\gamma_{SG} = \gamma_S - \pi_0$. Owing to the lack of experimental data, the value of π_0 is usually neglected, by assuming it to be small compared with γ_S and γ_L. At the same time according to Adamson's data,[8] the ratio $\pi_0/\gamma_L = 0.1$–0.3 for polar liquids, so that the above assumption is not always correct.

Thus for a correct representation of the physicochemical interaction of NLC with solid surfaces, further experimental studies in this field are essential, because only they can demonstrate the practical value of the models described above.

5. The Alignment of NLC on Cleavage Surfaces of Single Crystals

This aspect of the interaction of NLC with a solid surface has so far been little investigated, although the first experiments on the alignment of *p*-azoxyanisole on fresh cleavage surfaces of NaCl crystals were carried out as early as the beginning of this century. It has been shown that the layer of NLC on the cleavage surface of a single crystal can be divided into separate regions, within which the director is aligned in certain cases along simple crystallographic directions: for example, this is the [110] or [1$\bar{1}$0] direction for the (001) face of the NaCl crystal.[9] In the general case the alignment of the director in the cleavage plane depends on the symmetry of the single crystal[212] and for ferroelectric materials it also depends on the direction of the spontaneous polarisation vector and on the dielectric anisotropy of the NLC.[213]

The study of the characteristics of the alignment of liquid crystals on the cleavage surfaces of single crystals of different structure should make an additional contribution to the understanding of the mechanism of the physicochemical interaction of NLC with a solid surface.

6. The Elastic Interaction of NLC with a Textured Surface

In order to account more fully for the orienting effect of the support, it is necessary to consider, apart from physicochemical forces, also anisotropic-elastic forces in the NLC layer. A simple explanation of the homogeneous alignment of NLC on surfaces having a relief in the form of parallel grooves has been proposed.[178,214] It is based on the calculation of the additional elastic energy ΔW which the NLC molecules would have had as a consequence of deformation near the textured surface if they had been oriented at right angles and not parallel to the grooves. In the absence of other orienting factors, ΔW is the azimuthal anchoring energy W_α. If the surface relief is described by a sinusoidal function with an amplitude A and a wavelength λ, then the above energy is defined by the following expression on the assumption of strong anchoring of the NLC to the support:

$$\Delta W = 2\pi^2 k A^2/\lambda^3 \qquad (6)$$

where k is the elastic constant of the NLC.

The anchoring energies W_α, calculated by Eqn.(6) for different anisotropic surfaces, are listed in Table 5. Evidently there is a satisfactory agreement between the calculated and experimental W_α and, owing to their finer texture, the films sputtered at an angle make it possible to obtain an anchoring energy higher by an order of magnitude than for rubbed surfaces.

The low tilt angle of NLC molecules on rubbed supports can apparently be accounted for by the asymmetric form of the grooves arising under the conditions of a non-uniform mechanical action.[151] The minimisation of the energy of elastic deformation on sputtered films leads to different tilt angles of the director as a function of the parameters of the surface relief of the films.[139,188]

According to the elastic mechanism of orientation, the azimuthal energy of the anchoring of the NLC to the support can be regulated by altering the amplitude and wavelength of the surface relief. However, competition between the anisotropic physicochemical forces and the anisotropic-elastic forces can prevent the alignment of the NLC molecules along the grooves. Thus when during the coating of the working cell the stream of the liquid crystal material is directed at right angles to the grooves, the direction of the director deviates from that of the grooves by an angle which increases with the width of the grooves and gives a smaller value of ΔW. The energy W_α of the anchoring of NLC to the surfaces of surfactant films having an ordered molecular structure is of the same order of magnitude as ΔW for rubbed surfaces (Table 5). In particular, as a result of this agreement, the rubbing of extended polymer films in a direction which does not coincide with that of the long molecular axis of the polymer leads to the breakdown of the orientation of the NLC.[93] The anisotropy of the surface energy of sputtered films[206,219] and films which have been rubbed on[206] also indicates the need to allow for the physicochemical properties of the support together with the geometry of its surface.

Thus the interfacial interaction of NLC with a solid surface determines characteristics such as the polar angle ϕ and the polar anchoring energy W_ϕ, while the direction of the director α and the azimuthal anchoring energy W_α are specified both by anisotropic-elastic forces, related to the geometry of the surface of the support, and by anisotropic physicochemical forces.

VI. EXAMPLES OF THE PREPARATION AND APPLICATIONS OF ALIGNED NEMATIC LIQUID CRYSTALS

In the technology of the preparation of liquid crystal displays, the selection of the method for orienting the NLC whereby the required tilt angle of the director can be achieved necessitates the allowance for factors such as the chemical structure of the NLC, the composition of the glass employed for the support, the technological intermediate layers, the dimensions of the support, and the temperature regime of the subsequent operations. The correct choice of the method of cleaning the surface plays a very important role. In order to eliminate the influence of alkali metal ions diffusing from the glass, it is desirable to employ a sublayer of an oxide or polymeric material. Certain examples of technological processes for the creation of various types of orientation are given below.

1. Homogeneous Alignment of NLC

Deposition of PVA Films with an Ordered Molecular Structure (by the Langmuir–Blodgett Method)

Glass plates with an electrode pattern are coated with silicon oxide, washed in an ultrasonic bath with a peroxide–ammonia mixture, washed with deionised water, and dried by centrifugation. A bath with a mobile barrier is filled with an aqueous PVA solution (0.03 wt.%) and cassettes with the plates are immersed in it. With the aid of the mobile barrier, an oriented monolayer of PVA molecules is established on the surface of water and the cassette is withdrawn from the solution, after which the plates are heat-treated at 150 °C for 20 min. The angle of tilt achieved is $\beta = 0° \pm 0.5°$ and the director is aligned at right angles to the direction of withdrawal. The orienting capacity of the films persists up to 160 °C.[191]

The Rubbing on of Polyimide Films

Glass plates with an electrode pattern are washed in hot chromic acid mixture and water and then treated with an aqueous solution of γ-aminopropyltriethoxysilane (0.1 wt.%) and dried by centrifugation. A solution of polypyromellitamidoacid in dimethyl formamide (5 wt.%) is deposited on the

plates by immersion with subsequent centrifugation at 3000 rev min^{-1}. The plates are maintained successively at 80°, 130°, and 300 °C, 30 min at each temperature. The polyimide film formed is rubbed with Kapron brushes; the tilt angle of the director achieved is $\beta \cong 1-3°$ and the director is aligned along the direction of rubbing. The orienting capacity of the film persists up to 450 °C.[95,103]

The Oblique Sputtering of Germanium Monoxide

A film of germanium monoxide 200–250 Å thick is sputtered onto glass plates by one of the technological procedures described with a temperature of the source of 800–850 °C, at a pressure of 5×10^{-3} Pa and at an angle $\psi = 30-50°$ relative to the surface of the support. The angle of tilt of the director achieved is $\beta = 0°$ and the director is perpendicular to the direction of the beam of the sputtered substance. The film retains its orienting capacity up to 450 °C.[145]

2. The Tilted Alignment

The Sputtering of Germa ium Mo oxide

The sputtering of GeO under the conditions described in the previous example at an angle of 5–8° relative to the surface of the support makes it possible to achieve a tilt angle of the director $\beta = 25-35°$.[145]

Double Oblique Sputtering of Silico Oxide

A second film ~10 Å thick is sputtered at an angle $\psi = 30°$, after rotating the support by 90° relative to the normal to the surface, on top of a film of silicon oxide 200–300 Å thick which had been sputtered at an angle of 5° relative to the surface of the support; the temperature of the source is 1300–1400 °C and the pressure is 10^{-2} Pa. The angle of tilt of the director achieved is $\beta = 0-30°$ and the orienting film withstands heating to 500 °C.[159]

Treatment of Sputtered Geo or Sio Films with a Solution of Lecithin

Plates treated by one of the methods described in previous examples are immersed in an alcoholic solution of lecithin (1 wt.%) and are then dried at 80 °C for 30 min. The angle of tilt β achieved increases to 60–90° and the azimuthal alignment is retained; the alignment does not change on heating to 200 °C.[7]

3. The Homeotropic Alignment of NLC

Deposition of Multilayers of α Cetylacrylic Acid by the Langmuir–Blodgett Method

Glass plates with an electrode pattern are washed in hot chromic acid mixture in water and are dried in a centrifuge. They are then immersed in a 60 × 15 × 8 cm^3 bath filled with deionised water on the surface of which 0.1 cm^3 of a 0.1% solution of α-cetylacrylic acid in heptane has been deposited. With the aid of a mobile barrier, an aligned monolayer of α-cetylacrylic acid is formed on the surface of water, whose surface tension then diminishes from 71 to 40 mJ m^{-2}. The plates are withdrawn from the bath, displacing the barrier so that the surface tension of water remains constant. They are then kept at 110 °C for 10 min. The orienting properties of the layer are retained up to 200 °C.[191]

Treatment of the Supports by Carboxylatochromium Complexes

Glass plates with an electrode pattern are washed as in the previous experiment and are then immersed in a solution of stearatochromium chloride [chromolin {Edoran in original—(Ed.of Translation)}] (0.1 wt.%) for 30–40 s, after which they are kept at 120 °C for 20 min. The orienting capacity of the layer is retained up to 400 °C.[50]

4. The Relation Between the Alignment Parameters and the Electro-optical Characteristics of the NLC

The choice of a particular type of alignment of NLC in liquid crystal displays is achieved depending on the electro-optical effect employed, the properties of the NLC, and the required parameters and design of the apparatus. Thus, in order to attain the *B*-effect, the "guest–host" effect (using dyes), and the cholesteric–nematic transition in thin layers, an initial homeotropic orientation is required. However, electro-optical effects involving the creation of an initial homogeneous alignment with $\beta = 0$, particularly with a twist structure for which the azimuthal directions of the director at the upper and lower supports form an angle which is usually close to $\pi/2$, are employed much more frequently.

The alignment parameters, especially the initial tilt angle of the director, exert a significant influence on the electro-optical characteristics of the NLC. Thus, with increase of the deviation from $\phi = 0$ or $\phi = \pi/2$, the threshold and controlling potentials diminish and the rapidity of the response improves; however, the contrast of the image and the steepness of the voltage–contrast characteristic are then somewhat impaired[142,220–221] and the range of angles of observation also diminishes considerably for displays based on the twist effect.[143] At the same time the use of a rigorously homogeneous or homeotropic alignment can lead to the appearance of various defects in the image caused by the equal probabilities of the rotation of the director in opposite directions under the influence of the electric field[148,149,222] and also by the curving of the potential field lines at the edges of the electrodes.[149,152] In preparing the displays, one therefore endeavours to achieve a small (by 1–5°) deviation of the director from $\phi = 0$ or $\phi = \pi/2$.

An interesting possibility for the attainment of optimum electro-optical characteristics has been demonstrated by the alignment effects under the conditions of a weak anchoring of the NLC to a solid surface.[133,223–225] A decrease of the anchoring energy W_ϕ promotes not only a decrease of the threshold potential and of the response time but also an increase of the steepness of the voltage–contrast characteristic, the overall effect of which makes it possible to increase the information capacity of the displays. For the twist effect, the realisation of this version is complicated by the additional requirement of a high anchoring energy W_α compared with the volume energy of twisting in order that the supports can maintain the twist deformation of the NLC.

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Thus intensive investigation of the orientation of NLC led to a diminution of the gap between theoretical studies in the physical chemistry of surfaces and the applied developments in the field of liquid crystal devices. The methods available at present make it possible to achieve a reliable specific alignment of NLC of various types. At the same time, a complete understanding of the mechanisms of the alignment process has not so far been achieved. In the immediate future questions concerning the interaction of NLC with a solid surface should apparently remain in the centre of attention of investigators. In particular, the study of electro-optical effects in NLC, under the conditions of their weak anchoring to the surface, in order to develop procedures for the attainment of the optimum characteristics of the indicator devices is of special interest.

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