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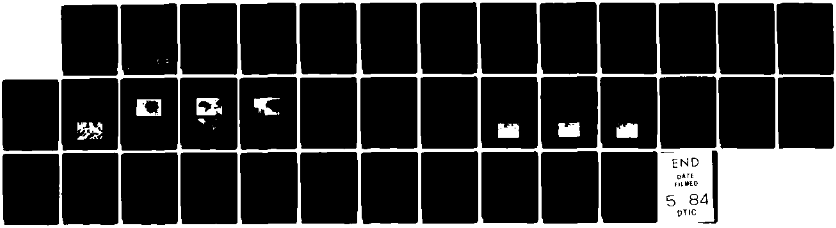

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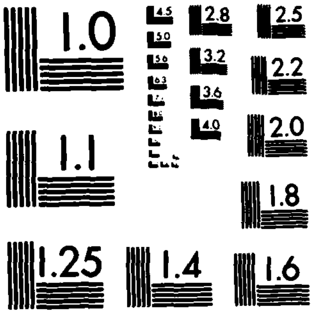

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FLUORESCENT GUESTS IN THERMOTROPIC AND CHIRALITY IN LYOTROPIC LIQUID CRYSTALS

FINAL REPORT

M. M. LABES

MARCH 1984

U. S. ARMY RESEARCH OFFICE

DAAG29-81-K-0003

DEPARTMENT OF CHEMISTRY
TEMPLE UNIVERSITY
PHILADELPHIA, PENNSYLVANIA 19122

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Three problems were examined under this program. Firstly, a novel electro-optic display concept has been developed in our laboratory involving the incorporation of fluorescent (emissive) guest molecules into a cholesteric liquid crystal host. Improvements were made in the contrast ratios of such displays via electrochemical quenching. Secondly, a fundamental study was completed on the nature of phase transitions in thermotropic liquid crystals confined in porous polymer films. Finally, new lyotropic liquid crystals were investigated to (a) try to develop non-aqueous lyotropic media, and (b) investigate

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20. orientational ordering and solubility of guest molecules in lyotropic nematics and cholesterics.

STATEMENT OF THE PROBLEMS STUDIED

Three problems were examined under this program. Firstly, a novel electro-optic display concept has been developed in our laboratory involving the incorporation of fluorescent (emissive) guest molecules into a cholesteric liquid crystal host. Improvements were made in the contrast ratios of such displays via electrochemical quenching. Secondly, a fundamental study was completed on the nature of phase transitions in thermotropic liquid crystals confined in porous polymer films. Finally, new lyotropic liquid crystals were investigated to (a) try to develop non-aqueous lyotropic media, and (b) investigate orientational ordering and solubility of guest molecules in lyotropic nematics and cholesterics.

SUMMARY OF IMPORTANT RESULTS

Fluorescent Liquid Crystal Cells

We have demonstrated that useful emissive liquid crystal displays can be constructed by incorporating appropriate rare earth chelates, fluorescent hydrocarbons and organo-metallic complexes into cholesteric and nematic liquid crystals. Most of these systems require uv backlighting to stimulate the emission, although a few systems seem possible with so-called "day-fluors", which both absorb and emit in the visible. During this program, several day-fluors were investigated but no completely satisfactory system was developed. We were able to show that contrast ratios of such fluorescent cells could be enhanced by combining a dc electrochemical quenching of fluorescence with a scattering-nonscattering ac field induced transition.

Liquid Crystals in Polymer Films

When a positive dielectric anisotropy liquid crystal is allowed to fill the 0.2-12 μm diameter cylindrical pores of the polymer thin film Nuclepore, the liquid crystal is forced, via wall effects, to adopt an alignment in which the center of the pore is a "singularity", i.e. the director or long axis is everywhere aligned with respect to the walls, except at the core. The behavior of these singularities in electrical fields was studied and found to display, in some cases, a critical destruction at a characteristic voltage. Transition temperature scaling with pore size was studied and models for understanding the depression in these transition temperatures as a function of pore size were developed.

Lyotropic Liquid Crystals -- Non-Aqueous

Although nematic lyotropic behavior is common in aqueous systems, the behavior is rare in non-aqueous systems. Development of the latter would allow for interesting electro-optic effects with totally different elastic constants for the media involved and therefore the possibility of totally different time frames for response and decay. The simplest non-aqueous nematic lyotropic system was accidentally observed in 1973 by Hoppe, consisting of a few wgt % of a fatty substituted urea in decane. A basic study was completed to understand this system. Unfortunately even at extremely low concentrations the nematic phase in this system is a gel which can be perturbed mechanically but not electrically. The study of this system has helped us to have a better understanding of the problem to guide future work into more appropriate systems.

Optical Spectroscopy in Aqueous Nematic Lyotropic Liquid Crystals

Since lyotropic nematic liquid crystals are readily oriented by magnetic fields, optical spectroscopy in such matrices allows for fundamental studies of polarization of water soluble molecules as well as the use of these molecules in probing the structure of the lyotropic phase itself. During this grant, we have initiated a broad study of such effects using UV-VIS-NIR, fluorescence and FTIR spectroscopy. The first paper (preprint) dealing with a study of rod-like and disc-like water soluble dyes is incorporated in this report. This work is to be continued in current studies in our laboratory.

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Electrochemical enhancement of contrast ratio in fluorescent liquid crystal cells

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(Received 26 July 1982; accepted for publication 7 September 1982)

Europium chelates in cholesteric or nematic phases show a brilliant red (612 nm) fluorescence which can be quenched electrochemically. Either cathodic or anodic quenching can occur depending on total electrolyte concentration, the latter process involving oxidation of the ligand. By combining the electrochemical effect with a field induced cholesteric–nematic transition, enhanced contrast ratios can be achieved for electro-optic display.

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INTRODUCTION

Cholesteric and nematic liquid crystal electro-optic cells can be prepared incorporating fluorescent guest molecules.[1–6] If fluorescent guests such as a europium chelate are employed, UV back lighting is required to cause the cells to be emissive. "Day-Fluors" can also be incorporated which both absorb and emit in the visible.[7] In all of these effects, contrast between "on" and "off" states depends on either a scattering nonscattering transition, the more emissive state being the scattering state of the liquid crystal, or orientation of a polarized guest molecule.

Another way of obtaining contrast in the fluorescence emission of a rare earth chelate is to quench the emission via an electrochemical process. For example, Hamblen and Clarke[8] have succeeded in preparing display panels containing a europium chelate in an isotropic liquid. In the panels, the europium chelate is dissolved in a moderately polar solvent such as N,N-dimethylformamide, a small amount of an organic salt is added to enhance the conductivity, and a dc potential is applied. A cathodic reduction of Eu^{+3} to Eu^{+2} occurs, fluorescence is quenched, and fluorescence returns upon reversal (oxidation of Eu^{+2} to Eu^{+3}).

In this work, electrochemical fluorescence quenching of Eu(III) chelates in liquid crystals is explored in nematic and cholesteric phases. By combining electrochemical quenching with the previously described scattering–nonscattering (cholesteric–nematic) transition, improvements in contrast ratios for electro-optic display are achieved.

EXPERIMENTAL

As host materials, ROTN-100 (Hoffmann-La Roche), a mixture of benzoyloxybenzoate esters, E_8 (E. Merck), a mixture of substituted biphenyls and terphenyls or PCH-1083 (E. Merck), a mixture of phenylcyclohexanes, were employed. Cholesteric phases were prepared by doping ROTN-100 with cholesteryl nonanoate (CN). Tris-[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanediono] europium III (EuTTA) was taken as the fluorescent guest molecule for all measurements. It shows a brilliant red fluorescence peaking at about 612 nm, with an effective excitation band of 320–380 nm. The measurements were done exciting at 360 nm. Some other europium compounds were used to investigate the nature of the anodic reaction that takes place in the presence of [illegible]: 1. europium(III)tris-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione; 2. europium(III)tris-2,2,6,6-tetramethyl-3,5-heptanedione; 3. tris-[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III). Compounds 1 and 3 hardly show any fluorescence and compound 2 leads to quenching at the anode in a manner similar to that described below for EuTTA. Tetrapentylammonium iodide (TPAI) was used as a salt to improve the conductivity of the liquid crystal. Several other salts were used to investigate the nature of the anodic reaction: 1. tetrabutylammonium bromide; 2. tetramethylammonium fluoborate; 3. tetramethylammonium bromide; 4. tetraethylammonium perchlorate; 5. tetramethylammonium perchlorate; 6. tetrabutylammonium nitrate; 7. tetrahexylammonium perchlorate; 8. tetrabutylammonium perchlorate; 9. tetrabutylammonium hexafluorophosphate. Salts 1 and 2 do not dissolve in liquid crystals sufficiently, whereas salts 3 to 9 lead to quenching at the anode in a manner similar to that described below for TPAI.

The liquid crystalline material was sandwiched between two untreated tin oxide coated glass plates, by the use of spacers, and the cell was mounted on an optical bench for transmission measurements. The thickness of the spacers was 23.4 μm. The UV light source for fluorescence measurements consisted of a 150 W xenon lamp (Bausch & Lomb) coupled to a grating monochromator (Bausch & Lomb high intensity grating monochromator). The intensity of the fluorescence was measured at room temperature with a Schoeffel GM-200 double monochromator and an RCA 4840 pho-

TABLE I. Contrast ratios for mixtures of E_8, EuTTA, and TPAI.

EuTTA (wt. %)	TPAI (wt. %)	Contrast ratio	Voltage dc	Polarity
12	0	3	5	-
		4	10	-
20	0	3	5	-
		5	10	
20	0.8	8	3.5	+
12	0.8	8	3.5	+
12	0.4	7	3.5	+
12	0.2	4	3.5	+
12	0.1	2	3.5	+

TABLE II. Contrast ratios for mixtures of ROTN-100, EuTTA, and TPAI.

EuTTA (wt. %)	TPAI (wt. %)	Contrast ratio 3.5 V dc	Polarity
0.5	0.6	4	+
1.0	0.6	14	+
1.5	0.6	35	+
2.25	0.6	25	+
2.75	0.6	12	+

tomultiplier tube which was connected to a Photovolt photometer.

RESULTS AND DISCUSSION

Tables I and II summarize data on the measured contrast ratios for the 612 nm emission of dc operated cells. When no supporting electrolyte is added to the liquid crystals, the conductivity is quite low and 5–10 V must be applied in order to observe quenching. Quenching occurs at the cathode in ~3 sec and is consistent with the reductive process $Eu^{+3} + e \rightarrow Eu^{+2}$ discussed by Hamblen and Clarke.[8] If the field is switched off, the cell recovers most of its fluorescence, but very slowly (minutes). If the field is reversed, however, the fluorescence recovery is more rapid (~3 sec).

Cells may be operated at lower dc voltages if supporting electrolyte is added. Data are presented for the salt TPAI, although many other salts (see Experimental) may be utilized with essentially similar results. As the conductivity is increased, much better contrast ratios are obtained at 3.5 V dc. However, the quenching now occurs at the anode exclusively. This anodic process is also reversible. In the presence of salt, switching occurs in 500 msec–2 sec. The maximum amount of TPAI that could be dissolved in E_8 was 0.8%. Decreasing the percentage of the salt decreased the contrast ratio. The polarity of the electrode at which quenching is observed changes back to the cathode process when the percentage of salt was reduced below 0.05%. The reversal of polarity with the addition of salt was also observed in the other liquid crystals studied, PCH-1083 and ROTN-100 (Table II). Various concentrations of EuTTA were studied using 0.6% of TPAI. The quenching took place at the anode in all cases, and the contrast ratio was a maximum (35) at 1.5% EuTTA. ROTN-100 based samples showed an overall decrease in fluorescence when the voltage was increased above 4 V, whereas E_8 based samples were stable to about 6 V.

TABLE III. Contrast ratios of cells containing 3% EuTTA in ROTN-100, to which TPAI and CN are added, operated in three modes. dc voltage applied was 3.5 V for all quenching effects.

			Contrast Ratios		
TPAI (wt. %)	CN (wt. %)	ac (V)	Quenching	Ch→N transition	Quenching + Ch→N transition
0.1	0	0	2.8	...	2.8
0.1	4	20	1.8	1.3	3.7
0.1	8	35	2.25	1.7	4.5
0.05	0	0	1.75	...	1.75
0.05	4	20	1.6	1.3	2.0
0.05	8	35	1.7	1.7	2.7
0.05	12	45	2.2	2.2	4.0
0.05	16	55	2.3	2.3	4.2
0.05	20	65	2.0	2.3	4.0

The anodic oxidative process most likely involves an electrochemical attack on the organic ligands. Several attempts were made to control this electrochemical event or to inhibit it. All of the variations in salt or ligand were of little or no consequence to the anodic attack. Careful purging of samples of moisture and oxygen caused only minor suppression. However, when a specific inhibitor for sulfur oxidation was added, the anodic reaction was indeed suppressed, and the cathodic process was observed. The inhibitor employed was dithiothreitol (Sigma Chemical Co.) which is reported to stabilize sulfur compounds.[9] Thus it seems likely that the sulfur containing ligand in EuTTA is being (reversibly) oxidized to the sulfoxide.

Since fluorescent electro-optic display with good contrast can be achieved via inducing a scattering–nonscattering (cholesteric–nematic) transition,[2-5,7] an attempt was made to combine the dc electrochemical effect (quenching) with such an ac induced transition. The scattering effect leads to an extremely bright display as compared to that in an aligned liquid crystal state. Chirality in the nematic mixture containing EuTTA and the salt TPAI was obtained by adding cholesteryl nonanoate to it in various proportions. Low percentages of salt (0.1%, 0.05%) were taken to keep the conductivity low. This avoids excess heating upon application of the higher ac voltage required for conversion from the cholesteric to nematic state. The contrast is obtained by switching from a state of enhanced fluorescence (obtained by application of a reverse bias dc voltage on the scattered cholesteric state) to the quenched nematic state (obtained by simultaneous application of dc and ac). Table III indicates that the simultaneous application of a dc voltage (for the quenching effect) and an ac voltage (for inducing a cholesteric-nematic transition) gives a contrast better than either of the two effects alone.

This work was supported by the U.S. Army Research Office (Durham) under Contract No. DAAG29-81-K-0003. Helpful discussions with Dr. S. Takenaka gratefully acknowledged.

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A Nonaqueous Lyotropic Nematic Gel

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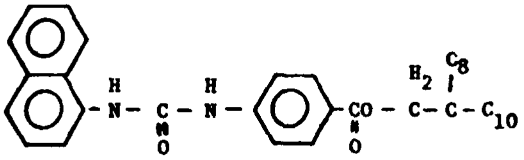
A nematic gel of a fatty substituted urea (3–4 Wt.%) in decane is studied optically and thermodynamically. Typical nematic schlieren textures are observed. Shear and compression forces distort these textures, but applied electric and magnetic fields are ineffective until one reaches the gel-isotropic transition temperature.

INTRODUCTION

Nematic lyotropic phases are frequently encountered in aqueous systems, but are extremely rare in other solvents. There have been, however, several recent observations of non-aqueous lamellar lyotropic phases.[1] Excluding polymeric systems,[2] the only nematic gel of which we are aware was reported by Hoppe, who observed anisotropic optical properties of gels of sunscreening substances in hydrocarbon solvents.[3,4] Although most of the preparations were lamellar phases, a "micellstructur" was reported for a solution of 2% of compound *I* (below) in heptane. In this paper, optical microscopy and differential scanning calorimetry (DSC) are applied to a study of *I* in decane.



I

4-[[(1-naphthalenylamino)carbonyl]amino]-benzoic acid,

2-octyldodecylester [Index Registry #34913-82-1]

We use the term nematic gel here to denote: (a) the occurrence of typical nematic schlieren textures in thin capillaries (~0.3 mm); (b) a system which undergoes elastic distortions in response to shear and compressive forces, or electric and magnetic fields.

EXPERIMENTAL

A small sample of *I* was kindly supplied to us by Hoppe.[11] 3–5 mg were weighed into polypropylene tubes and the appropriate amount of decane was then added. After sealing, the sample was heated and stirred until the solid matter dissolved. Samples for optical studies were made using 0.3 mm rectangular glass capillaries from Vitro-Dynamics, Inc., New Jersey, by heating the bulk sample to the isotropic phase and allowing capillary action to draw in the material. The sample was then sealed with a micro-torch. Reasonable consistency in transition temperatures was obtained. Some samples were made with a slide and coverslip. Only results on fresh samples made in this way are reported.

Optical observations were made between crossed polars on a Nikon microscope, whereas the thermodynamic data were obtained on a Perkin-Elmer DSC-2C differential scanning calorimeter (DSC) at relatively rapid (10–20°/min) heating rates in order to visualize the small enthalpies.

RESULTS AND DISCUSSION

Table I summarizes data on optically and thermodynamically observed transitions. Nematic to isotropic transition temperatures (T_{NI}) were difficult to obtain optically because of the small birefringence and represent the visual observation of $\Delta n \rightarrow 0$. The DSC measurements along with macroscopic observation of samples in a stirred water bath confirm the existence

TABLE I

Sample compositions, transition temperatures, and enthalpies of I in decane

Wt. % I	Molar ratio $\frac{\text{decane}}{\text{I}}$	T_{NI} Optical °C	T_{NI} DSC °C	ΔH Kcal mole^{-1}
3.0	135.1	71	81	.17
3.5	114.9	71	80	.10
4.0	100.0	73	78	.08
5.0	79.4	74	76	.24

of a gel-fluid transition T_{GI} which does not appear to coincide with T_{NI} observed optically.

Figure 1 demonstrates the typical nematic schlieren textures obtained. These textures typically developed when the sample was quenched from the isotropic phase to room temperature rapidly.[4] When stored at room temperature, the texture did not relax over a three-week period of observation. The brushes around the singularities did not move in response to ±10° temperature changes within the nematic gel phase. Even close ($T_{NI} - T \cong 2°$) to the transition, mobility of the brushes was very small in comparison with ordinary thermotropic nematics. As $T \rightarrow T_{NI}$ the already small birefringence ($\Delta n \sim 10^{-4}$) decreases uniformly over the sample. Figure 2 shows a nematic-isotropic transition under strong illumination.

Figure 3 shows the result of a shear applied to a sample with a coverslip. The textures in Figure 4 arise from shear induced orientation as the isotropic liquid of low viscosity is drawn into a cold capillary. Noticeable in both Figures 3 and 4 are faint striations running perpendicular to the direction of shear, and are possibly hydrodynamically induced defects. In general, the director field appears "locked" to the amorphous gel lattice. At room temperature, the director does not reorient in a magnetic field of 25 k Gauss applied in any of three orthogonal directions over a period of three days. In a large applied electric field of ~ 10^7 V/cm on a 23 μm

FIGURE 1 Nematic schlieren texture of 3.5% I in decane at 22. Magnification 130X, crossed polars.

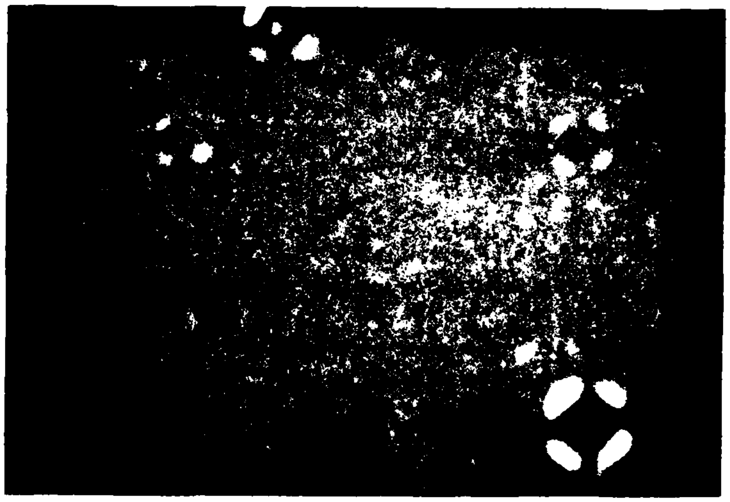
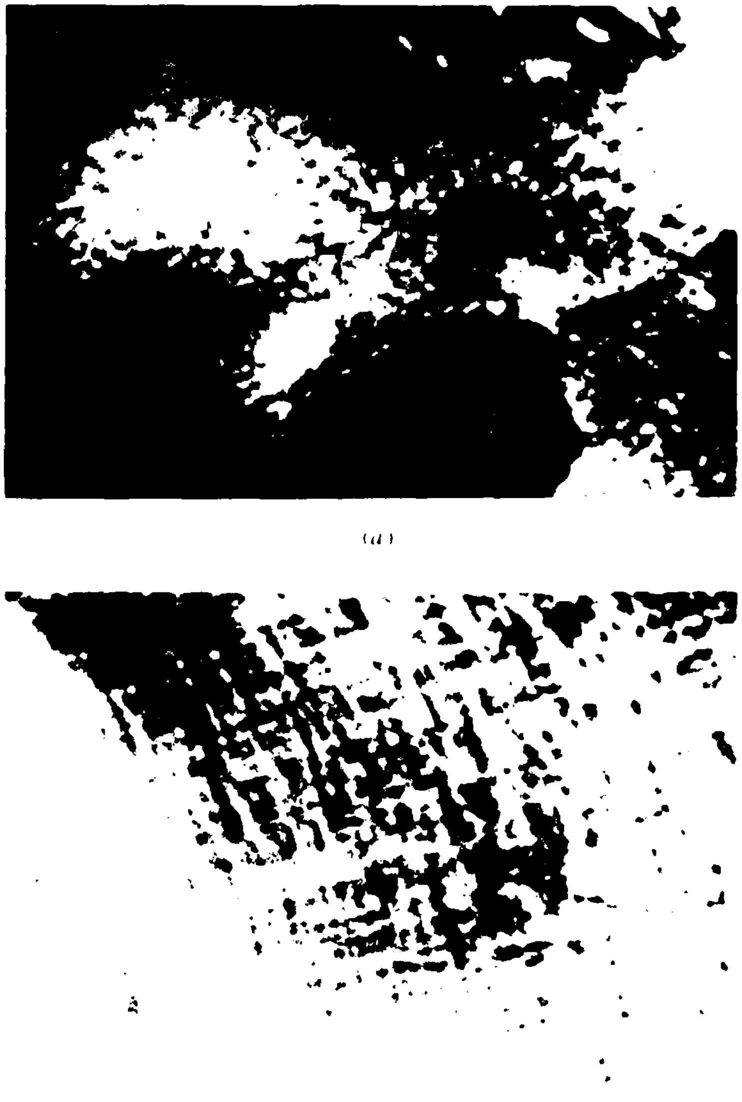


FIGURE 2 Nematic → isotropic transition of 3.5% *I* in decane at 71.4°. Magnification 130×, crossed polars.

thick cell no observable instability occurred until $T \approx T_{GI}$ when electrohydrodynamically induced turbulence occurred. By periodically varying an applied pressure of $\sim$0.5 Kg cm^{-2} on the coverslip or the voltage in the electrooptical cell (condenser forces causing the compression), the elastic response of the system was qualitatively verified to quite low frequencies ($\sim$1 – .1 sec^{-1}) by observing the relative distances between dust particles and bubbles.

DSC measurements rarely show a peak on cooling. On slowly cooling samples from $T > T_{GI}$ to room temperature, the samples remained optically isotropic but the gel properties were retained. After 24 hours at room temperature they were still optically isotropic. The samples were then placed in an oven at 55° and within three days the samples became uniformly birefringent. Textures obtained in this way showed little structure except for an occasional +½ singularity with broad brushes along the capillary edge. Supercooling into an isotropic gel is the most likely explanation of these effects.

It seems most likely that the nematic gel is composed of extended inverse micelles held together by dispersion and dipolar forces. If this is true, the existence of textures with splay deformations implies either the micelles are finite in extent, or break apart and reform easily in response to thermal fluctuations and diffusive processes. Why such a small amount of a rela


(*a*)

(*b*)

FIGURE 3 Shear in [illegible] of 3.5% *I* in decane at 22 Magnification 62X crossed polars. Sample [illegible] horizontal direction by moving [illegible] (a) Before shearing. (b) [illegible]

FIGURE 4 Striated birefringent texture of 3.5% *I* in decane at 22. Magnification 62X, crossed polars. Sample flow into the capillary occurred in the horizontal direction.

tively low molecular weight amphiphile is able to establish an extended micellar phase with a high viscosity is the interesting materials question which remains unanswered.

Acknowledgment

We wish to thank Dr. U. Hoppe for furnishing us samples of these compounds. This work was supported by the U. S. Army Research Office under Contract No. DAAG29-81-K-0003.

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Liquid Crystals in Cylindrical Pores: Effects on Transition Temperatures and Singularities

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(Received March 25, 1983)

Positive dielectric anisotropy liquid crystals are studied in cylindrical pores in a 10 μm thick polymer membrane of diameters 0.2–12 μm. Transition temperature depressions increase with decreasing pore size. Singularities of strength 1 are observed in the center of the pores, accompanied by some strength ½ singularities. By applying a voltage across the membrane, the $S = 1$ singularities are shown to be "escaped" singularities. $S = +½$ singularities show a critical destruction at a characteristic voltage.

INTRODUCTION

Porous media[1] and thin films[2,3] have provided convenient systems to measure the effect of surface interactions on the physical properties of liquid crystals. For example, for sufficiently small pore radius the isotropic-nematic transition temperature, T_{NI}, decreases while the width of the transition region increases.[1] In general, a rounding or weakening of thermodynamic singularities may occur in finite systems.[4] In thin films, T_{NI} is predicted to increase with decreasing film thickness,[5] $\sim .1°C$ for 10^3 Å. However, experimental investigations show either little effect[2] or a decrease[3] in T_{NI} for thin films.

A particularly appropriate porous membrane for investigation of these effects is the polycarbonate film "Nuclepore" which has been "drilled" by nuclear bombardment to create a series of cylindrical pores of quite uniform size (Figure 1). These pores are almost perfect cylinders with diameters ranging from 0.1 μm to 12 μm. Via optical microscopy, it is possible to observe these pores filled with liquid crystals in the size range 0.2 μm to

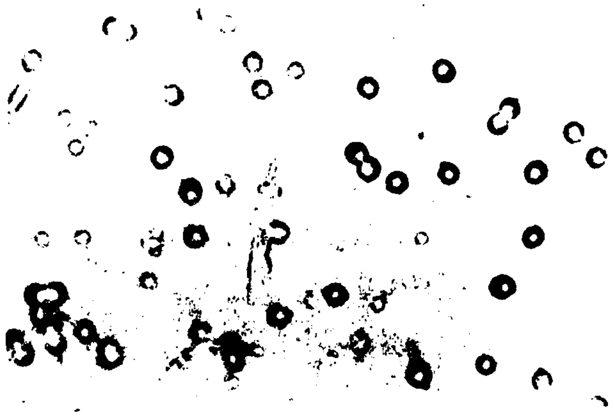

FIGURE 1 Photomicroscopic view perpendicular to microporous membrane Unpolarized light, magnification ≈ 375 X.

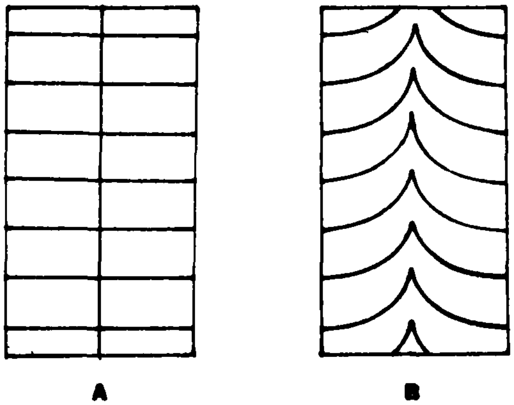

FIGURE 2 Side view of cylindrically symmetric director fields in capillary: (a) $S = +1$ singularity; the director field is in a radial direction everywhere except in a core region surrounding the center where the director field is not defined; (b) "escaped" $S = +1$ singularity with no core.

12 μm, and in this paper data are presented on transition temperature depressions, the behavior of singularities of strength 1 and ½ within the pores, and the effect of electric field on the strength 1 singularities. Studies of the stability of $S = +1$ singular lines[6] in cylindrical capillaries have indicated that deviations of the director field from a planar solution always occur for sufficiently large radius. In this case, the director field corresponds to that shown in Figure 2, and upon application of an electric field

parallel to the axis of the capillary, one might expect a continuously tunable birefringence for a positive dielectric anisotropy material.

EXPERIMENTAL

The liquid crystals employed are p-cyano-p′-*n*-nonylbiphenyl (K27, T_{NI} 50.3°C) and p-cyano-p′-*n*-pentylbiphenyl (K15, T_{NI} 35.3°C) obtained from EM Chemicals, both having a positive dielectric anisotropy. The Nuclepore membranes are 10 μm thick and the pores are essentially perpendicular to the film. Pore density increases with decreasing pore size, *e.g.* 1 μm, density $\cong 5 \times 10^{6}$ cm^{-2}; 0.2 μm, density $\cong 5 \times 10^{7}$ cm^{-2}.

A sample is prepared by allowing a small amount of isotropic liquid crystal to wet the membrane. They are quickly adsorbed indicating a good mutual attraction between the liquid crystal and the membrane. The membrane is then pressed between a clean glass slide and coverslip and placed in a Mettler hot stage. The sample is allowed to sit in the isotropic phase for approximately ½ hour. Uncovered samples left overnight exposed to air showed no measurable shift in transition temperature, either in bulk or confined to the membrane pores. The Nuclepore membrane was used as obtained. No observable change occurred in transition temperatures of liquid crystals when either new membrane material or membrane material exposed to the atmosphere ($T = 22$°C) for 24–48 hours are used.

Figure 3 gives the transition temperature depression determined on both cooling and heating the samples as follows. In the isotropic phase, with the sample between crossed polars, the membrane could be oriented so that an

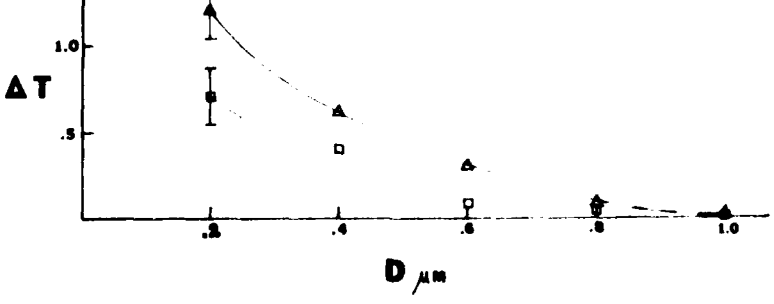

FIGURE 3 Nematic-isotropic transition temperature depression ($\Delta T = T_{\mathrm{bulk}} - T_{\mathrm{confined}}$) vs pore diameter.
△ $K27$, T_{NI} = 50.3°C (bulk)
□ $K15$, T_{NI} = 35.3°C (bulk).

almost complete extinction of light could be obtained. The polymer membrane in an oriented birefringent material, presumably because of stretching during manufacture. On decreasing temperature, the isotropic-nematic transition in the smaller pores (< 1 μm) is observed as a sudden non-uniform increase in the birefringence (Δn) over the whole field of the microscope. The non-uniformity in Δn is due to both a spatial distribution in pore sizes and to incomplete filling of the pores by liquid crystal. It is possible, however, to select a relatively uniform area for observation. Material on the surface of the membrane also underwent an isotropic-nematic transition which could be distinguished from the pore transition in two ways: (1) it generally occurred at the same temperature for different pore size; (2) a nucleation front could be observed continuously sweeping across the microscope field. Portions of the sample were chosen for observation in which these effects were minimized.

RESULTS AND DISCUSSION

In the 12 μm diameter pores we first observed, upon decreasing T, an increase in Δn on the perimeter of a pore where nucleation of a nematic phase by the pore surface began.[7] As T is lowered to just below T_{NI}, a texture corresponding to Figure 4 resulted. Figure 2 is a rationalization of the occurrence of "escaped" $S = 1$ singular lines[8] for the director field in the pores.

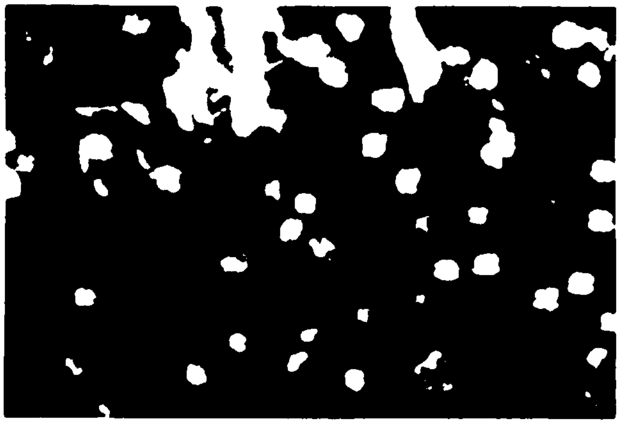

FIGURE 4 Membrane with 12 μm pores filled with $K27$. $T = 50.2$°C, magnification $\approx 375\ X$, crossed polars. Note singularities in pores at extreme right of picture

Some time ago Meyer[9] and Cladis and Kleman[6] had demonstrated that a lower free energy is attained by a three dimensional cylindrical system if a coreless solution to the elastic equations is selected. Such a solution applies strictly to an infinite cylinder; however, the coreless solution will still appear in two dimensions as long as the director is not constrained to a plane.[10] Surface tension effects at the ends of a short cylinder should be taken into account for a proper determination of the director field.

That the observed $S = 1$ singularities are "escaped" singularities can be demonstrated by a method suggested by Meyer.[9] Electro-optic cells were prepared of 36 μm thickness and a 10 Kc voltage was applied across the cell. Upon application of 30 V parallel to a pore axis, the birefringence is observed to slightly decrease in the center of a pore (Figure 5). With continuously increasing electric field (up to 100 V) the decrease in birefringence continuously spreads to the perimeter of the pore.

We also observe $S = +\frac{1}{2}$ singularities in the pores under increasing electric field. Above a critical voltage, the director field discontinuously "snaps" to a lower energy configuration to accommodate the electric field. Upon lowering the electric field below a critical value, the director field in many pores relaxed back to the original configuration ($S = \pm\frac{1}{2}$).

The proximity of the smectic A phase in K27 ($T_{N \to SA} = 48.8°$, bulk value) rendered the escaped structure unstable with decreasing temperature, due to anomalous increase in the bend and twist elastic constants K_{33} and K_{22}. In a few pores, true $S = 1$ singularities were observed in the smectic A

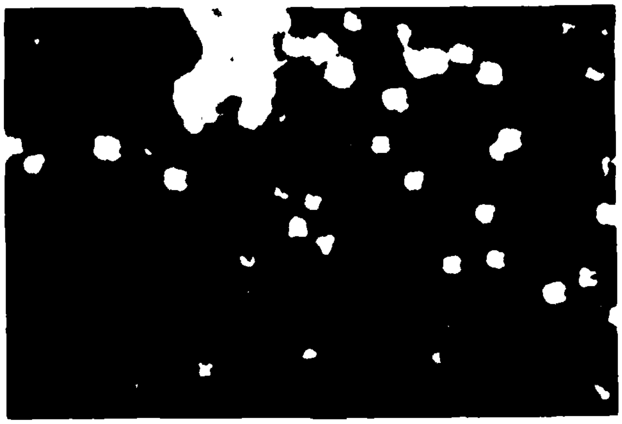

FIGURE 5 12 μm porous membrane in Figure 4 under the influence of an applied voltage (30 volts at 10 kilocycles). The electric field is perpendicular to the membrane. Membrane thickness $\simeq$ 10 μm.

phase. In the A phase, the fan texture aligned with the stretching direction of the membrane (Figure 6).

The temperature depression (Figure 3) is likely due to finite size effects (barring impurity effects). Two of the possible mechanisms involved are: (1) The assumed well aligned nematic material on the surface of the cylinder acts as an imposed deformation. The nematic material in the interior of the cylinder must arrange to minimize the elastic energy in accordance with this distortion. (2) Surface tension effects may cause temperature depression.

We may simplify mechanism (1) by considering only fluctuations in S, the nematic order parameter, to arrive at a formula for ΔT, the temperature depression. The free energy density for $T > T_{NI}$ is[10]

$$g = a_2S^2 + a_3S^3 + a_4S^4 + \frac{\kappa_0}{2}(\nabla S)^2 + \cdots \tag{1}$$

where $a_2 = a_{20}(T - T^*)$, T^* is the lower temperature boundary of the N–I two phase region (supercooling temperature), a_{20}, a_3, a_4, and κ_0 are constants. The nematic-isotropic transition temperature is defined as $T_{NI} = T^* + a_3/4a_{20}a_4$. For $T > T_{NI}$ keeping only quadratic terms in g, we find the correlation function for fluctuations in S of wave number q is[11]

$$G(q) \sim \left(a_2 + \frac{\kappa_0}{2}q^2\right)^{-1}.$$

FIGURE 6 Smectic A phase of surface film. Pore diameter 12 μm, T = 48.5°C, magnification 375 X. Note alignment of the fan texture

In an infinite system we let $q \to 0$ and identify[11] the susceptibility $\chi \sim G(0)$. χ has a singularity at $T = T^*$. In a finite system, however, $q \to q_o = 2\pi/R$, where R is now the pore radius. Thus we can write

$$\chi \sim (T - T_R)^{-1}$$

where $T_R = T^* - \Delta T$ and

$$\Delta T = \frac{\kappa_o}{2a_{20}}\left(\frac{2\pi}{R}\right)^2 = 4\pi^2 T^*\left(\frac{\xi_o}{R}\right)^2 \qquad (2)$$

where $\xi_o^2 = \kappa_o/2a_{20}T^*$.

Assuming $\kappa \simeq \kappa_o S^2$ where κ is a Frank elastic constant, we estimate a value for κ_o using $\kappa(T \leqslant T_{NI}) \simeq .5 \times 10^{-6}$ dyne and $S \simeq .3$ as appropriate values for cyanobiphenyls;[12] thus, $\kappa_o \simeq 5.5 \times 10^{-6}$ dyne. Also $a_{20} \simeq 9.0 \times 10^5$ erg/cm^{3}K,[13] so that $\xi_o \simeq 10$ Å. Substituting $R \simeq 10^3$ Å, $T^* \simeq 310$ K, we obtain $\Delta T \simeq 1.2$ K. Thus the temperature scale is shifted downwards by $\approx .4\%$.

The crude method used to derive Eq. 2 ignores interaction of fluctuations and overestimates the effect of boundary conditions treating the imposed deformation as a body force, not a surface force. Eq. 2 represents the temperature shift in a free energy per unit volume for an infinite system with an imposed deformation of wavelength R. This estimate is therefore to be used with caution.

For the second mechanism involving surface tension effects the formula[14]

$$\Delta T = \frac{\Delta\sigma T_{NI}}{R\Delta H n} \qquad (3)$$

may be useful. Here $\Delta\sigma$ is the difference in surface tension between the nematic and isotropic phases, ΔH is the N–I transition enthalpy, and n is the number density of liquid crystal. We take $\Delta\sigma \sim .026$ dyne/cm, $\Delta H \simeq .3$ kcal/mole,[15] $R = 10^{-5}$ cm, $T = 310$ K, and $n \simeq .5 \times 10^{22}$ cm^{-3} and arrive at

$$\Delta T \simeq 8 \times 10^{-3}\,\text{K} \sim .01\,\text{K}.$$

We conclude distortion effects are dominant in lowering T_{NI} for nematic materials in cylindrical pores with strong surface alignment. However, the data are insufficient to confirm this mechanism.

Porous membranes allow easy investigation of singularities in cylinders and also of the effect of finite size on transition temperature. An interesting possibility also exists that, with increased surface density of pores, a matrix for a nematic phase may be obtained for which the relaxation time of molecular reorientation, $\tau_R \cong (\gamma/\kappa)(R/\pi)^2$ (γ = effective viscosity,

κ = elastic constant, R = radius of pore), can be varied at constant electric field without changing the thickness of the cell. This may be interesting with respect to display applications.

Acknowledgments

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Optical Spectroscopy of Ordered Dyes in Aqueous Lyotropic Nematic Liquid Crystals

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Abstract

Aqueous lyotropic nematic liquid crystals can be uniformly ordered by magnetic fields of ∿ 20 Kilogauss in flat glass capillaries up to ∿ 1 mm in path length. Once removed from the field the orientation decays very slowly, and optical spectra of the oriented samples can easily be recorded in conventional instruments. In this manner, the visible spectra of a substituted porphine ($TPPS_4$) and the dye Congo Red were recorded in three nematic lyotropics which consist of rod-shaped micelles. The polarization of the absorption bands can easily be assigned. $TPPS_4$ orients with its plane perpendicular to the optic axis of the lyotropic rods with a low order parameter, and the long axis of Congo Red also orients perpendicular to the optic axis with a considerably higher order parameter. In the nematic system (potassium laurate/decanol/D_2O) addition of $TPPS_4$ at a sufficiently high concentration stabilizes a biaxial nematic phase.

Introduction

Lyotropic nematic liquid crystals are readily oriented by a magnetic field and have frequently been utilized as solvent systems to study solute molecules by NMR spectroscopy.[1] However, relatively little advantage has been taken of this orientational capability for optical spectroscopic studies. Once a lyotropic nematic is oriented in a magnetic field between glass plates separated by up to 1 mm, the sample remains aligned for many hours when removed from the field. Thus samples may be prepared, aligned in an electromagnet, and placed in a conventional optical spectrometer for recording polarized spectra. Examples of such a technique have appeared in studies of fluorescence depolarization[2] and uv-visible spectra of hydrophobic solutes.[3]

In this paper we report observations on the polarized absorption spectra of the water soluble dye molecules tetrasodium-meso-tetra-(4-sulfonatophenyl)porphine ($TPPS_4$) and Congo Red (CR) dissolved in several lyotropic nematic systems.

The nematic systems used as solvents are (see Table I): (A) disodium cromoglycate[4,5] (DSCG) and H_2O with negative diamagnetic anisotropy ($\chi_a < 0$); (B) potassium laurate (KL)[6,7] decanol and D_2O ($\chi_a > 0$); (C) KL, KCl and H_2O[8] ($\chi_a > 0$). Homogeneous planar alignment of the above phases by magnetic fields ∿ 10 kG and surface interaction persists for a considerable time (weeks) provided exposure to temperature and velocity gradients are kept to a minimum.

At room temperature, all three nematic systems are classified as N_c phases having rod-like or cylindrical micelles. In the case of system A, Lydon[9] suggested on the basis of x-ray evidence and a high degree of hydration that DSCG molecules form hollow finite cylinder micelles which are partially aligned. For systems B and C, the hydrophobic chains of the KL form the inside of the cylinder micelle with the polar head pointing outwards. The perpendicular cross section of the column may be circular or elliptical.[10]

Finally we report preliminary observations of an interesting dye induced stabilization of a biaxial nematic (N_{Bx}) phase in system B.

Experimental

The DSCG was provided by Fisons Ltd. and the KL was synthesized as per Ref. (7). Sample compositions in weight % are given in Table I. For each system one sample was made without the dye; transition temperatures and deuterium magnetic resonance splittings agreed with quoted literature values[4,6,10] to within acceptable limits. When the dye was added, changes in transition temperatures occurred as shown in Table I. A few studies were also performed using trans azobenzene (Aldrich Chemical Co.) and a dichroic azo dye D1 (E. Merck), the latter of which is known to have a high order parameter ($\sim$ .7) in thermotropic nematics.

The dye mixtures were prepared from stock solutions of 10^{-3} - 10^{-5}M of $TPPS_4$ in D_2O, and 10^{-3}M of CR in triply distilled H_2O. The pH of the water was $\approx$ 5. The solubility calculated from absorbancy at room temperature of CR in the KL/KCL/H_2O system was $\simeq 6 \times 10^{-5}$M, and in the DSCG/D_2O system approximately 8×10^{-5}M. The samples were centrifuged to remove any salted out dye crystals that were suspended in the solution. The concentration of dye quoted in Table II was determined from the absorbance of the solution assuming Beer's Law to hold. The extinction coefficients found by standard methods were: $\varepsilon[TPPS_4,\text{Soret band}] \simeq 45 \times 10^4$ and $\varepsilon[CR,495nm] \simeq 5 \times 10^4$.

The components were weighed into glass test tubes with air-tight screw top caps and stirred magnetically overnight in a water bath. The bath temperature was held below the expected nematic-isotropic transition temperature. This is particularly important for the DSCG system. This system has a wide two-phase temperature region and the nematic volume fraction contains a higher density of DSCG than the isotropic volume fraction.[5] Thus concentration gradients easily occur in this region. Samples were always examined for homogeneity in bulk before use.

The absorption polarization spectra were recorded on a Cary 14 spectrophotometer. Polarizers in the reference and cell compartments were placed in front of and behind the sample to correct for instrumental polarization and sample depolarization effects. The absorbancy, A, was recorded with light polarized either parallel ($A_{\parallel}$) or perpendicular ($A_{\perp}$) to the liquid crystal optic axis n. Consistent with the solubilities of the dyes, larger path lengths were employed. Two types of sample cell were used: (1) standard 1 mm thickness spectroscopic cell, and (2) stacks of equal thickness glass capillaries. The capillary thickness varied from .2 - .3 mm. A torch was carefully used to seal the capillaries.

Both 1 mm thick or stacked capillary cells were used for the more viscous system C. Uniform alignment was obtained within hours. The less viscous systems A and B aligned in the capillaries within minutes and the number of capillaries in a stack was varied to obtain an optimum absorbancy. Because DSCG absorbs below 400 nm, one is restricted to observation of visible absorption bands only.

Results and Discussion

Studies of CR in stretched polyvinyl alcohol films[11] indicate that the CR transition moment giving absorption at 495 nm is oriented at an angle of about 15° with the stretching direction. The orientation of the transition moment at 360 nm is deduced (see Table II) as approximately perpendicular to the 495 nm moment. Making the reasonable assumption that the long axis of CR aligns in the stretching direction, we conclude the transition moment (495 nm) is approximately parallel to the long axis of the molecule. For $TPPS_4$ it is well known[12] that the transition moment associated with the Soret band is in the plane of the molecule. It should be mentioned that we observed only the monomer spectrum of CR[11] and $TPPS_4$[13] in lyotropic nematics.

Remembering these points we write for the degree of order of the transition moment for a selected absorption band[14]

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} = 1/2 \left\langle 3\cos^2\beta - 1 \right\rangle . \qquad (1)$$

$A_{\parallel}(\lambda_m)$ and $A_{\perp}(\lambda_m)$ are absorbancies at the wavelength of maximum absorption, taken parallel and perpendicular to the director respectively. The angle between the transition moment and the director is β and the brackets mean a thermal average over molecular motions.

Congo Red

As shown in Table II, the basic result for the CR dye is the same for both systems A ($DSCG/D_2O$) and C ($KL/KCl/H_2O$), namely the CR molecule orients with its long axis on the average perpendicular to the director in accordance with the above discussion of the 495 nm transition in CR. The magnitude of the long axis order parameter of the CR molecule should be slightly higher than the order parameter of the transition moment due to the nonparallelism of the molecular long axis and the transition axis.

The simplest model to explain this behavior is that the CR molecules (length $\simeq$ 25 Å) are incorporated into the cylindrical micelle such that the

CR molecule spans the diameter of the cylinder with the hydrated SO_3^- group near the polar region of the micelle. For the DSCG system a similar argument applies.

The bulkiness of the CR molecule does not aid in its incorporation into the micelle and this property may account for the relatively low order parameter. Magnitudes of order parameters obtained by NMR for small solute molecules, e.g. benzene, in the N_L phase of a (KL/KCL/decanol/water)[15] system range between .023 and .046.[1]

$TPPS_4$

For low concentrations of $TPPS_4$ (10^{-4}, 10^{-5}M) in systems A and B an N_c phase was observed at room temperature. An order parameter of the in-plane (Soret) transition moment (see Table II) was obtained as $S \cong -0.006$ for both the above systems. The negative value of the order parameter of the in-plane transition moment[12] of $TPPS_4$ indicates the plane of the molecule slightly prefers to orient perpendicular to the director.

Considering the size and shape of the porphyrin molecules and the presence of the phenyl rings, which are almost perpendicular to the plane of the porphine nucleus,[15] it seems plausible to conjecture that a significant portion of the porphine molecules may be wedged between rather than incorporated into the micelles.

We have also tried some hydrophobic dyes in system B, in particular trans-azobenzene, solubility $\sim 10^{-3}$M; and D1, solubility in B $\sim 10^{-4}$M, T = 22°C. Little orientation was detected $|S| < 10^{-3}$. The azobenzene solutions gave an N_L phase (disc-like micelles). Since the alignment of the symmetry axis of the N_L phase was parallel to the wave-vector of the incoming light for our experiment, no anisotropy in absorption could be observed in this case.

The existence of the N_L phase was verified in two ways: (1) a uniform homeotropic texture was observed, and under conoscopic examination the system was determined to be uniaxial with positive dielectric anisotropy; (2) observation of the proton line width[17] or deuterium splitting[6,8] under spinning the sample shows $\chi_a < 0$.

Finally we note as a preliminary report that at relatively high concentrations ($\simeq 1.3 \times 10^{-3}$M) of $TPPS_4$ in system B we observed a biaxial nematic phase (N_{Bx}). For system B with no added $TPPS_4$ only an N_c phase was observed at room temperature. The stabilization of the N_{Bx} phase from the N_c phase is probably due to a combination of two effects: (1) a salt effect due to the 4 sodium ions of $TPPS_4$ which tends to decrease the curvature (through electrostatic screening) of the surfactant headgroup/water interface;[18] (2) the disc shape of the porphyrin molecule sterically favors lamellar aggregates.

The biaxial phase when oriented by a magnetic field parallel to the flat surfaces of the capillary gave a psuedo-isotropic texture which, using a conoscope, presented the characteristic "baseball" interference figure. It should be mentioned that the empty glass capillaries in general show a weak biaxial strain birefringence; however, this is easily distinguished from N_{Bx}.

Phase diagrams of Yu and Saupe[6] for the (KL/decanol/K_2O) system show we are in a sensitive region ($N_c - N_{Bx} - N_L$) of the phase diagram near room temperature; it is therefore not surprising that perturbations induced by solubilized $TPPS_4$ or azobenzene causes an $N_c \rightarrow N_{Bx} \rightarrow N_L$ transition. It is to be noted that a recent study by Hendrix et al[10] on the above system failed to reveal a biaxial phase. Clearly care must be used to control ionic impurities and maintain a consistent pH.

In summary, we find: (1) the long axis of the dye CR is oriented on the average perpendicular to the director in both systems A and C (see Table I), the order parameter of the 495 nm transition moment being $S = -0.030 \pm .002$; (2) the planes of the $TPPS_4$ molecules orient perpendicular to the director with an order parameter $S = -0.006 \pm 0.002$ in systems A and B; (3) an $N_c \rightarrow N_{Bx}$ transition was caused in system B by $TPPS_4$ ($\sim 10^{-3}$M), and an $N_c \rightarrow N_L$ transition by azobenzene ($\sim 10^{-3}$M).

Investigations using a variety of dye stuffs are underway, as is a closer study of the $TPPS_4$ induced $N_c \rightarrow N_{Bx}$ transition.

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Table I. Effect of Dye Concentration on Transition Temperature of Three Nematic Lyotropic Phases

Sample wt%	Dye Concentration (M)	Transition Temperature[a] (^oC)
A (15% DSCG/85% H_2O)	0	32.0 ($N_c \rightarrow N_c + I$)
	1.0×10^{-4} ($TPPS_4$)	33.1 ($N_c \rightarrow N_c + I$)
	8.0×10^{-5} (CR)	33.5 ($N_c \rightarrow N_c + I$)
B (26.36% KL/6.24% decanol/ 67.40% D_2O)	0	42.6 ($N_c \rightarrow N_c + I$)
	8.0×10^{-5} ($TPPS_4$)	39.0 ($N_c \rightarrow N_c + I$)
C (33.03% KL/2.20%KCl/ 64.77% H_2O)	0	41.5 ($N_c \leftrightarrow N_c + M$)
	6×10^{-5} (CR)	37.6 ($N_c \leftrightarrow N_c + M$)

[a] Transition temperatures are assigned for the lowest temperature boundary of the observed two-phase region. I and M denote isotropic and middle soap respectively. N_c and N_L denote cylindrical and disc-like micelles respectively.

Table II. Absorbancies and Order Parameter of Dyes in Nematic Lyophases

Sample	Dye	λ_{max}(nm)	Absorbancy		Sample Thickness	Order Parameter
			$\parallel$	$\perp$	mm	S
A	$TPPS_4$	424	0.648	0.661	0.2	-0.007
	Congo Red	517	0.475	0.520	1.2	-0.030
B	$TPPS_4$	418	0.718	0.730	0.2	-0.006
C	Congo Red	495	0.330	0.368	1.2	-0.036
	Congo Red	360	0.441	0.352	1.2	+0.078