

Lyotropic nematics

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The current status and prospects are examined of the rapidly developing field that studies the structure and properties of lyotropic nematic liquid crystals. Typical amphiphiles are presented, and systems based on them. Typical textures and their optical properties are examined. The physical properties of nematics are described in detail: diamagnetic, dielectric, and viscoelastic. A special section is devoted to biaxial nematics, which have no analogs among the thermotropic nematic liquid crystals. The features of their order parameter and elastic properties are examined. Textures and optical properties are described. Further, molecular ordering (from NMR data) and features of phase transitions are discussed. In closing, lyotropic cholesterics are discussed, both those based on individual chemical compounds and those induced by chiral additives.

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INTRODUCTION

A year after the discovery of thermotropic liquid crystals that form ordered phases upon melting, in 1889, Leman found that these same phases also arise upon dissolving certain organic materials. Thus, ordered solutions were formed in a mixture of ammonium oleate, water, and alcohol. These liquid crystals became called lyotropic ($\lambda\nu\omega$ — I dissolve).

The study of lyotropic liquid crystals proceeded practically independently of the thermotropic type. The latter were immediately drawn into the sphere of interest of physicists, whereas lyotropic liquid crystals for a long time were an object for colloid chemistry.

It was established at the end of the 50s that only amphiphilic molecules (literally—loving both sides) form lyotropic mesophases. They contain two fragments: a hydrocarbon chain soluble in fat (lipophilic part) and a polar head soluble in water (hydrophilic part). Upon dissolving such amphiphilic molecules in water, they are concentrated about the polar heads, thus orienting the hydrocarbon tails in a certain direction. Analogous processes occur also in a nonpolar solvent—a hydrocarbon or fat. In this case the molecules of the solvent are concentrated about the lipophilic part of the amphiphilic molecule. Ordered structures or micelles (micrain) are formed in both cases,—groups of molecules of the amphiphile that in turn are packed to form a superstructure.

Toward the end of the 60s two principal superstructural lyomesophases were known^{1,2}: the so-called “pure” phase

having a layered (lamellar) structure, and the “intermediate” phase—a hexagonal packing of cylindrical micelles. At low concentrations of the amphiphile these phases are preceded by an isotropic micellar solution containing spherical micelles. A solid phase is formed at high concentrations of the amphiphile.

All these facts, together with the analogy with thermotropic liquid crystals, ought to lead to the thought that phases must exist between isotropic micellar solutions and superstructural mesophases having an ordered arrangement of individual structural units. In line with the accepted terminology, these phases must be called nematic. In general the structural unit can be an individual molecule, as in the cases of the systems poly- γ -benzylglutamate-chloroform or DNA-polyethylene glycol. However, since in this case the original phase is a micellar solution, we should have expected that the role of the structural elements would be played by anisometric (cylindrical or discotic) micelles. These systems are also generally regarded as being nematic.

The assumption of their existence rested on a number of facts. First of all, the theory of micelle formation had predicted^{3,4} that the shape of the micelles can change from spherical to ellipsoidal at a certain concentration of the amphiphile. Further, direct experimental proofs existed by the methods of light scattering,^{5–8} small-angle x-ray scattering,⁹ and diffusion¹⁰ of the existence of asymmetric micelles in a large number of aqueous solutions of various amphiphiles.

However, as often happens, lyotropic nematics were

discovered as the result of experiments formulated to elucidate completely different problems.

It was known¹¹ that thermotropic nematics are a good medium for studying various substances by the NMR method. They are rather rapidly and completely oriented by a magnetic field. However, these phases suffer from one essential defect—only quite definite, most often lipophilic, substances are well soluble in thermotropic nematics. This restricted the use of thermotropic nematics in the NMR method. It was necessary to seek other media that are well oriented in a magnetic field and that dissolve as broad a class of substances as possible.

In 1967 Lawson and Flautt¹² reported such a medium. They found that a mixture of octyl- or decylsulfates (40 mass percent),¹¹ the corresponding alcohols (5%), sodium sulfate (5%), and water (50%) in the temperature range 10–75 °C dissolves well both hydrophilic and lipophilic compounds and is oriented by a magnetic field.

Studies of the preparations that were obtained using a polarizing microscope showed that they form filamentous and “schlieren” textures typical of thermotropic nematics. The conclusion was drawn from these two facts—orientation in a magnetic field and a typical texture—that lyotropic nematics had been obtained.

In subsequent years these lyotropic nematics have been widely used in studying the NMR spectra of various compounds (see, e.g., Refs. 13–26).

Soon other lyotropic nematics were found. Thus, as early as 1973, Long²⁷ proposed the system of 30% potassium laurate (KL), 4% potassium chloride, 6% decanol, and 60% D₂O, which orients well in a magnetic field, is stable in the temperature range 10–70 °C, and is more stable to hydrolysis than the system with sodium decylsulfate (NaDS). In this same year Reeves and his associates²⁸ found a nematic lyomesophase in the system decylammonium chloride, ammonium chloride, decanol, and water. In subsequent years many more new lyotropic nematics have been found, and their number now amounts to more than twenty. Lyotropic cholesterics having a helical superstructure have also been obtained.

The interest in the physical properties of nematic lyomesophases has become especially notable in recent years.²⁹ However, for the present it is mainly centered on the optical study of textures and magnetic properties. Single studies have been devoted to such fundamental properties as elasticity, viscosity, and Fredericks transitions.

However, on the whole a rather interesting picture is being drawn of a new class of liquid crystals having their specific properties and their fields of application.

The onset of study of lyotropic nematics opens a new chapter in the study of liquid crystals. The point is that the types of lyotropic liquid crystals existing up to now have been highly conservative. Electric and magnetic fields and mechanical deformations have practically no effect on them. Therefore one can alter the degree of order in these phases only by changing the temperature and concentration. This restricts the possibility of obtaining information on the different properties of the lyomesophases. It suffices to say that the elastic, magnetic, and electrooptical properties of lamellar and hexagonal phases have been unknown up to now.

Lyotropic nematics are oriented by a magnetic field and by flow. Mechanical deformations also affect their order.

There are no grounds for stating that an electric field will act on them differently from what it does on thermotropic nematics. These properties offer completely new potentialities in the study of lyomesophases. Here we should expect very interesting results comparable in significance with those obtained in studying thermotropic nematics. The physical parameters of systems of anisometric micelles will prove accessible—viscoelastic, dielectric, magnetic, optical, and electrooptical, and their dependence on the order parameter. Yet this is not all. In contrast to thermotropic nematics, in lyonematics all the properties arise not only from the state of the structural elements (micelles) as such, but also from their structure. This implies that physics acquires the possibility of studying delicate processes of self-assembly of molecular aggregates and their rearrangement under the influence of physical and chemical factors, and creation and breakdown of superstructures. This is all very significant for the physics and chemistry of dispersed systems and phase boundaries.

Yet the study of lyotropic nematics is especially important for biophysics. As is known, a large number of materials in living organisms exist in the liquid-crystalline state. This includes a large number of organelles of cells, such as membranes, myelin, and mitochondria. They include such non-cellular forms as protein filaments of muscles, the lens of the eye, and the head of the spermatozoon. The products of life activity—bile, urine, and blood—also contain substances in mesomorphic states. At present liquid crystals in living organisms are being intensively studied, and it has become evident that mesophases are remarkably adapted to the occurrence of life processes. Moreover, one can say that, if liquid crystals were not formed in nature for any reason, life would be impossible.

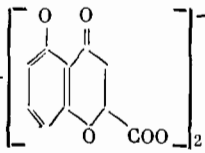
At present the existence in living organisms of lyotropic lamellar and hexagonal mesophases is firmly known. However, their presence is not correlated with high lability of the living medium, in particular, with reactions to external electric and magnetic fields that can be distinctly fixed. This problem can be clarified by a search among materials of organic origin for lyotropic nematics, especially near temperature and concentration phase transitions from highly ordered to disordered states. If the search proves successful, then quite possibly it will be found that the anisometric micelles participate in transport of materials in living organisms. Here it is essential that the shape of these micelles can be easily altered, depending on the concentration, pH, and composition of additives. But, apart from further studies, already at present lyotropic nematics are a good model for various biophysical processes. In particular, one can use them to model many processes of self-assembly of organelles of cells and viruses, and as is most important, the influence of electric and magnetic fields on the form and properties of various biological objects such as erythrocytes.

1. COMPOSITION AND STRUCTURE

1.1. Chemical composition

Nematic lyomesophases have been obtained with a few types of amphiphilic molecules (Table I). They include negative amphiphilic ions such as decylsulfate (DS), laurate (L), and positive ions such as decylammonium (DA). A special place is occupied by the alcohols—decanol and oc-

TABLE I. Chemical formulas of typical amphiphiles of nematic lyomesophases.

Name	Chemical formula
Decyl sulfate (DS)	$\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{SO}_4^-$
Octyl sulfate (OS)	$\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{SO}_4^-$
Decanoate (DeO)	$\text{CH}_3(\text{CH}_2)_8\text{COO}^-$
Laurate (L)	$\text{CH}_3(\text{CH}_2)_{10}\text{COO}^-$
Laurylsarcosinate (LS)	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{NCOCH}_2\text{COO}^-$
Hexadecyltrimethylammonium (HDTMA)	$\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)^+$
Hexadecylpyridinium (HDPyr)	$\text{CH}_3(\text{CH}_2)_{15}\text{N}_5\text{H}_4^+$
Decylammonium (DA)	$\text{CH}_3(\text{CH}_2)_{10}\text{N}(\text{CH}_3)^+$
Myristyltrimethylammonium (MTA)	$\text{CH}_3(\text{CH}_2)_{13}\text{N}(\text{CH}_3)^+$
Decanol (DeOH)	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OH}$
Octanol (OeOH)	$\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{OH}$
Perfluorooctanoate (PFO)	$\text{C}_7\text{F}_{17}\text{CO}_2^-$
Hexyloxybenzoate (HxB)	$\text{C}_6\text{H}_{13}\text{O}(\text{C}_6\text{H}_5)\text{CO}_2^-$
Chromoglycate (CG)	$\text{CH}_2-\text{CHOH}-\text{CH}_2-$ 

tanol. They take part in practically all the nematic lyomesophases. However, they themselves do not form mesophases in solvents, in particular, in water.

All these ionophiles are ionogenic. Quite recently³⁰ nonionogenic lyonematics have been obtained—hexapolyethyleneoxy-derivatives of triphenylene.

We see from Table I that the lipophilic part of most of the amphiphilic molecules amounts to simple, unbranched hydrocarbon chains with a number of carbon atoms greater than eight. The polar heads are also not highly varied: SO_4^- , CO_2^- , $\text{N}(\text{CH}_3)^+$, and $\text{N}(\text{C}_5\text{H}_{10})^+$.

The classification of nematic lyomesophases can be patterned according to structural characteristics.³¹ It has now been reliably established³¹⁻³³ that two fundamental types of nematics exist. Nematics of the first type are constructed of cylindrical micelles (Fig. 1). They are often called calamitics (calamus—reed) and are denoted as N_C or CM (cylindrical micelle). The micelles of nematics of the second type have the form of disks (see Fig. 1). Hence they are called discotics. They are denoted in various ways: N_D , N_L (lamellar micelle) or DM (discotic micelle). Below we shall use the first of the cited designations.

Table II gives the composition of the systems in which nematic lyomesophases have been found. Water and heavy water have been used everywhere as the solvent.

One compound is known³⁴—the surface-active dye, *n*-

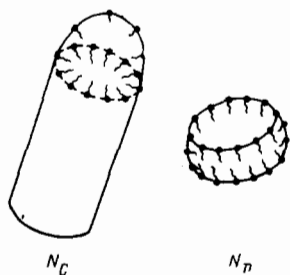


FIG. 1. Schematic drawing of the structure of the micelles of lyotropic nematics.

octylphenolaminopoly (ethylene oxide)—which forms an N_C phase in diluted methyl alcohol. The only nonaqueous nematic is the 2-octyldodecyl ester of 4-[1-naphthalenylamino]carbonyl]-aminobenzoic acid in decane.³⁵ There is an indication³⁶ of the existence of nonaqueous nematics in the system tetraoxyethyleneglycol-hexadecane-pentane.

The nematic lyomesophases presented in Table II are formed only in a narrow interval of concentrations, which will be discussed below in describing the concrete mixtures.

The best studied is the NaDS-DeOH- H_2O system.^{31,32,36} In general this system, just like the NaOS-OeOH- H_2O system, had repeatedly previously been studied carefully,² but no nematic mesophase was found. The corrected phase diagram in the region containing the nematic mesophase is shown in Fig. 2.³⁷ It has been constructed from a study of the textures and small-angle x-ray scattering data at a temperature of 22 °C.

The small nematic region is surrounded by three extensive regions. In the micellar-solution region (M) two phases were found at different weight concentrations of NaDS. If c is the concentration in grams per gram of solution, then at $c < 0.191$ an isotropic solution (M_1) of spherical micelles exists (mean radius 35 Å, mean distance between micelles 50 Å). A micelle contains 26 molecules on the average. At $c > 0.191$ the solution remains isotropic (M_2), but the micelles are no longer spherical. Owing to the closeness of this phase to the region of existence of the nematic phase N_D , one can assume that the micelles are disk-shaped.

This phase is very interesting. It is dark between crossed polarizers, but upon shear deformation transmitting regions appear. That is, anisotropic regions arise. The same sort of anisotropic regions arise when the isotropic specimens are placed in a magnetic field. In this regard, one can classify the M_2 phase as a disordered micellar phase.

The other phases can be conveniently examined along the line shown as a dotted line in Fig. 2. This line corresponds to a constant water content (~48%) and to an increase in the ratio DeOH/NaDS from 0 to 10.8%. At DeOH/NaDS ratios from 0 to 5.0% the hexagonal phase G exists and amounts to a dense packing of infinite cylindrical micelles 26 Å in diameter. A hexagonal lattice with a period

TABLE II. Composition of systems forming nematic lyomesophases with water.

Amphiphiles	Counterions	Electrolytes
a) N_C : DS, DeOH	Na^+ , Cs^+ , Rb^+ , Li^+ NH_4^+ , $C_2H_5NH_3^+$ Cs^+ , Na^+	Na_2SO_4
DS	Na^+	KCl
CG	K^+	
L	Br^-	
MTA	$CH_3C_6H_4SO_3$	
MTA	Cs^+	
HxB		
b) N_D : DS, DeOH	Na^+	Na_2SO_4 $(NH_4)_2SO_4$ CH_3NH_2Cl $(CH_3)_3NHCl$ $(CH_3)_4NCl$ $[(CH_3)_4N]_2SO_4$ Na_2SO_4
DS, DeOH	$CH_3NH_3^+$, $(CH_3)_2Sn^+$, ND_4^+ , ND_3H^+ , NH_4^+ $(CH_3)_2NH^+$, $(CH_3)_3N^+$	
DS, DeOH	Na^+ Na^+ , CH_3Pb^+	CH_3HgNO_3 $(CH_3)_3SnNO_3$, $NaNO_3$ $(CH_3)_3PbNO_3$ Na_2SO_4
OS, OeOH	Na^+	KCl
DeO	Na^+ , K^+	KCl
DeOH, DeO	Na^+ , K^+	KCl
HDTMA	Br^- , Cl^- , NO_3^-	$NaBr$, $NaCl$, $NaNO_3$
HDPyr, DeOH, HDTMA	Cl^- , Br^-	$NaCl$
L, DeOH	Rb^+ , Cs^+ , K^+ , Na^+	$NaBr$, KCl , $RbCl$, $CsCl$
L, HDTMA	K^+ , Br^-	$NaBr$
DA	Cl^- , BF_4^-	$NaCl$, NH_4Cl , NH_4Br
DA, DeOH	Cl^- , CH_3COO^- $[(CH_3)_2AsO_2]^-$ BF_4^- , F^-	NH_4Cl , NH_4BF_4 , CH_3COONa
DA, HDTMA, DeOH	Br^- , Cl^-	$NaCl$
LS, DeOH	Na^+	Na_2SO_4
MTA, DeOH	Br^-	NH_4Br
MTA, DeOH	Br^- , $CH_3C_6H_4SO_3$	NH_4Br
PFO	Cs^+	
NxB	Na^+	Na_2SO_4

of 36.5 Å is formed. Upon increasing the DeOH/NaDS ratio up to 8.5%, an orthorhombic phase *R* arises. It consists of infinite micelles having a rectangular cross-section (dimensions 19 × 49 Å). The micelles are packed in a centered rectangular lattice. At high decanol concentrations a transition occurs to a lamellar phase *L* having a layer thickness 19 Å and distance between layers 18.3 Å.

The nematic lyomesophases is found in the narrow concentration range: NaDS (37–41%), H₂O (50–56%), and DeOH (5–9%). This is shown in Fig. 2.

In this nematic region three phases are distinguished. The region of existence of discotics N_D and calamitics N_C are shown in Fig. 2. Between them another, biaxial nematic mesophase has been found,³⁸ shown in Fig. 2 by dotted lines.

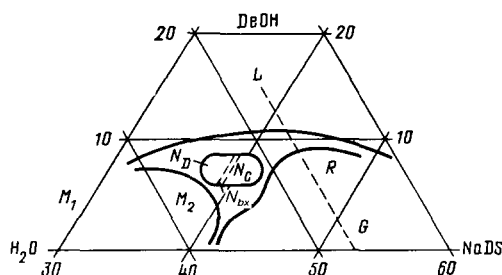


FIG. 2. Phase diagram of the NaDS-DeOH-H₂O system at room temperature.⁸⁷

We shall discuss it separately below, along with other biaxial phases.

One can use the phase diagram to estimate the concentration regions where calamitics and discotics exist: N_D -NaDS (37–39%), H₂O (51–56%), DeOH (5–9%); N_C -NaDS (39–41%), H₂O (52–55%), DeOH (5–9%). We see from the diagram that the concentration of decanol remains constant throughout the region of the nematic phase. However, one must treat all these numbers with great caution. They are only estimates, since the exact phase diagram in this region are only estimates, since the exact phase diagram in this region is unknown. It has been constructed from a few points only.³⁷ Other studies have cited other concentration ranges of existence of the nematic phase. Thus, in the already cited paper³⁸ on biaxial nematics, it is stated with a citation to Ref. 37 that a nematic mesophase at a constant water concentration equal to 57% exists at the concentrations NaDS (35.50–38%) and DeOH (5–7%). In Ref. 39 a region of the phase diagram was studied with a constant 7% concentration of decanol over a broad temperature range. One can estimate from this diagram that at 22 °C the N_C phase exists at the concentrations NaDS (35–38%), H₂O (55–58%), and the N_D phase at NaDS (34.4–35%) and H₂O (58–58.6%).

Apparently such a scatter in the concentration values arises from the fact that the region of existence of the nematic phase and the types of it depend substantially on the purity of the starting materials. Without at present discussing

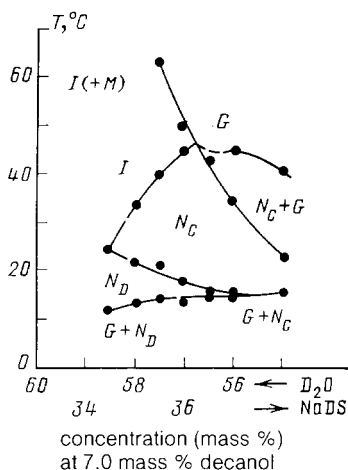


FIG. 3. Phase diagram of the NaDS-DeOH (7%)-H₂O system at different temperatures.³⁹

this problem in essence, we shall state that, when one adds only 0.3% Na₂SO₄ to the NaDS-DeOH-H₂O mixture, the calamitic transforms to a discotic.⁴⁰ Figure 3 shows the phase diagram of the NaDS-DeOH-H₂O mixture at a constant decanol concentration of 7% and at different temperatures. The narrow region of the discotic mesophase is well marked. It narrows with decreasing water concentration and disappears completely at 54% H₂O. Upon cooling, the N_D and N_C phases transform to the G phase. A calamitic having a water concentration above 57% transforms on heating to an isotropic phase with a small region of the L phase. At higher temperatures these phases disappear and the typical texture of the G phase appears. Upon further heating the G phase transforms to an isotropic liquid. At water concentrations below 57% the N_C phase transforms to the G phase, while in most cases one observes coexistence of the N_C and G phases. If the decanol concentration becomes greater than 7.5%, a layered solution is formed. The upper layer of it is the L phase. The lower layer at constant decanol concentration with decreasing H₂O concentration varies from an isotropic micellar solution to the N_D phase, and then to the N_C phase. At a decanol concentration below 6.5% the phase composition varies with decreasing water concentration from a viscous isotropic solution to the N_C phase, and then to the G phase.

1.2. Structure

The structure of a calamitic has been studied^{37,41} in the NaDS-DeOH-H₂O system. It amounts to a system of long, extended cylinders whose long axes are approximately parallel. The mean diameter of the cylinders is about 38 Å. It was not possible to determine the length of the cylinders. However, if we assume that their length is the same on the average, then it must be no more than 150 Å. Yet if the length of the cylinders varies substantially, then one could draw no conclusions on their dimensions.

The structure of the calamitic phase has also been studied in detail^{42,43} in the KL-KCl-H₂O system. A radius of the micelles of 14.2 Å at 22 °C was found by small-angle x-ray scattering, and the mean distance between the micelles was 47.0 Å. The micelles are extended, of finite length, with their long axes oriented approximately in the same direction.

The lengths of the cylindrical micelles for the NaDS-DeOH-H₂O and KL-DeOH-H₂O systems have been estimated⁴⁴ from x-ray and neutron scattering data. Here it was assumed that the diameters of the micelles are equal to the diameters of the cylindrical aggregates in the hexagonal G phase, being respectively 26 and 36 Å for the former and the latter systems. Then the length of the micelles in the NaDS-DeOH-H₂O system is no greater than 60 Å, while in the KL-DeOH-H₂O system it is 60-66 Å. The number of molecules in these aggregates was determined from the volume of the micelles. It is ~90 for the former and 175-195 for the latter system.

The structure of a discotic has been studied³⁷ in the NaDS-DeOH-H₂O system. Disk-shaped micelles were found with a mean thickness of 20 Å and diameter 60 Å. These micelles lie approximately parallel to one another at a mean distance of 37 Å in the direction parallel to their axes, and at 72 Å in the perpendicular direction.

Similar results (thickness of micelles 20 Å and diameter 65 Å) were found in the same system upon adding 0.3% Na₂SO₄.

In the discotic phases of the NaDS-DeOH-H₂O and KL-DeOH-H₂O systems the diameters of the micelles were estimated^{44,45} under the assumption that their thickness equals the thickness of the double layer of the lamellar N_D phase. They proved to be equal to 57 Å for the former and 64 Å for the latter system. The number of molecules per micelle of the former system was estimated as 145, and 215 for the latter system. It was shown⁴⁴ that, within the limits of the N_D phase, the dimensions of the micelles do not depend on the concentration of the amphiphile and the temperature.

In the discotic phase of the NaDS-DeOH-H₂O-6% Na₂SO₄ system, a superstructural packing of the micelles was found by small-angle x-ray and light scattering, with a characteristic distance of 1000 Å, called the micellar microdomain.⁴⁶ The same sort of superstructural organization has been found^{47,48} in a system containing 5% Na₂SO₄ and several other concentrations of the starting components. In these same studies the distance was found more precisely between the micelles along the direction of the director. It proved to be equal to 114 Å.

It is not clear what the micellar microdomains are. Perhaps they are cybotactic groups that precede the transition to the lamellar mesophase. This is indicated by the direction of the periodicity—along the direction of the director.

In general the distances between the micelles are not constant. They vary with varying temperature within the limits of the nematic phase. This is confirmed by direct x-ray studies on the discotic phase of KL-DeOH-H₂O. It was shown⁴⁹ that the distance between the micelles in the direction of the director is 46 Å and does not depend on the temperature, whereas the distance between the micelles in the perpendicular direction varies symbatically with the order parameter. Quite recently⁵⁰ neutron scattering was studied in partially deuterated KL and DeOH, which form a calamitic. These data showed that KL and DeOH are not homogeneously distributed in the cross-section perpendicular to the long axis of the micelle. Then these cross-sections are ellipses, while the micelle itself is an ellipsoid of general form. The hypothesis was advanced on the basis of these data that all lyomesophases are built of these universal micelles. In the calamitic phase they freely rotate about their long

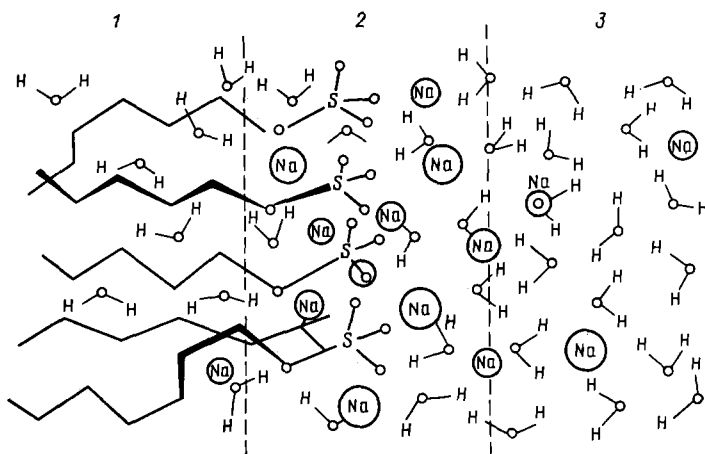


FIG. 4. Structure of the boundary region of a micelle.²⁵

axes, but about their short axes in the discotic phase, while in the biaxial phase all rotation is hindered.

As Holmes and Charvolin⁵¹ showed with the example of the DACl-NH₄Cl-H₂O system, the transition from the lamellar to the nematic phase is complex in character. The infinite layers break up into large regions (cybotactic groups?), separated by water. With increasing temperature these groups diminish and are converted into ribbons, which then transform to discotic micelles.²⁾

The question is of interest of how the transition region from the micelle to the surrounding solution is organized. Studies performed by NMR have shown²⁵ that the structure of the transition regions is practically the same for all types of lyotropic liquid crystals (Fig. 4). The region 1 belongs to the micelle and consists mainly of hydrocarbon tails, shown as bent lines in Fig. 4. A small amount of water molecules diffuses into this region. In region 2, which is the transition region proper, the polar heads are concentrated, such as (-SO₃), and counterions, such as Na⁺. A considerable amount of water molecules is concentrated about these ions. And finally, region 3, which belongs to the intermicellar solution, practically consists of pure water with a small amount of ions, e.g., Na⁺.

Attempts have been undertaken⁵² to study theoretically the problem of interaction between micelles. Within the framework of the Deryagin-Landau-Ferveci-Overbek theory with allowance for Coulomb repulsion and van der Waals attraction, the free energy of interaction between the micelles was calculated while varying the parameters of the structure of the mesophases. It was found that for calamitics the interaction energy $\sim kT$ corresponds to a length of the cylindrical micelles ~ 1000 Å at a diameter of 34 Å and mean distance between the centers of the cylinders of ~ 50 Å. For discotics the interaction energy $\sim kT$ corresponds to a diameter of the micelle of ~ 80 Å at a thickness of 28 Å and distance between micelles ~ 40 Å. All these results do not contradict the structural data.

1.3. Textures and optical properties

One of the fundamental arguments favoring the classification of the lyotropic mesophases with asymmetric micelles as nematics is the fact that they form textures typical of thermotropic nematics.

In the melting of a solid material in a narrow gap (20–100 μm) between two glass plates, a calamitic forms the so-

called planar texture, in which all the long axes of the micelles are oriented parallel to the glass plates. Optically such a texture behaves like a plate cut from an optically uniaxial crystal parallel to the optic axis. Conversely, a discotic often forms the so-called homeotropic texture, where the short axes of all the micelles lie perpendicular to the glass plates. Such a structure is completely analogous to a plate cut from a solid, optically uniaxial crystal perpendicular to the optic axis.⁵³

Often for a more graphic presentation of textures and their changes depending on the amount of solvent, one uses the concentration-gradient method. Figure 5 shows a micrograph obtained⁵⁴ from a specimen having a concentration gradient. One can see well the sequence of phases (with increasing water content): lamellar nematic, isotropic. The nematic mesophase is identified by the schlieren texture.

Observations of textures by the concentration-gradient method have shown^{37,51,54} that, in all mixtures studied thus far, the lamellar phase transforms to the N_D phase with increasing water content, and the hexagonal to the N_C phase.

In the presence of two phases, N_D and N_C, the latter is manifested upon temperature or concentration change in the form of anisotropic regions on a dark background.

Optical studies performed^{32,52,55} on oriented specimens have shown that the N_C phase is uniaxial negative, and the N_D phase uniaxial positive. This arises from the fact that the

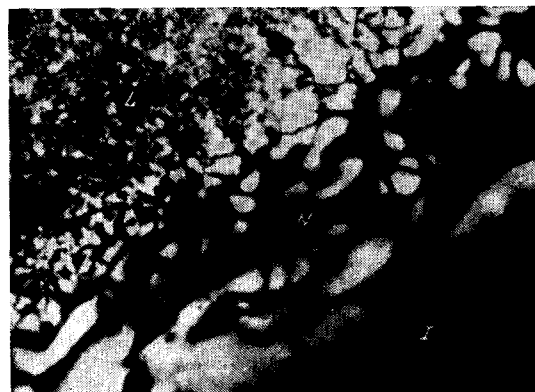


FIG. 5. Sequence of textures in a concentration gradient.⁵⁴ MTABr (14.75%)–MTATS (16.34%)–DeOH (3.28%)–NH₄Br (8.20%)–H₂O (57.38%) system.

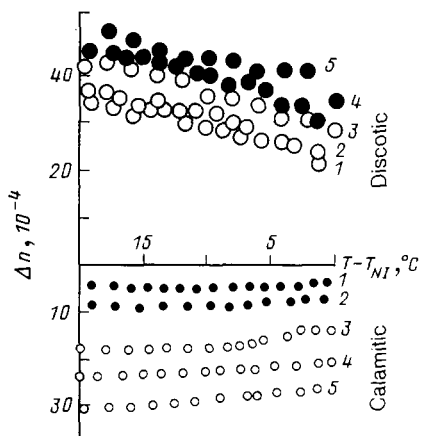


FIG. 6. Temperature dependence of the birefringence for discotics and calamitics in the tetradecyltrimethylammonium bromide-tetradecyltrimethylammonium phenylsulfonate (TDTMAFS)-DeOH-CsCl-D₂O system.⁵⁸ Concentration of TDTMAFS (mole percent): 0.2 (1); 15 (2); 30 (3); 45 (4); and 60 (5).

amphiphile molecules in the former case lie perpendicular to the director, and parallel in the latter case.

The birefringence of lyonematics is an order of magnitude smaller on the average than that of thermotropic nematics.⁵⁶⁻⁵⁸ Typical values are seen well in Fig. 6, which shows the data for the tetradecyltrimethylammonium bromide-DeOH-CsCl-H₂O system in the discotic and calamitic phases.

Vedenov and Levchenko²⁹ derived a simple formula for the birefringence of a lyonematic depending on the order parameter and the fraction of the volume of the solution occupied by micelles. Estimates by this formula yield values of the birefringence coinciding with the experimental values.

2. PHYSICAL PROPERTIES

2.1. Diamagnetic anisotropy

The pioneer study of Lawson and Flautt¹² showed that the nematic lyomesophase of composition NaDS—36%, DeOH—7%, D₂O—50%, Na₂SO₂—7% has a positive diamagnetic anisotropy $\chi_a = (\chi_{\parallel} - \chi_{\perp}) > 0$. Here χ_{\parallel} and χ_{\perp} are the diamagnetic susceptibilities in the direction of the director and perpendicular to it, respectively.

Soon Reeves and his associates^{59,60} established the existence of nematic mesophases having a negative diamagnetic anisotropy ($\chi_a < 0$). They are formed in the same NaDS-DeOH-H₂O system, either upon a small change in the con-

centrations of the starting components, or upon adding the counterions K⁺, Li⁺, or Cs⁺.

Systems having $\chi_a > 0$ were called type I, and systems having $\chi_a < 0$ type II. The hypothesis was advanced⁴¹ that the diamagnetic anisotropy in the NaDS-DeOH-H₂O system arises from the shape of the micelles: calamitics have $\chi_a > 0$, and discotics $\chi_a < 0$. However, the nematic phase in the CsPFO-H₂O system with micelles of discotic form has $\chi_a > 0$.⁶¹ This contradiction stimulated Boden and his coauthors⁵⁴ to study systems having polymethylene and perfluoropolymethylene chains. The former have $\chi_a < 0$, and the latter $\chi_a > 0$. Consequently it proved possible to "construct" nematic discotics and calamitics, both with $\chi_a > 0$ and $\chi_a < 0$. Examples of such systems are presented in Table III. Thus it was shown⁵⁴ that the sign of the diamagnetic susceptibility is not determined by the type of micelles. This viewpoint was confirmed when discotics were found⁶² with $\chi_a > 0$ and calamitics with $\chi_a < 0$ in the NaHxB-Na₂SO₄-DeOH-H₂O system.

The problem of the cause of the diamagnetic anisotropy of micelles has been examined in detail in Refs. 29 and 63. The orientation of diamagnetic micelles by a magnetic field can arise from two factors: first, from the diamagnetic anisotropy of the shape, and second, from the diamagnetic anisotropy of the molecules themselves.

The orientation of a diamagnetic ellipsoid having the mean susceptibility $\bar{\chi}$ placed in a medium having the susceptibility χ_0 does not depend on the sign of $(\bar{\chi} - \chi_0)$, and is determined unambiguously—the principal axis of the ellipsoid is established parallel to the field. Therefore cylindrical micelles will orient with their long axes, and discotic micelles with their short axes along the field.

If the difference in energies corresponding to configurations in which the principal axis of the ellipse is parallel or perpendicular to the magnetic field is ΔW_{shape} , then we have

$$\Delta W_{\text{shape}} \approx -\frac{V}{2} H^2 (\bar{\chi} - \chi_0) (D_c - D_a) \bar{\chi}; \quad (1)$$

Here V is the volume of the ellipsoid, and D_c and D_a are the diamagnetic factors in the directions of the least and greatest axes of the ellipsoid, respectively.

The greatest value of ΔW_{shape} will occur in the case of asymmetric ellipsoids ($a \approx 10c$). In this case we have $D_a = 0$, while $D_c = 4\pi$ for an oblate, and 2π for a prolate spheroid. If we assign typical values of χ and χ_0 (see below), then we find from the condition $\Delta W_{\text{shape}} > kT$ that $H^2 V \sim 1 \text{ G}^2 \text{ cm}^3$. Hence, for the usually employed values of

TABLE III. Lyotropic systems having different diamagnetic anisotropies at a temperature of 20°C.⁵⁴

χ_a	Type of micelles	Symbol	Composition, mass percent				
			MTABr	MTAΦSO ₃	H ₂ O	DeOH	NH ₄ Br
> 0	Cylinder	N _C ⁺	36,0	—	64,0	—	—
< 0	Disk	N _D ⁻	26,6	—	63,3	3,8	6,3
< 0	Cylinder	N _C ⁻	—	38,0	62,0	—	—
> 0	Disk	N _D ⁺	15,6	14,1	59,2	3,7	7,4

MTABr is myristyltrimethylammonium bromide; MTAΦSO₃ is myristyltrimethylammonium toluenesulfonate.

the magnetic fields (~ 1 kG), this implies that $V \sim 10^{-6}$ cm³. This means that only macroscopic diamagnetic particles can be subjected to orientation due to shape.

As is known,⁶⁴ orientation owing to the diamagnetic anisotropy of molecules depends on the sign of χ_0 . The difference between the energies of micelles corresponding to configurations along the magnetic field and perpendicular to it involves the number N of molecules in the micelle, its volume V_0 , and the order parameter S_{mol} , which characterizes the ordering of the molecules in the micelle:

$$\Delta W_{\text{mol}} = W - W_{\perp} = -\frac{H^2 N V_0}{2} S_{\text{mol}} \chi_a. \quad (2)$$

Yet if the ordering of the principal axes of the micelles in a nematic is described by the order parameter S_{mic} , then the difference between the energies indicated above for a system of M micelles will be

$$\Delta W_{\text{mic}} = -\frac{H^2 M N V_0}{2} S_{\text{mol}} S_{\text{mic}} \chi_a. \quad (3)$$

One can define the quantity $S_{\text{mol}} S_{\text{mic}} = S$ as the macroscopic order parameter. We shall examine these quantities in greater detail below in a special section.

By using Eqs. (1) and (3), we can easily find the ratio of the energy differences caused by the shape and the molecular anisotropies:

$$\frac{\Delta W_{\text{mol}}}{\Delta W_{\text{shape}}} = \frac{S \chi_a}{(\bar{\chi} - \chi_0) (D_c - D_a) \bar{\chi}}. \quad (4)$$

The calculation of this ratio is impeded by the lack of experimental data on the diamagnetic susceptibilities and the anisotropy. However, one can estimate the latter by using the additive scheme of atomic susceptibilities. Thus, for $\bar{\chi} = (\chi_{\parallel} + 2\chi_{\perp})/3$ the following values were obtained (in CGS units/mole): for NaDS -165×10^{-6} , for KL -155×10^{-6} , for DeOH -124×10^{-6} . By using the known compositions (see above), one can adopt the typical values $\bar{\chi} = -6 \times 10^{-7}$ CGS units/cm³, and $\chi_0 = -7 \times 10^{-7}$ CGS units/cm³. Estimates of $\chi_0/\bar{\chi}$ have been obtained under the assumption that the diamagnetic anisotropy arises only from the anisotropy of the methylene groups. Typical values for all the systems are equal to about 0.1.

Upon using these values of the diamagnetic constants as well as the typical values of S equal to 0.5–0.6 (see below), we find that

$$\frac{\Delta W_{\text{mol}}}{\Delta W_{\text{shape}}} \approx 10^4.$$

Hence it is clear that the orientation of a lyotropic nematic is caused by the molecular diamagnetic susceptibility.³⁾

2.2. Orientation in a magnetic field

The orientation of diamagnetic configurations depends on the sign of the diamagnetic susceptibility. When $\chi_a > 0$ the director takes up a position parallel to the direction of the magnetic field, and perpendicular when $\chi_a < 0$.

The process of orientation of nematics in above-critical fields has been studied in rather great detail in the N_C^+ , N_C^- , and N_D^- mesophases.

Calamitics with $\chi_a > 0$ (N_C^+) have been studied⁵⁹ in the

NaDS–DeOH–H₂O system using the change in the dichroism in fields from 5.5 to 15 kG. In fields above 10 kG orientation occurs in the course of several minutes. In smaller fields the orientation process is mainly completed in an hour, while in the initial interval the orientation occurs very rapidly (proportionally to H^2), and then approaches saturation.

The orientation of sodium chromoglycate (DSCG) in water (N_C^- mesophase) has been studied in a 19-kG field applied perpendicular to the glass plates.⁶⁵ It turned out that, depending on the processing of the support glasses, a planar disordered texture (a planar) is realized, in which the long axes of the micelles, though lying parallel to the glass plates, are random in orientation in this plane, or else a homogeneous ordered texture, in which the long axes of the micelles are ordered in one direction in the plane of the glass plates. When the support glasses are treated with chromic acid and alcoholic KOH solution, a planar is formed after 4 hours stay in the magnetic field. When the glass plates are rubbed, a planar is formed at first, and a homogeneous texture after 4 hours.

Discotics having $\chi_a < 0$ (N_D^-) have also been studied in detail in the NaDS–DeOH–H₂O system, both on pure specimens and on specimens with addition of about 1% of ferrofluid.⁶⁶ In the latter case the orientation proceeded 10^3 times faster. The initial orientation was an inhomogeneous planar, reflecting the velocity profile in filling the capillary by flow. It was shown that in both cases the discotic is oriented with its principal axes perpendicular to the field. The time dependences of the orientation of the pure discotic in a 6-kG magnetic field are exponential in character with a time constant of 9 min. The orientation law of the ferronematic differs from exponential.

The process of orientation of a discotic in the same system has been studied⁶⁷ by the change in textures and birefringence in a 5-kG magnetic field. The initial orientation was homeotropic, and the final orientation planar. The entire process took a time of the order of an hour.

In the initial stage of orientation the homeotropic texture is slightly deformed, and birefringence appears. The texture looks uniformly dark, but gradually lightens. As a rule, already after 3–5 min after introduction into the field, individual point regions arise that are visible in the microscope. Their number increases with time. Then the texture becomes wavy (Fig. 7a). Then the wavy deformation goes over into a more complex deformation, and contours of loops are formed. They grow and continue to gain in contrast.

Two forms of loops are distinguished quite clearly. Loops of the first type (Fig. 7b) amount to inversion walls that penetrate across the specimen. The same type of loops has been observed in the N_C^+ ,³² and N_C^- ⁶⁵ calamitics. The amount to the boundary between regions where the director is rotated by 180°. Loops of the second type are inclined walls (Fig. 7c). Sometimes at the instant of application or immediately after removal of the magnetic field, a domain structure is formed (Fig. 7d). An analogous structure has been found in the N_C^+ ,^{32,39,41,68,140} N_C^- ,^{65,69} and N_D^- ¹⁴¹ calamitics. The physical cause of this domain structure is reverse flow, which leads to appearance of cylindrical lenses.⁷⁰

The onset of a domain structure is governed by three main conditions: homeotropic orientation, strong adhesion, and a magnetic field intensity greater than the three critical

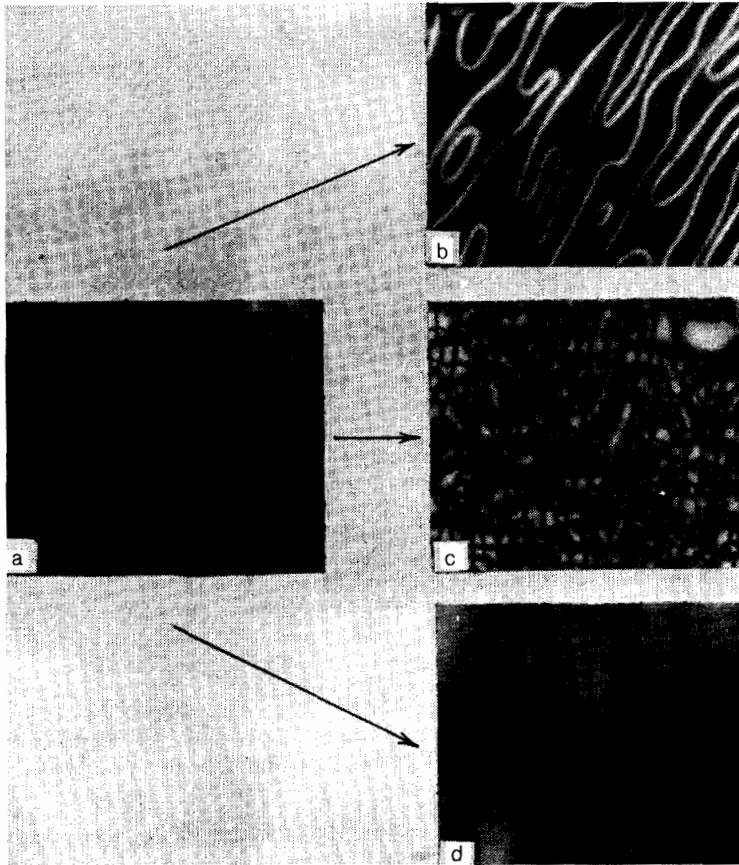


FIG. 7. Textures at different stages of reorientation from a homeotropic to a planar texture⁶⁷ in a 5-kG magnetic field. NaDS (4%)–DeOH (7%)–H₂O (53%) system.

values for the Fredericks transition.⁷⁰ Apparently a domain structure is formed only in those specimens in which a good initial homeotropic orientation exists. Specimens with a diverging cross form inversion walls upon reorientation in a magnetic field.

As is known,⁷¹ the angle of orientation by flow θ is determined by the following relationship:

$$\cos 2\theta = \frac{\gamma_1}{\gamma_2}. \quad (5)$$

Here γ_1 and γ_2 are the Leslie coefficients of viscosity. For calamitics that form a planar layer during flow, $\theta \rightarrow 0$ and $\gamma_1 \geq \gamma_2$. For discotics upon flow we have $\theta \rightarrow \pi/2$ and $\gamma_1 \leq \gamma_2$.

At the same time, the solution of the equation of motion for reverse flow is determined by the sign of the ratio of the Leslie coefficients. For transition from a homeotropic to a planar we have

$$\lambda^* = \frac{\gamma_2 - \gamma_1}{2\gamma_1}, \quad (6)$$

and for transition from a planar to a homeotropic

$$\lambda' = \frac{\gamma_2 - \gamma_1}{2\gamma_1}. \quad (7)$$

Upon taking account of the relationship between γ_1 and γ_2 , we obtain⁵⁵ $\lambda' < 0$ for calamitics, and $\lambda' > 0$ for discotics. This implies that, when one applies a magnetic field perpendicular to the initial orientation, the rate of reverse flow for calamitics will be larger than for discotics. Therefore, as experiments show, domains are formed more easily for calamitics and less easily for discotics.

2.3. Viscoelastic properties

The temperature dependences of the longitudinal and transverse bending and rotational viscosity constants have been studied only for the N_D phase.^{72,73} The DACl–NH₄Cl–H₂O⁶⁹ and NaDS–DeOH–Na₂SO₄–H₂O⁷³ systems were studied. The usual experimental methods applicable to thermotropic nematics were used. The results were processed according to the continuum theory of Oseen and Frank.⁶⁴ On the whole, the results obtained for the two completely different systems agree well.

Figure 8 shows the temperature dependences of K_{33}/χ_a for two specimens of differing composition in the DACl–

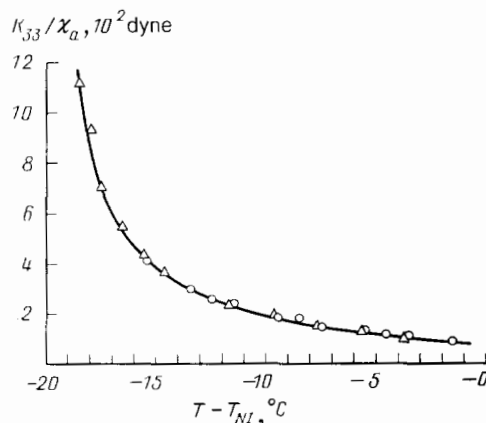


FIG. 8. Temperature dependence of K_{33}/χ_a of the N_D in the DACl (7 mole percent)–NH₄Cl (2.53%)–H₂O (90.47%) system.⁵⁷

TABLE IV. Temperature dependence of K_{11}/K_{33} and K_{11}/χ_a for an N_D of composition DACI (7.57 mole percent)- NH_4Cl (2.73 mole percent)- H_2O (89.70 mole percent).⁷²

Temperature, °C	K_{11}/K_{33}	K_{11}/χ_a , dyne	Temperature, °C	K_{11}/K_{33}	K_{11}/χ_a , dyne
61,3±0,1	0,512±4%	52±6%	49,5±0,1	0,470±4%	74±6%
59,4	0,518	68	48,5	0,428	70
57,4	0,533	82	47,5	0,098	69
55,4	0,360	70	47,0	0,075	70
53,4	0,320	76	46,5	0,052	59
50,4	0,185	68			

NH_4Cl - H_2O system, while Table IV shows the values of K_{11}/χ_a and K_{11}/K_{33} for a specimen having $T_{NI} = 65.5^\circ\text{C}$. As we approach the lamellar phase, all the measured quantities increase with a critical index apparently equal to 2/3. The data for K_{33}/χ_a for two specimens having a different water content fit a single curve well (see Fig. 8), which indicates the magnitude of the order parameter to be independent of the concentration of water.

The following values were obtained for the NaDS (37.8%)-DeOH (6.2%)- H_2O (51.7%)- Na_2SO_4 (4.3%) system at room temperature: $K_{33}/\chi_a = 87.4$ dyne, $K_{11}/K_{33} = 0.119$, $K_{11}/\chi_a = 10.4$ dyne.⁷³ With increasing temperature K_{33}/χ_a sharply declines, while K_{11}/χ_a declines insignificantly.

Since $\chi_a \sim 10^{-9}$ CGS units,¹³⁹ we have $K \sim 10^{-7}$ dyne, i.e., of the same order of magnitude as the elasticity constants of thermotropic nematics. This is as yet not very understandable since, according to the self-consistent-field theory, we have $K \sim V^{1/3}$, where V is the volume per molecule. Since a micelle contains at least 10^3 molecules, the elastic constants of lyotropic nematics should be an order of magnitude larger than for thermotropic nematics. The lack of such an increase can indicate the ease of deformation of the micelles themselves.¹⁴² This makes it necessary to take account of the elasticity of the micelles themselves, since the constant describing this elasticity has the magnitude $5 \cdot 10^{-8}$ dyne.²⁹

The relaxation times and the magnitudes of γ_1/χ_a , where γ_1 is the rotational viscosity, are given in Table V. The composition of the specimen is the same as is given in Table V. These data imply that, if we assume that $\chi_a \sim 10^{-9}$ CGS units, then $\gamma_1 \sim 10^{-1}$ poise. For the NaDS-DeOH- Na_2SO_4 - H_2O system the estimates yield⁷³ a rotational viscosity two orders of magnitude larger.

However, analogous measurements performed by NMR⁷⁴ in thin, round capillaries for the N_C phase yielded completely different results. Thus, for the NaDS (39.8%)- Na_2SO_4 (4.5%)- D_2O (55.7%) system, it was found that

$\chi_a/\gamma_1 = 1.8 \cdot 10^{-12} \text{ s} \cdot \text{cm}^{-2}$, while for the KL (33.2%)-KCl (2.2%)- D_2O (64.6%) system, it was found that $\chi_a/\gamma_1 = 5.89 \cdot 10^{-13} \text{ s} \cdot \text{cm}^{-2}$. If we assume as before that $\chi_a \sim 10^{-9}$ CGS units, then we have $\gamma_1 \sim 10^4$ poise. Apparently such high values of the rotational viscosity involve the strong orienting influence of the walls of the thin, round capillaries.

2.4. Dielectric properties

Since the overwhelming majority of lyotropic nematics are aqueous solutions, it is very difficult to measure their dielectric anisotropy. Vedenov and Levchenko²⁹ have derived a formula for calculating the dielectric anisotropy by analogy with the diamagnetic anisotropy. It implies that $\epsilon_a > 0$ for discotics and $\epsilon_a < 0$ for calamitics.

The conductivity (k) has been studied only for the N_D phase, both with $\chi_a < 0$ (DACI- NH_4Cl - H_2O),⁷⁵ and with $\chi_a > 0$ (CsPFO- H_2O).⁷⁶ In both cases it was found that $k_{\perp} > k_{\parallel}$. This fact was convincingly and elegantly demonstrated⁷⁶ as follows.

One can transform the matrix of the conductivity tensor k_{ij} by separating the isotropic component k_i , which does not depend on the director, and the anisotropic component k_a , which depends on the order parameter:

$$k_{ij} = \frac{1}{3}(2k_{\perp} + k_{\parallel}) + \frac{2}{3}(k_{\parallel} - k_{\perp}) \begin{vmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{vmatrix} = k_i + \frac{2}{3}k_a \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right). \quad (8)$$

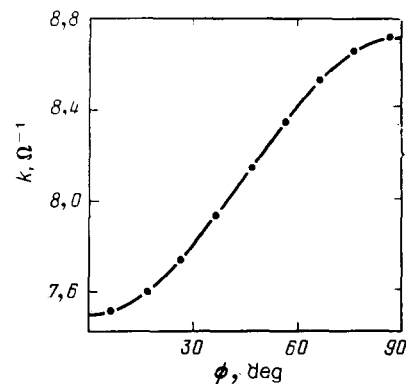


FIG. 9. Dependence of the electrical conductivity on the angle between the director and the electric-field direction for the N_D^+ in the CsPFO- H_2O (45%) system.⁷⁶

TABLE V. Relaxation times τ and rotational viscosities γ_1/χ_a of the N_D phase of the DACI- NH_4Cl - H_2O system.⁷²

Temperature, °C	τ , s	γ_1/χ_a , 10^8 P
57,4	41,2	3,13
53,5	47,6	5,59
40,5	54,3	11,68

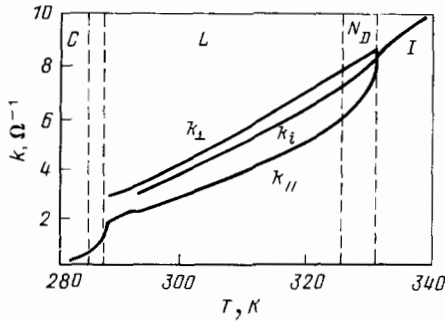


FIG. 10. Temperature dependence of the electrical conductivity k_{\perp} , k_1 , and k_{\parallel} (measured at an angle of $54^{\circ}44'$ to the director) for N_D .⁷⁶ Composition of the system is the same as in Fig. 9.

The dependence of the conductivity on the angle θ between the direction of the electric field and the director was studied experimentally. These results are shown by the dots in Fig. 9, while the curve is calculated by Eq. (8). The agreement is very good. It was found from these data for the CsPFO-H₂O system that $k_{\parallel} = 7.519$ and $k_{\perp} = 8.658$ $\text{cm} \cdot \text{m}^{-1}$.

The temperature measurements showed that the slopes of the $k_{ij}(T)$ curves change at the phase transitions, while the derivatives have maxima. These data are shown in Fig. 10 for the CsPFO-H₂O system. The conductivity k_1 was measured at $\theta = 54^{\circ}44'$, at which angle the second term in Eq. (8) is zero.

The phase transitions (S-L and N_D -I) are manifested as "steps" and are accompanied by sharp peaks in the derivatives of k_{ij} with respect to temperature. The L- N_D transition is manifested more sharply in the variation of k_{\parallel} and leads to practically no change in k_{\perp} .^{75,76}

The charge carriers in lyotropic nematics are the counterions. The small change in the conductivity along the director in the N_D -L transition and the analogous temperature variation of k_{ij} in both phases indicate an identical mechanism of conduction in these phases.

A more detailed examination of the mechanism of conduction has been performed for the CsPFO-H₂O system.⁷⁶ Here charge can be transported by the C_s^+ and $C_7F_{15}CO_2^-$ ions. The latter ions are almost all bound in micelles. Part of the C_s^+ ions is also strongly bound to the surface of the micelles, but a certain quantity of them forms a diffuse boundary. These are the ions that move freely and participate in the conduction process. The proof of this is the close coincidence of the ratios of the diffusion coefficients of the cesium ions and water molecules calculated from the data on the conductivity of this system and those experimentally measured in cesium chloride.

Attempts have been undertaken⁷⁷ to calculate the conductivity of N_D and N_C phases by using simple models. Thus it has been assumed that the micelles in the N_C phase lie at the nodes of a body-centered tetragonal cell, while their long axes are oriented along the chosen direction. The details of the calculation are not reported. However, by varying the parameters of the problem (the length and diameter of the micelles, the ratio of the minimum distances between the micelles along and perpendicular to the director), one can obtain either a positive or negative anisotropy of conductivity.

3. THE BIAXIAL PHASE

3.1. The order parameter

The existence of a biaxial nematic phase has long been assumed in thermotropic liquid crystals.⁷⁸⁻⁸² It has been considered possible to form it via ordering of the short axes of the molecules^{78,79} or in a mixture of elongated and disk-shaped molecules.^{80,81}⁴⁾ The methods of describing the order parameter of a biaxial phase proposed in these studies can be used in studying lyotropic biaxial nematics.

The biaxial phase is considered to be orthorhombic (*mmm*). The ordering in this phase is characterized by two mutually perpendicular unit vectors n and m . One of them describes the ordering of the long axes of the molecules, and the other the short axes. In lyotropic nematics n describes the ordering of the long axes of the micelles, and m of the short axes, if the micelles are orthorhombic. Yet if the biaxial phase is formed in a mixture of calamitics and discotics, then n and m respectively characterize the ordering of their principal axes. Then the tensor order parameter can be written as follows:

$$S_{ij} = S_1 \left(n_i n_j - \frac{1}{3} \delta_{ij} \right) + S_2 \left(m_i m_j - \frac{1}{3} \delta_{ij} \right). \quad (9)$$

Here $S_1 > 0$ and $S_2 < 0$ are the scalar order parameters, and δ_{ij} is the Kronecker symbol. In matrix notation we have

$$S_{ij} = \begin{pmatrix} \left(\frac{2}{3} S_2 - \frac{1}{3} S_1 \right) & 0 & 0 \\ 0 & -\frac{1}{3} (S_1 + S_2) & 0 \\ 0 & 0 & \left(\frac{2}{3} S_1 - \frac{1}{3} S_2 \right) \end{pmatrix}. \quad (10)$$

If $S_2 = 0$, then

$$S_{ij} = S_1 \begin{pmatrix} -\frac{1}{3} & 0 & 0 \\ 0 & -\frac{1}{3} & 0 \\ 0 & 0 & \frac{2}{3} \end{pmatrix} \quad (11)$$

describes a uniaxial nematic phase I, in which the principal axes are oriented along the Z axis.

If $S_1 = 0$, then

$$S_{ij} = S_2 \begin{pmatrix} \frac{2}{3} & 0 & 0 \\ 0 & -\frac{1}{3} & 0 \\ 0 & 0 & -\frac{1}{3} \end{pmatrix} \quad (12)$$

describes a uniaxial nematic phase II, in which the principal axes are oriented along the X axis.

The scalar order parameters are often expressed^{78,80} in terms of the parameters r and θ defined in the plane of the order parameter (Fig. 11). The parameter $r > 0$ gives the deviation from an isotropic phase, while $0 \leq \theta \leq \pi/3$ —the "asymmetry parameter"—gives the deviation from uniaxial phases. Then in a nematic phase I we have $r > 0$ and $\theta = 0$, and in phase II $r > 0$ and $\theta = \pi/3$. A biaxial phase corresponds to $r > 0$ and an intermediate state of θ .

The scalar order parameters are related to r and θ by the following relationships^{78,80}:

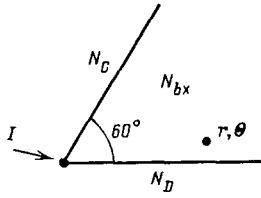


FIG. 11. Order-parameter plane.⁸⁰

$$\begin{aligned} S_1 &= \frac{\sqrt{3}}{2} r (\sqrt{3} \cos \theta - \sin \theta), \\ S_2 &= -\sqrt{3} r \sin \theta. \end{aligned} \quad (13)$$

Upon substituting Eq. (13) into the matrix (10), we obtain after transformations:

$$S = r \begin{vmatrix} -\cos\left(\frac{\pi}{3} - \theta\right) & 0 & 0 \\ 0 & -\cos\left(\frac{\pi}{3} + \theta\right) & 0 \\ 0 & 0 & \cos \theta \end{vmatrix}. \quad (14)$$

This matrix describes the ordering of a calamitic for $\theta = 0$ and a discotic for $\theta = \pi/3$.

A thermodynamic theory of the biaxial phase has been developed⁸² in the spirit of the Landau-de Gennes theory. Upon applying an expansion of the free energy G in the two principal invariants $r^3 \cos 3\theta$ and r^2 ,⁷⁸ we obtain

$$G = ar^2 + br^2 \cos 3\theta + cr^4 + dr^5 \cos 3\theta + cr^6 + fr^6 \cos^2 3\theta. \quad (15)$$

If we neglect the terms in r^6 , then Eq. (15) will describe only uniaxial nematic phases, with the sign determined by the value of θ . For an N_D we have $b + r^2d < 0$. For an N_C this expression is greater than zero. The transition between the two uniaxial phases occurs when $b + r^2d = 0$.

In a first approximation one can describe the temperature dependence of r near the transition as

$$r = \frac{3}{2} \left| \frac{\beta(T - T_m)}{4a} \right| + \left(-\frac{2a}{c} \right)^{1/2}. \quad (16)$$

Here T_m is the transition temperature. At this temperature r reaches a minimum, and $T - T_m$ varies continuously from a negative to a positive value during the transition.

Taking account of the sixth-order terms in Eq. (15) leads to formation of a biaxial phase. The uniaxial-biaxial phase transition occurs when

$$|b + r^2d| = 2r^3f, \quad (17)$$

with $f > 0$. Thus we have $r > 0$ for a biaxial phase. In this region we find

$$\cos 3\theta = -\frac{b + r^2d}{2r^3f}. \quad (18)$$

Near the phase transition and in the biaxial region, if it is narrow enough, we can assume that

$$b + r^2d = \beta(T - T_m). \quad (19)$$

Here $T_m = (T_1 + T_2)/2$, and T_1 and T_2 are the tempera-

tures of the $N_D - N_{bx}$ and $N_C - N_{bx}$ transitions, respectively. We obtain the following expression from Eqs. (18) and (19) for the region of existence of the biaxial phase:

$$T_2 - T_1 = \frac{4r^3f}{\beta}. \quad (20)$$

Along the line of the transition from the uniaxial to the biaxial phase we have the following from Eq. (18):

$$(b + r^2d) \cos 3\theta = -2r^3f \cos^2 3\theta. \quad (21)$$

Then the expansion (15) will have the following form:

$$G = ar^2 + cr^4 + er^6 - fr^6 \cos^2 3\theta. \quad (22)$$

We see from this expression that the transition from a nematic to an isotropic phase at the point where the lines of the uniaxial-biaxial phase and nematic-isotropic phase transitions meet can be a second-order phase transition. Here the biaxial phase disappears (for more details see Secs. 4.2 and 4.3).

3.2. Features of the viscoelastic properties

Saupe⁸³ has developed a theory of elasticity of biaxial nematics. This phase is considered orthorhombic (mmm), and in keeping with the matrix of the sixth-order tensor used to describe it, we need nine nonzero elasticity constants. If a , b , and c are the unit vectors along the three twofold axes associated with the local coordinate system X , Y , and Z , then the elasticity constants have the following meaning: K_{aa} , K_{bb} , and K_{cc} are the torsion constants about the vectors a , b , and c , respectively; K_{ab} and K_{ac} are the longitudinal bending constants of the vector a in the XY and YZ planes, respectively, K_{ba} and K_{bc} are the longitudinal bending constants of the vector b in the XY and YZ planes, respectively, and K_{ca} and K_{cb} are the longitudinal bending constants of the vector c in the XZ and YZ planes, respectively.

There are as yet no experimental data on the elasticity constants of biaxial nematics.

The equations of motion of biaxial nematics with allowance for viscosity have been solved in Refs. 84–87. Twelve coefficients are required to describe incompressible nematics, and 15 for compressible.

3.3. Textures and optical properties

Biaxial N_{bx} lyomesophases were discovered in 1980 by Yu and Saupe⁸⁸ in the KL-DeOH-H₂O system. Figure 12 presents⁸⁹ part of the phase diagram showing the region of existence of the N_{bx} phase. It was obtained at a constant concentration of decanol equal to 6.24%. As we see from this diagram, the biaxial phase exists in a narrow temperature range.

The proof of optical biaxiality was obtained by NMR and optical conoscopic patterns.

A detailed study of the biaxial phase in this system has been conducted by Saupe and his associates,⁸² and also by Galerne *et al.*⁸⁹⁻⁹¹ The $N_D - N_{bx}$ transition is manifested on the homeotropic texture in the form of grey spots of irregular shape (Fig. 13). This involves the change in the circular cross-section of the optical indicatrix to elliptical, for which the condition of complete darkening in crossed polarizers is no longer fulfilled. In homogeneous regions the axis along

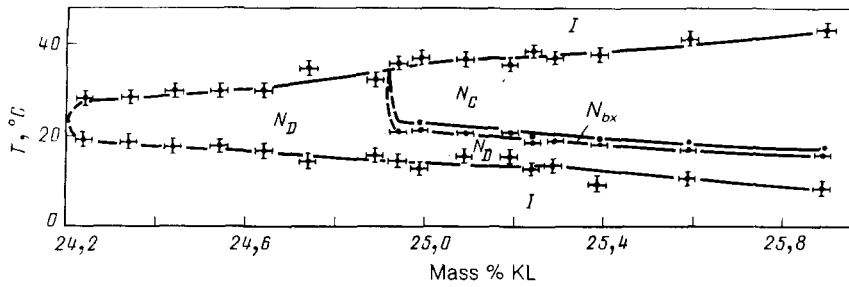


FIG. 12. Phase diagram of the KL–DeOH (6.24%)–H₂O system.⁸⁹

which the diamagnetic susceptibility is minimal lies parallel to the glass plates, while the axis with the maximal susceptibility is perpendicular to them.

A conoscopic pattern typical of an optically biaxial crystal has been observed⁸¹ in a thick (2.5 mm) specimen oriented by a magnetic field so that the axis of maximal diamagnetic susceptibility is directed normal to the glass plates (Fig. 14).

Thermodynamic theory can be used to describe the temperature dependence of the birefringence and the magnitude of splitting of the NMR line.

Since any tensor property of a liquid crystal depends on the order parameter, one can show⁷⁸ that the difference between the two principal refractive indices n_1 and n_2 can be determined by the following expression:

$$n_1 - n_2 = \frac{a_\epsilon}{2n_2} (S_1 - S_2) = -\frac{a_\epsilon}{2n_2} r \cdot \sqrt{3} \sin \theta. \quad (23)$$

Here a_ϵ is a constant that does not depend on the temperature and the concentration.

Upon substituting Eq. (16) into Eq. (23), we obtain

$$n_1 - n_2 = -\frac{a_\epsilon}{2n_2} \cdot \sqrt{3} r \sin \left[\frac{1}{3} \cos^{-1} \frac{2(T - T_m)}{T_1 - T_2} \right]. \quad (24)$$

In particular, near the N_D – N_{bx} transition, where we can set $T = T_1 - \delta(T_1 - T_2)$, we have

$$n_1 - n_2 = -\frac{a_\epsilon}{n_2} \frac{r}{\sqrt{3}} \delta^{1/2}. \quad (25)$$

Near the N_C – N_{bx} transition, where $T = T_2 + \delta(T_1 - T_2)$, we have

$$n_1 - n_2 = -\frac{3}{4} \frac{a_\epsilon r}{n_2} + \frac{a_\epsilon}{n_2} \frac{r}{\sqrt{3}} \cdot \frac{1}{2} \delta^{1/2}. \quad (26)$$

The experimental results⁷⁸ for the KL (25.6%)–DeOH (6.3%)–D₂O (68.1%) system agree well with this treatment. The birefringence in the biaxial phase increases with

increasing temperature. In this region the axis with the smallest diamagnetic susceptibility is established perpendicular to the support glass plates. In the N_C phase the birefringence slowly declines. In this study⁷⁸ a reversed biaxial and a discotic phase were found above N_C .

Galerie and Marcerou^{90,91} repeated the measurement of the temperature dependence of the birefringence using practically the same composition, but with addition of a small amount ($< 10^{-4}$ mass fraction) of a ferrofluid for better orientation of the specimens. Their results, approximately up to 30 °C, agree well with the data of Ref. 78. However, neither in this study nor in the later study⁸⁹ were recurrent biaxial and discotic phases found.

The temperature dependences of the diagonal elements of the anisotropic part of the permittivity tensor at optical frequencies were calculated from the birefringence data:

$$\begin{aligned} \epsilon_{a1} &= -\frac{4}{3} \langle n \rangle \left[(n_2 - n_1) + \frac{1}{2} (n_3 - n_2) \right], \\ \epsilon_{a2} &= \frac{2}{3} \langle n \rangle [(n_2 - n_1) - (n_3 - n_2)], \\ \epsilon_{a3} &= \frac{4}{3} \langle n \rangle \left[\frac{1}{2} (n_2 - n_1) + (n_3 - n_2) \right]. \end{aligned} \quad (27)$$

Here $\langle n \rangle$ is the mean refractive index, which is equal to 1.375.

The symmetric invariants of this tensor, which can be treated as parameters, are written^{90,91} as follows:

$$\begin{aligned} \sigma_1 &= \epsilon_{a1} + \epsilon_{a2} + \epsilon_{a3} = 0, \\ \sigma_2 &= \frac{2}{3} (\epsilon_{a1}^2 + \epsilon_{a2}^2 + \epsilon_{a3}^2), \\ \sigma_3 &= 4\epsilon_{a1}\epsilon_{a2}\epsilon_{a3}. \end{aligned} \quad (28)$$

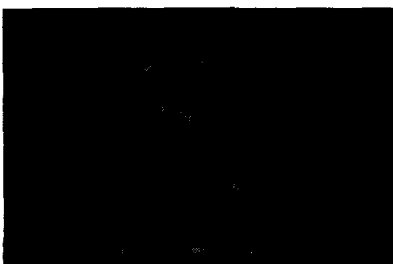


FIG. 13. Texture of a biaxial nematic. KL (26.6%)–DeOH (2%)–H₂O (67.8%) system.



FIG. 14. Conoscopic pattern of a biaxial nematic.⁸⁰ KL (26%)–DeOH (6.24%)–H₂O (67.76%) system. Thickness of specimen 2.5 mm. Temperature 20 °C.

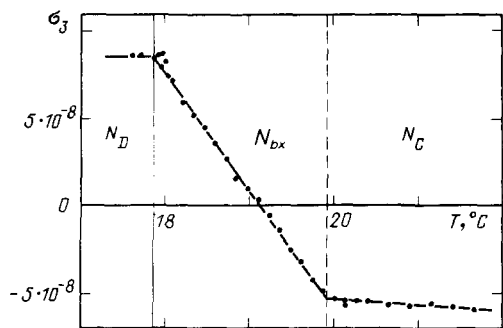


FIG. 15. Temperature dependence of the invariant σ_3 of the order parameter in the transition $N_D-N_{Bx}-N_C$.⁹¹ KL(25.6%)-DeOH(6.3%)-H₂O(68.1%) system. Thickness of specimen 100 μm . Magnetic field 10 kG.

These quantities are proportional to the molecular order parameter S .

In the uniaxial phases we have $\sigma_3 = \pm \sigma_2^{3/2}$, and the sign is completely the same as the sign of S : positive for discotics and negative for calamitics. In the biaxial phase we have

$$-\sigma_2^{3/2} \leq \sigma_3 \leq \sigma_2^{3/2}. \quad (29)$$

Figure 15 shows the temperature dependence of the invariant σ_3 in the biaxial nematic phase. In agreement with the inequality, σ_3 varies linearly while changing sign.

A biaxial phase has also been observed³⁸ in the NaDS-DeOH-H₂O system. A cross section of the system was studied at the constant water concentration 57%. The biaxial phase exists at room temperature in the NaDS concentration range from 36.05 to 36.15 mass percent. Conoscopic patterns were observed and the dependence of the birefringence on the temperature and the concentration was measured.

The hypothesis was advanced³⁸ that the transition to the biaxial phase can be explained by aggregation of discotic micelles along the optic axis into completely anisotropic aggregates. Further aggregation leads to formation of calamitic micelles.

This same group of authors⁹² studied light scattering near the transition to the biaxial phase. They found a strong depolarization of the scattered light at the transitions from the discotic to the biaxial and from the biaxial to the calamitic phase. This agrees well with the second-order character of these phase transitions.

Estimates have been made⁹² of the angle between the optic axes in the biaxial phase. They proved very small, of the order of 10^{-3} radian.

4. MOLECULAR ORDERING AND PHASE TRANSITIONS

4.1. NMR data

Lytotropic nematics are widely used as phases for studying NMR spectra. This has made it possible in recent years to amass a rather extensive experimental material that enables characterizing the molecular ordering.

The measure of molecular ordering is the magnitude of the quadrupole splitting, which is associated with the order parameter by the following relationship⁹³:

$$\Delta\nu = \frac{3}{2} QS \cdot \frac{1}{2} (3 \cos^2 \Omega - 1). \quad (30)$$

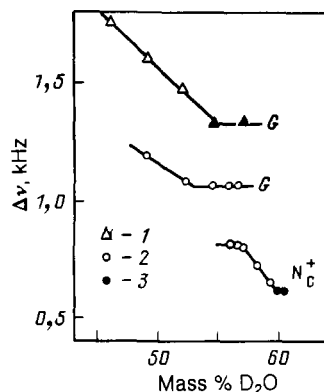


FIG. 16. Dependence of the deuterium quadrupole splitting of D₂O molecules in the NaDS-D₂O-Na₂SO₄ (mass ratio of NaDS to Na₂SO₄ = 8.75) on the D₂O concentration.⁹⁴ 1—NaDS-D₂O (phase G); 2—NaDS-D₂O-Na₂SO₄ (4%) (phase G); 3—the same (phase N_C⁺). Temperature 30.3 °C.

Here Q is the quadrupole splitting constant, S is the experimentally determined order parameter, and Ω is the angle between the director of the mesophase and the direction of the external magnetic field. For nematics having $\chi_a > 0$ we have $\Omega = 0^\circ$, and for nematics having $\chi_a < 0$, $\Omega = 90^\circ$.

In most cases one uses the quadrupole splitting of ²D atoms. However, data exist on using ²³Na, ⁷Li, ¹³³Cs, ¹³C, and ²¹Cl. In the former case the quadrupole splitting of the deuterium atoms of D₂O and of amphiphiles specially introduced into the main chain has been studied.

First of all it was found that the formation of a nematic phase from hexagonal and lamellar mesophases leads to a decrease in the order parameter.^{94,95} This can be seen well from Fig. 16, which presents the NMR data for the NaDS-D₂O-Na₂SO₄ system. With increasing D₂O concentration the quadrupole splitting in the G phase declines linearly. At 52% D₂O a two-phase region is formed: along with the G phase a N_C⁺ phase arises. On increasing the water concentration the nematic phase prevails. This leads to a linear decline in the quadrupole splitting. The pure N_C⁺ phase has minimal order and a minimal value of the quadrupole splitting.

On the whole, an analogous pattern is observed also upon temperature change.⁹⁴

The nature and concentration of the counterions considerably affect the ordering of lyotropic nematics.^{60,96,97} In the general case addition of salt expands the temperature and concentration range of existence of the nematic phase, and hence increases the order parameter. However, sometimes the influence of the counterions can be more radical. Thus, the replacement of 5–8 mole percent of the Na⁺ ions in the NaDS-DeOH-H₂O system with Cs⁺, Rb⁺, and K⁺ ions leads to a N_C⁺-N_D⁺ phase transition. Analogous transitions are induced by 20 mole percent NH₄⁺ and 15 mole percent C₂H₅NH₃⁺. This transition occurs jumpwise.

We also see from these data that the ordering of the polar groups in the N_C⁺ phase is smaller than in the N_D⁺ phase. In the N_C⁺ phase also the carbon chains are less ordered. This has been precisely established by measuring the quadrupole splitting of deuterium atoms introduced into the carbon chain in the positions 3,3,4,4.⁹⁵ Figure 17 shows the dependence of the quadrupole splitting of deuterium in D₂O and in the methylene group—CD₂—in the NaDS-DeOH-

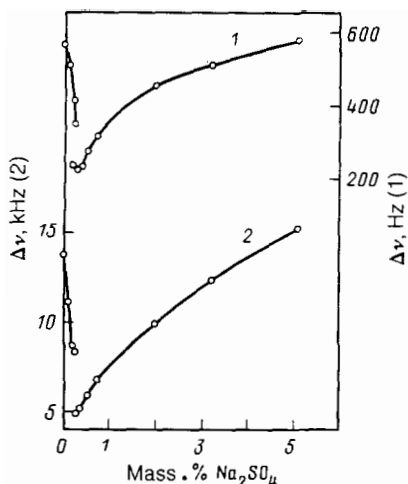


FIG. 17. Dependence of the deuterium quadrupole splitting of D_2O molecules (1) and methylene groups— CD_2 (2) in the $NaDS-NaDS-3,3,4,4-d_4$ (37.63%)— D_2O (54.84%)— $DeOH$ (7.53%) system on the Na_2SO_4 concentration. Temperature $24^\circ C$.

D_2O system on the concentration of Na_2SO_4 . Addition of the latter in the amount of 0.272% leads to a $N_C^+-N_D^+$ transition. Here the quadrupole splitting varies jumpwise by a factor of 1.64. We can easily find from these data using Eq. (31) that $S_{C-D}(N_C^+)/S_{C-D}(N_D^+) = 0.82$. Thus the ordering of the C—D bonds with respect to the director in micelles of calamitics is slightly smaller than in the micelles of discotics.

An increase in the water concentration reduces the order of both the polar groups and the hydrocarbon chains.⁹⁵ Thus, in the $DACl-D_2O-NH_4Cl$ system this can be seen well from the dependence of the quadrupole splitting of deuterium of the end groups ND^+ and $\alpha = CD_2$ on the concentration of heavy water. The N_D^- phase exists at a D_2O concentration above 50%, and in this region the order linearly declines with increasing water concentration. The curves have breaks at 59% D_2O . As one can suppose, they correspond to a second-order phase transition to a phase where an isotropic liquid and an N_D^- mesophase coexist. A second phase transition is observed at 63.87% D_2O to a phase whose nature has not been established.

Many different motions occur in nematics and they all affect the experimentally established order parameter. In the general case⁹⁸ we have

$$S = S_{MO}S_{CO}S_{h/j}S_{diff}; \quad (31)$$

The right-hand side contains the order parameters arising from different motions: S_{MO} —vibrations of the micelle as a whole with respect to the director; S_{CO} —vibrations of the long axis of the carbon chain with respect to the normal to the surface of the phase boundary; $S_{h/j}$ —segmental motion of the trans-gauche type⁵⁾ in the hydrocarbon chain; and S_{diff} —an edge effect—diffusion of the amphiphile at the boundary of the micelle.

It is impossible at present to distinguish and analyze all these motions. However, we can still draw some conclusions.

The most general considerations imply that the ordering of the different segments of the hydrocarbon chains of amphiphilic molecules must vary. However, it is not evident *a priori* how the order varies in going toward the tail of the chain inside the micelle. This problem has been clari-

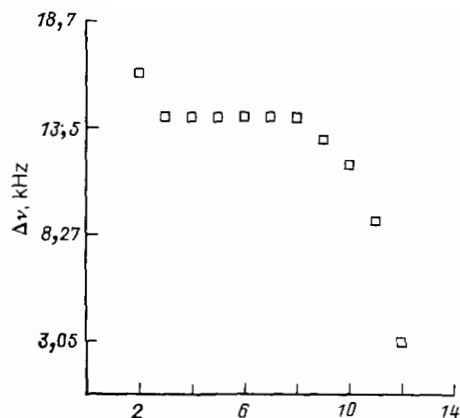


FIG. 18. Quadrupole splitting of deuterium atoms in different segments of hydrocarbon chain of KL in the N_D^- phase.¹⁰¹ $KL(33.7\%)-DeOH(5.2\%)-KCl(5.1\%)-D_2O/H_2O(56.0\%)$ system.

fied⁹⁹⁻¹⁰¹ by introducing deuterium atoms into different segments of the chain. Figure 18 presents the results of one such experiment. We can see well that the order varies weakly up to the ninth carbon atom, then sharply declines. The idea has been advanced^{102,103} to explain this fact of an equilibrium distribution of gauche conformations in the region of the chain up to C_9 , with formation of a sole gauche configuration at the end of the chain.

It was possible to calculate the order parameter of each CD_2 segment of the hydrocarbon chain from the data of Fig. 18 and to determine their temperature dependence. As we should expect, all the order parameters decline almost linearly with increasing temperature and drop to zero at $69^\circ C$, where the system transforms to the isotropic and the G (or L) phase. The order parameter of the region C_3-C_8 behaves interestingly. At about $45^\circ C$ the NMR signal splits into three components with an intensity ratio of 4:1:1. This leads to a situation in which the character of the temperature dependence of the order parameter for the two methylene groups varies appreciably. Apparently this is due to the increase at this temperature in the number of gauche configurations.

In the transition from the lamellar to the nematic N_D^- phase in the $DACl-H_2O$ and $DACl-H_2O-NH_4Cl$ systems, the ordering of the different segments differs appreciably.¹⁰⁴ The end segments practically do not "sense" the phase transition, whereas the ordering of the segments closest to the polar part varies rather considerably. This allows us to state that the end segments behave to a certain degree independently of the rest of the molecules of the amphiphile.

Interesting data have been obtained¹⁰⁵⁻¹⁰⁸ in studying the segmental motions of the trans-gauche type. For different segments x and y of a single chain we can write

$$\frac{S_x}{S_y} = \frac{(S_{h/j})_x}{(S_{h/j})_y}. \quad (32)$$

If we take the y segment to be the end methyl group, then we find that the ratio $S_x/S_y = 3.00$ for the trans conformations of the segment. For the end methyl group under these conditions this ratio is unity. Deviation from these rules would indicate the presence of gauche conformations.

Figure 19 shows such a situation for the $NaDS-DeOH-H_2O$ system. We can see well that the order in $NaDS$ and

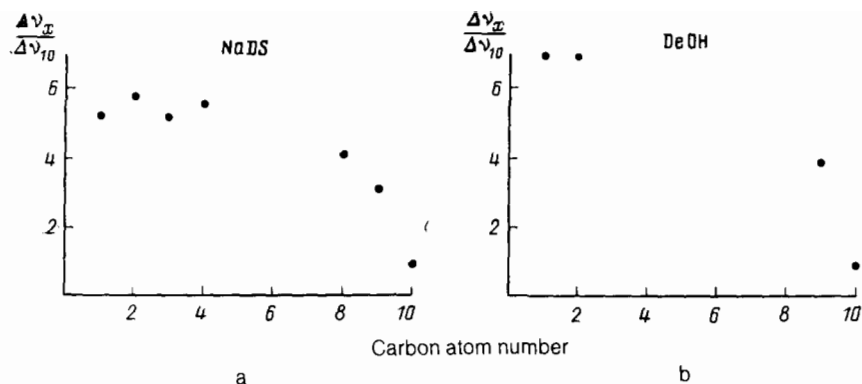


FIG. 19. Ratio of the quadrupole splittings for different segments of the hydrocarbon chain of NaDS and decanol in the NaDS (41.1%)-DeOH (3.6%)-H₂O (55.3%) system in the N_D phase.¹⁰⁷

DeOH is approximately constant for segments 1-8 and rapidly declines for the end groups. For NaDS an "even-odd" effect is clearly marked: the degree of order of segments 1 and 3, and 2 and 4, are equal. The order in DeOH on the average is greater. This shows that the contribution of the gauche configurations in the decanol chain is far greater than in the NaDS chain.

In some cases the angular dependences of the quadrupole splitting enable one to calculate the components of the order-parameter tensor of a deuterated segment. Data of this type have been obtained¹⁰⁹ in studying the NaDS-DeOH-Na₂SO₄-H₂O and DACI-NH₄Cl-H₂O systems with substituted phenols, where the molecules of the amphiphiles were deuterated in the α -position (see Table VI). These systems were studied in the N_D phase. We see well that the order of the CD₂ segment closest to the polar part in the single lyotropic nematic phase practically does not depend on the nature of the amphiphile. At the same time, the low values of the order parameter cannot be understood.

4.2. Model calculations

The common features of the phase transitions and the temperature-dependences of ordering are well manifested in model calculations performed within the framework of a lattice model by the method of Flory.¹¹⁰ We have already mentioned them above. The model is based on dividing space into cubic cells, each of which contains anisometric particles in three orientations with their principal axes along the coordinate axes. Two types of particles are considered: rods and square plates. The forces of interaction among them are taken into account. The early studies of Alben^{80,81} allowed only

TABLE VI. Components of the order parameter of the NaDS (0.1 mole percent)-Na₂SO₄ (0.24)-DeOH (0.22)-H₂O (19.36)-substituted phenols (0.055) and DACI (0.1 mole percent)-NH₄Cl (0.26)-H₂O (16.23)-(0.055) and DACI (0.1 mole percent)-NH₄Cl (0.26)-H₂O (16.23)-substituted phenols (0.054) systems.¹⁰⁹

Components of the order-parameter tensor	NaDS	DACI
S_{33}	+0,155	+0,146
S_{22}	-0,043	-0,039
S_{11}	-0,113	-0,107

for the short-range repulsion. Nevertheless, for a certain anisometry of square plates it was found that, besides the first-order phase-transition line separating the isotropic and nematic phases, two lines appear on the phase diagram of second-order phase transitions that converge to a single point with this line. The second-order phase-transition lines mark out the optically biaxial phase.

Chen and Deutch¹¹¹ have recently examined this model in greater detail. In addition to the short-range repulsion, they allowed for a long-range attraction between the particles of the same two types. The long-range action potential was chosen in the form

$$\omega^{\alpha\beta} = b + cB^{\alpha\beta}\Delta. \quad (33)$$

Here b and c are constants, Δ is the volume of the cell, and $B^{\alpha\beta}$ is a matrix whose elements are products of the linear dimensions of the particles.

If $c > 0$, then the long-range attraction tends to order the particles exactly as the short-range repulsion does, i.e., so that their long axes become parallel. Then a nematic phase is realized. In this case the phase diagram differs in no way from that obtained by Alben. However, this model enabled calculating the temperature dependence of the mole fractions of particles in different given orientations, which enables one to decide on the change in orientation in transition to different phases. As an example Fig. 20 shows these results for certain concrete values of the parameters of the theory.

The model yields an isotropic phase at high temperature. With decreasing temperature a first-order phase transition to a nematic phase arises. Depending on the concentration of the particles, this will be either a discotic (as in Fig. 20) or a calamitic. In the discotic phase, as we see from Fig. 20, most of the plates and the smaller part of the rods are oriented along the Z axis. Here most of the rods are oriented in the XY plane. However, in a uniaxial nematic phase most of the rods (or plates) are ordered in one direction, while the rest of the rods (or plates) are uniformly ordered in the two other directions. With decreasing temperature this equality breaks down, a second principal axis is formed, and the system is converted via a second-order phase transition into a biaxial phase.

Yet if $c < 0$ in Eq. (33), the attraction tends to establish a perpendicular orientation, while the repulsion tends to form a nematic phase. This case is especially interesting. It leads to recurrent phases.

The calculations show that at high temperature, just as

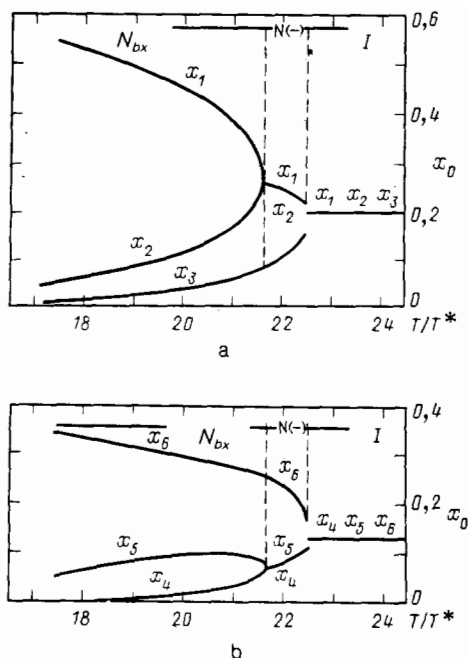


FIG. 20. Temperature dependence of the distribution of rods (a) and plates (b) in the model of Chen and Deutch.¹¹¹ Dimensions of particles: rods (length = 1, diameter = 0.1), plates (length = 0.5, thickness = 0.04). Here x_1 is the mole fraction of rods oriented along the X axis, x_2 along the Y axis, and x_3 along the Z axis; x_4 is the mole fraction of plates oriented along the X axis, x_5 along the Y axis, and x_6 along the Z axis.

in the previous case, only an isotropic phase arises. At intermediate temperatures the state of the system is determined by the competition of the long- and short-range forces. Depending on the concentration of particles, discotic, calamitic, or biaxial phases can arise. However, at low temperatures the long-range attraction proves to predominate in the configurational energy, and when $c < 0$ the molecules will tend toward a disordered arrangement, so that the system will revert from a biaxial phase to a uniaxial nematic phase, and from it to an isotropic phase.

Figure 21 shows the phase diagram as calculated for certain values of the parameters of the theory.

Interestingly, the biaxial region is asymmetric, and the

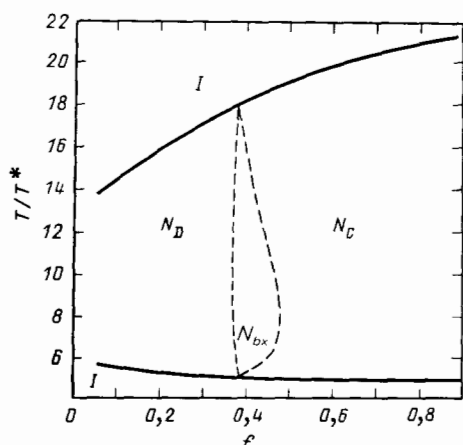


FIG. 21. Phase diagram calculated for certain values of the order parameter in the model of Chen and Deutch.¹¹¹

degree of asymmetry depends on the degree of asymmetry of the particles being studied. The phase diagram presented in Fig. 21 describes the sequence of phases $I \rightarrow D \rightarrow N_{bx} \rightarrow D \rightarrow I$. Such a sequence has not been observed experimentally. However, with high asymmetry of the particles the biaxial region acquires a large slope toward the calamitic phase, and then one can easily realize the experimentally observed sequence of phases $I \rightarrow D \rightarrow N_{bx} \rightarrow C \rightarrow N_{bx} \rightarrow D \rightarrow I$.⁷⁸

In the model under study the critical points for the biaxial and the recurrent biaxial phase correspond to identical concentrations. However, this arises only from the adopted simplified relationship between the repulsive and attractive forces. Upon taking a more exact account of this balance the critical points will generally be manifested at different concentrations.

The critical points have not been studied experimentally. However, we can consider a proof of their existence to be the concentration narrowing of the biaxial phase in the KL-DeOH-H₂O system.^{78,80}

The model being studied is fully equivalent to the phenomenological approach within the framework of the theory of phase transitions of the Landau-de Gennes type. Hence one can find simple relationships between the parameters of the model and the coefficients of the expansion of the free energy in terms of the order parameter.¹¹¹ Here one finds simple equations describing the first- and second-order phase transition lines between the isotropic and nematic phases and the uniaxial and biaxial phases, respectively. Yet if these phase transitions occur simultaneously, then the N-I transition will be a second-order transition.

4.3. Critical indices

As we have already seen, phenomenological models of the Landau-de Gennes type and calculations by the mean-field method yield the result that the N-I and N-L phase transitions are first-order transitions, while the uniaxial-biaxial nematic transition is second-order. The experimental data on the refractive indices, light scattering, and NMR spectra^{38,78,81,92} that we have mentioned above agree as a whole with this pattern. Information also exists¹¹² on thermal effects of the transitions obtained with a differential scanning calorimeter. The DSCG (13%)–H₂O–ethylene glycol system in the L-N transition showed $\Delta H \sim 0.8$ cal·g⁻¹, while $\Delta H \sim 0.6$ cal·g⁻¹ for the N-I transition. However, all these data were not obtained under equilibrium conditions, and it is very difficult to draw conclusions from them on the features of the phase transitions in lyotropic nematics.

However, studies have recently appeared specially designed to meet all the requirements for a careful study of phase transitions, from which we can draw the first conclusions.

Kumar, Yu, and Litster¹¹³ studied the first-order transition between an isotropic and an N_D phase by the light-scattering method. They worked with the DACI-NH₄Cl-H₂O system in the isotropic phase. The specimens were thermostatted to an accuracy of $\pm 0.001^\circ$. Figure 22 shows the dependence of the reciprocal of the light-scattering intensity on the temperature. Behavior typical of thermotropic nematics is shown, and far from the transition over a broad range the reciprocal of the intensity depends on the temperature as $(T - T_{NI}^*)^{-1}$, where T_{NI}^* is the extrapolated temperature

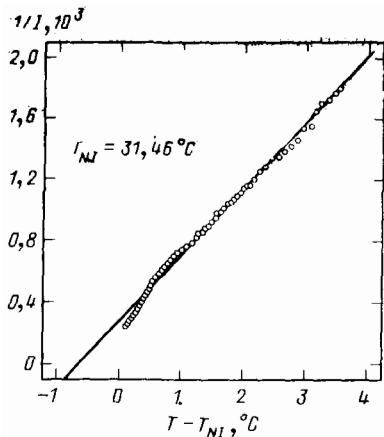


FIG. 22. Temperature dependence of the reciprocal of the light-scattering intensity in the DACI (44.4%)–NH₄Cl (4.4%)–H₂O (51.6%) system. Temperature of the N–I transition is 63 °C.¹¹³

at which only the nematic phase is stable. For the given system we find $T_{NI}^* = T_{NI} - 0.8$ °C. The two-phase region is fixed in a range of 0.3 °C below T_{NI} . However, hysteresis was not observed.

These same authors¹¹³ studied light scattering near the nematic-lamellar phase transition. They determined a critical index for the smectic correlation length that proved equal to 0.64 ± 0.05 . This value is contained in the interval of critical indices for thermotropic liquid crystals. However, it agrees with neither the value from mean-field theory nor with that from similitude theory.

Another interesting result is that the intensity of the scattered light obeys a power law in an interval of 11 °C above T_{NL} . This indicates a prevailing role of smectic fluctuations. We recall that for thermotropic nematics a deviation from a power law is already observed above 3 °C.

We should especially consider the N–I phase transition in the CsPFO–H₂O system. It has been thoroughly studied using the temperature dependence of the birefringence induced by a magnetic field^{114–117} and of the ordinary birefringence.¹¹⁸ If we choose the quantity $T_{NI} - T_{NI}^*$ as the characteristic of the transition, then with decreasing CsPFO concentration the phase transition approaches second order (Table VII). We note the unusual narrowness of the interval $T_{NI} - T_{NI}^*$ for this system. For thermotropic nematics and such a typical lyotropic nematic as DACI–DeOH–H₂O we find $(T_{NI} - T_{NI}^*)/T_{NI} \sim 3 \cdot 10^{-3}$. For the CsPFO–H₂O system this quantity is $\sim 5 \cdot 10^{-5}$.

The study of the magnetic birefringence in the isotropic phase showed a linear dependence of $\Delta n/H^2$ with a critical index $\gamma = 1.01 \pm 0.04$, which agrees well with the value

from mean-field theory. In an interval of 0.3° from T_{NI} a deviation was observed from linear dependence caused by strong fluctuations in the order parameter.

The extrapolation of Δn to zero field allowed calculating the critical index for the order parameter. It proved equal to $\beta = 0.34 \pm 0.6$.¹¹⁵ A similar value

$$\beta = 0.40 \pm_{-0.06}^{+0.04}$$

has also been found from measuring the temperature dependence of the birefringence.¹¹⁸ These critical indices differ both from mean-field theory (0.5) and from the tricritical value (0.25), but are close to the *mean-field* value when one takes into account sixth-order terms in expanding the free energy (0.34). This phase transition is described just as well by using the scaling theory with the dimensionality $d = 3$ and number of components of the order parameter $N = 5$.

Near T_{NI} ($\sim 0.75 \cdot 10^{-3}$ K), the estimates of the jump in the order parameter yield a value of 0.18, and $K \leq 2 \cdot 10^{-8}$ dyne for the elasticity constant. The strong fluctuations in this region diminish the order parameter by a factor of almost two. (For thermotropic nematics a 2–3% decrease is typical.)

Addition of Cs⁺ ions increases $T_{NI} - T_{NI}^*$; that is, the transition approaches first order. Here T_{NI} and T_{NL} increase, but the region of existence of the lamellar phase decreases. Hence one concludes that it is possible to form intermicellar complexes involving Cs⁺ ions. The dimensions of these complexes decrease with increasing concentration and temperature.^{116,117}

We have already spoken above of the interesting phase transitions between optically uniaxial and biaxial nematics. These transitions have the features of second-order phase transitions. They have been studied in detail by using the temperature dependence of the birefringence and the magnetic-field-induced birefringence in the KL–DeOH–H₂O system by Saupe and his associates.^{82,119} In the first study a value of the critical index for the order parameter was found that agrees with the mean-field theory. However, it was found in the later work¹¹⁹ that the critical index β describing the behavior of the order parameter near the N_D – N_{bx} transition equals 0.37 ± 0.03 , while γ , the critical index of the temperature behavior of magnetic-field-induced birefringence, is 1.33 ± 0.04 . These data indicate the possibility of describing the N_D – N_{bx} transitions by using scaling theory with $d = 3$ and $N = 5$. Cajas, Swift, and Brand¹²⁰ arrived at the same theory by examining the critical dynamics near the N– N_{bx} transition. At the same time, light-scattering experiments near the N_D – N_{bx} transition¹²¹ in the KL–DeOH–H₂O system showed that its behavior is described well by the critical indices of mean-field theory.

Such discrepancies are quite explainable by the difficulty of the experiments in the region of the uniaxial-biaxial nematic transition (narrow temperature interval of existence of the biaxial phase, breakdown of the stoichiometry of composition of the mixture in the process of the experiment, impurities, etc.).

5. CHOLESTERIC

5.1. Influence of chiral additives

As early as 1976 Fujiwara and Reeves¹⁰⁵ studied the influence of adding cholesterol (up to 4.6 mole percent) on

TABLE VII. Change in the character of the phase transition as a function of the molar concentration of CsPFO in water.¹¹⁶

c, mole	$T_{NI} - T_{NL}^*$, K	c, mole	$T_{NI} - T_{NL}^*$, K
0,30±0,005	< 0,025	0,49±0,005	0,07±0,03
0,37	0,03±0,01	0,53	0,10±0,03
0,40	0,035±0,01	0,57	0,25±0,05
0,43	0,06±0,02	0,61	0,60±0,1



FIG. 23. Cholesteric texture induced in the $\text{NH}_4\text{DS}-\text{DeOH}-\text{H}_2\text{O}-(\text{NH}_4)_2\text{SO}_4$ system by adding BS.¹²²

the NMR spectrum in the $\text{DACl}-\text{NH}_4\text{Cl}-\text{H}_2\text{O}$ system. They reported a broadening of the lines in the spectrum with increasing content of cholesterol and interpreted this effect as the formation of a lamellar phase. Lyotropic cholesterics were first obtained two years later by Radley and Saupe.¹²² They used three systems:

1. $\text{CsDS}-\text{DeOH}-\text{H}_2\text{O}-d$ -tartaric acid.
2. $\text{NH}_4\text{DS}-\text{DeOH}-(\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{O}$ + brucine sulfate.
3. $\text{DACl}-\text{NH}_4\text{Cl}-\text{H}_2\text{O}$ + cholesterol.

The concentrations of the chiral additives were the following: tartaric acid from 7.2 to 18.8 mole percent, brucine sulfate (BS) from 0.113 to 8.28 mole percent, and cholesterol from 0.50 to 3.85 mole percent. In all cases typical disordered cholesteric textures were observed. Upon applying a magnetic field in the plane of the specimen a well-ordered texture was formed (Fig. 23), which easily allowed measuring the pitch of the helix. Since the axis of the helix is established parallel to the magnetic field, the diamagnetic anisotropy of the specimens was negative.

The specific rotation was measured experimentally. It was found to be equal to 550 for BS, 1100 for cholesterol, and 1800 deg/cm for tartaric acid.

BS and tartaric acid induce a right-handed helix, and cholesterol a left-handed one. For all the systems a decrease in pitch was found with increasing concentration of the additive, while in the case of cholesterol a subsequent increase was observed.

Yu and Saupe³⁹ studied the influence of BS addition to the $\text{NaDS}-\text{DeOH}-\text{H}_2\text{O}$ system. They obtained cholesterics both from discotics (Ch_D) and calamitics (Ch_C). In both cases the pitch of the helix decreased with increasing concentration of BS. However, the pitch of the helix for Ch_C is almost twofold greater than for Ch_D . A comparison of the magnitudes of the helical pitch presented in this study and in Ref. 122 shows that in the latter the specimens of system 2 possessed a calamitic phase.

An optically active additive also affects the phase-transition temperatures: with increasing BS concentration the temperature of the Ch_D-Ch_C transition was elevated (by approximately 3 °C at 0.2 mole percent BS) and the temperature of the transition to the lamellar phase was depressed.

An optically active additive also affects the phase-transition temperatures: with increasing concentration of BS the

temperature of the Ch_D-Ch_C transition was elevated (by about 3 °C at 0.2 mole percent BS) and the temperature of the transition to the lamellar phase was depressed.

The Ch_D phase is easily ordered by a magnetic field, the axis of the helix being aligned parallel to the field. The Ch_C phase in a strong magnetic field forms an untwisted texture owing to the fact that its helical axis is aligned perpendicular to the field ($\chi_a > 0$) and it is untwisted into a nematic.

Discotic and calamitic cholesteric phases induced in the $\text{KL}-\text{DeOH}-\text{KCl}-\text{H}_2\text{O}$ system by adding cholesterol (0.13–0.26 mole percent) were first observed by Alcantara *et al.*¹²³ In a magnetic field they observed typical cholesteric textures, while by using NMR spectra they found a decline in the degree of micellar mobility as compared with the nematic phases.

Neto, Liebert, and Levelut¹²⁴ have studied in detail the influence of a magnetic field on the properties of lyotropic cholesterics. They worked with the $\text{NaDS}-\text{DeOH}-\text{H}_2\text{O}$ and $\text{KL}-\text{DeOH}-\text{H}_2\text{O}$ systems. They added 0.05% of a ferrofluid to reduce the orienting magnetic field intensity in these systems. It was shown that the ferrofluid does not affect the optical properties of the mesophases that were obtained.

Just as in the previous studies, it was found that for Ch_D the helical axis is aligned parallel to the magnetic field. The specific rotation for a BS concentration of 0.4 mole percent was 380 deg/cm, and it declines with increasing concentration of the chiral additive.

The Ch_C phase is untwisted by a magnetic field. When the latter is applied in the plane of the preparation, a planar nematic texture is formed in several hours. However, after removing the field a texture arises from both sides of the specimen that amounts to straight, parallel lines lying perpendicular to the initial application of the field. They gradually fill the entire specimen, but break down after several hours, and the texture again becomes homogeneous without lines. This homogeneous texture is optically active. In it the helical axis is perpendicular to the plane of the specimen. In this configuration the axes of the cylindrical micelles remain perpendicular to the helical axis and parallel to the plane of the specimen.

The intermediate banded structure arises owing to hydrodynamic instability caused by backflow. The situation here is the following. In the presence of the magnetic field the micelles are oriented along the field and parallel to the support glasses throughout the specimen except at the ends. After removing the field the micelles lying at the ends of the specimen are also oriented by the glass plates parallel to their surfaces. This leads to flow and establishment of a configuration of cylindrical tubes.

The specific rotation for the same concentration of BS in Ch_C is an order of magnitude larger than in Ch_D .¹²⁴

Cholesteric Ch_D phases have also been obtained by adding chiral compounds to the $\text{DSCG}-\text{H}_2\text{O}$ system.^{65,125,143} Numerous chiral additives were used, chosen by the principle of solubility in water and hydrogen-bonding capability. They were added to the starting system in amounts of 1–30%. The most effective (yielding the smallest helical pitch at the least concentrations) proved to be lysine·HCl, phenylalanine, proline, and *d*-glucose. Linear dependences of the reciprocal helical pitches on the concentration of the additives were obtained. Typical values of the pitch were 15–100 μm. Here there was no simple correlation

between the sign of the additive and the sign of the obtained cholesteric. Thus, *l*-alanine and *l*-proline induce right-handed helices, and their *d*-enantiomorphs left-handed helices. It was possible by combining additives to reduce the helical pitch to 3–5 μm . For example, in the DSCG (15.1%–*l*-alanine (9.5%)–*d*-lysine·HCl (9.5%)–H₂O (65.9%) system a helical pitch of less than 3 μm was found. Upon cooling this and analogous systems having a small pitch become colored, since the helical path becomes comparable with the wavelength of visible light.

A usual behavior of the systems in a magnetic field was found: the helical pitch decreases over the course of several hours until it reaches a stationary value equal to about 1/3 of the initial value. Apparently this effect involves the influence of the walls of the thin capillaries, which have a sharply marked untwisting action for cholesterics whose pitch is comparable with the thickness of the capillaries. Here the magnetic field is a stabilizing factor that converts the cholesteric to the equilibrium state.

A report¹²⁶ has been published on finding a blue phase in this system upon adding 26.07% allo-4-hydroxy-*l*-proline. However, it was ascertained later¹²⁷ that the obtained phase is lamellar.

Recently a biaxial cholesteric phase Ch_{bx} has been obtained¹²⁸ by adding 0.18 mass percent BS to a biaxial nematic in the NaDS–DeOH–H₂O system. The mesophase Ch_{bx} exists between Ch_{D} and Ch_{C} in the temperature interval 16–19 °C. The helical pitch of Ch_{bx} equals that of Ch_{D} and the long axes of the biaxial micelles lie parallel to the axis of the helix. Although it was expected *a priori* that the three cholesteric phases would have different values of the helical pitch and the Ch_{bx} mesophase would be analogous in structure to the blue phase, yet, owing to the large energy needed to form the latter, only one structure is realized with the axis of the helix along the long axes of the micelles.

Defects in the Ch_{bx} mesophase have been treated theoretically.¹²⁹ It was shown that, in contrast to uniaxial cholesterics, the λ -disclinations must have nuclei.

5.2. Chiral nematics

We are employing this generally accepted term for compounds that form cholesteric phases, but are not derivatives of cholesterol. The first such cholesteric was the system of the hydrochloride of the decyl ester of *d*- (or *l*-)alanine–Na₂SO₄–D₂O at a concentration of 11.3–11.85 moles of water per mole of amphiphile.¹³⁰ Typical cholesteric-type textures were observed, which became ordered in a magnetic field so that the axis of the helix became parallel to the field ($\chi_{\text{a}} < 0$). The racemic mixture of amphiphiles yields an N_{D} phase in this system. The enantiomorphous amphiphile yields, besides the cholesteric phase, (at lower water content) also an N_{D} phase, which transforms with increasing water concentration to a lamellar phase, and only then to a cholesteric phase. Unfortunately structural data are lacking on this interesting case of polymorphism, whereas this is the first case of coexistence in one system (albeit not in a single compound) of both a nematic and a cholesteric mesophase.

The group of Reeves¹³¹ has obtained a cholesteric calamitic. It is formed in the sodium lauryl-*l*-alanine (29.73%)–Na₂SO₄ (3.04%)–DeOH (4.8%)–D₂O (62.43%) system. The racemic mixture of amphiphiles forms a calamitic nematic phase.

Optically active sodium N-laurylaspartate forms both Ch_{D} and Ch_{C} phases.¹³² They arise in the presence of an electrolyte and decanol. The Ch_{C} phase is formed in the Na₂SO₄ (2.99 mole percent)–H₂O (70.38%)–D₂O (22.11%)–DeOH (1.29%) system, and the Ch_{D} phase in the NH₄Cl (5.91 mole percent)–H₂O (68.05%)–D₂O (20.42%)–DeOH (1.53%) system. The racemic compounds form N_{C} and N_{D} phases, respectively.

The Ch_{D} phase is well oriented in a magnetic field with the helical axis parallel to the field. A typical helical pitch lies in the range 60–80 μm . The Ch_{C} phase is oriented by a magnetic field with formation of typical λ^+ and τ^+ disclinations.

Continuing these studies on cholesterics having chiral anions, Covello *et al.*¹³³ obtained salts of other amino acids (serine, valine) and found that they also form typical cholesteric phases in aqueous systems. A cholesteric with a chiral cationic amphiphile has recently been obtained by Goozner and Labes.¹³⁴ They synthesized D-(2)-octylammonium chloride (D-OACl) and studied an aqueous system containing DACl and NH₄Cl in addition to this compound. A cholesteric Ch_{D} phase was found at the following concentrations: D-OACl (17.7%), DACl (36.6%), NH₄Cl (5.9%), H₂O (39.8%). The cholesteric phase exists in the temperature range 16–32.5 °C. A lamellar phase is formed at lower temperatures and an isotropic phase at higher. The cholesteric phase is formed very slowly from the smectic. Several hours are needed to reach thermal equilibrium. The helical pitch increases linearly with increasing temperature: it is ~35 μm at 16 °C, and 45 μm at 32 °C. Moreover, the pitch is very sensitive to the concentration of electrolyte: a twofold increase in its concentration decreases the helical pitch. Moreover, one can control the helical pitch by adding optically active glucose.

A chiral nematic has been obtained¹³⁵ in the potassium N-dodecanol-*l*-alaninate–DeOH–H₂O system. It was shown by NMR with this example that a change in the concentration of amphiphile and DeOH alters the dimensions of the micelles. This is accompanied by a change in the helical pitch: the helical pitch increases with increasing concentration of amphiphile, and decreases with decreasing concentration of DeOH.

In closing this Section we point out the formation of a cholesteric phase in an aqueous solution of the polysaccharide schizophyllan.¹³⁶ Although the latter is a lyotropic liquid crystal, yet it belongs generally to the high-molecular-weight compounds.

CONCLUSION

Broad studies of lyotropic nematics are just beginning. And although important results have already been obtained, the most interesting material still lies ahead.

First of all, one must establish the connection between the nature and structure of the molecules constituting the system and the possibility of formation of certain types of mesophases. At present, as in the time of Leman for thermotropic liquid crystals, all lyotropic nematics have been obtained fortuitously, and there is yet no guiding idea that might indicate the pathway of "molecular construction." A more special, but very important problem is to obtain non-aqueous nematics having a large electric resistivity. These systems would make it possible to extend to lyotropic nematic

tics the entire arsenal of means of study of the dielectric and electrooptic properties that have made such a great contribution to studying thermotropic liquid crystals.

Undoubtedly the physics of lyotropic nematics will expand our view of the molecular mechanisms of all the physical properties of liquid crystals. It is already evident in studying the elastic, diamagnetic, dielectric, and optical properties of lyotropic nematics that one must take into account the contribution made by the properties of the molecules of the amphiphiles, counterions, and solvent, as well as the characteristics of the micelles themselves as a whole. Further studies in this field will enable a close approach to be made to the construction of a molecular physics of liquid crystals.

Here the most important problems are the construction of a complete phenomenological theory of the physical properties of uniaxial and biaxial nematics, the elucidation of the structure of the micelles and the changes that they undergo in phase transitions, and the accumulation of experimental data on the entire complex of physical properties, including the electrooptic properties.

Studies of lyotropic nematics in earnest are just beginning. Therefore it is not yet clear what practical application they can find. However, already lyotropic nematics are being successfully applied as solvents in studying NMR spectra. Perhaps they will find application as ordered solvents enabling one to control chemical reactions that occur in them.

¹¹Everywhere below, unless specially indicated, the concentration is given in mass percent.

¹²Electron-microscopic studies¹³⁸ have shown that the transition to the lamellar phase involves only partial combination of discotic micelles.

¹³The value of the diamagnetic anisotropy has been measured¹³⁹ for the DACl (43.2–45%)–NH₄Cl (4.8–5%)–H₂O (52–50%) system in the discotic phase. It was found that χ_a varies from $2 \cdot 10^{-9}$ near the nematic-isotropic liquid transition to $5 \cdot 10^{-9}$ CGS units near the nematic-lamellar phase transition.

¹⁴Recently two crucial experiments have been proposed¹³⁷ that enable one in principle to distinguish biaxial phases formed by a mixture of discotic and calamitic micelles from genuine biaxial phases. The experiment consists in orienting the micelles with a field and with shear flow. In the light of this, the analysis of certain synchrotron experiments compels us to assume that the biaxial phase is genuine, at least in the LK–DeOH–D₂O system.

¹⁵In the trans- and gauche-conformations the substituents in the rotational isomers lie respectively opposite and alongside one another.

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