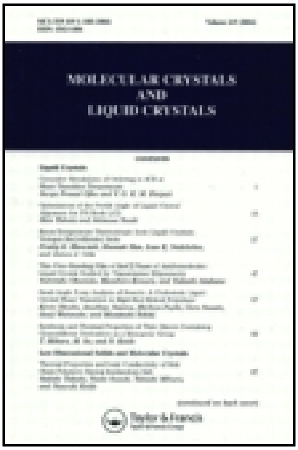

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Polarized Absorption Spectroscopy as a Tool in Studying Guest-Host Interactions in a Nematic Lyotropic Liquid Crystal

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Magnetically aligned samples of the nematic lyotropic liquid crystal prepared by dissolving disodium cromoglycate in water were studied via polarized absorption spectroscopy. The order parameters of the host as well as those of a wide variety of guest dye molecules were determined and correlated with structure of dye, ionic strength of medium, and temperature effects. In general, order parameter of guests increases with ionic strength, and decreases with increasing temperature. Very large molecules tend to orient parallel to the axis of the nematic cylinder, whereas small molecules lie perpendicular to this axis. The order parameter of the host is $S = -0.20$, consistent with values obtained by other methodologies.

INTRODUCTION

The facile alignment of nematic lyotropic liquid crystals in a magnetic field allows one to utilize these matrices as solvents for studying orientation and polarization of guest molecules. The earliest use was in NMR spectroscopy,[1] but more recently there have been several investigations of the ordering of dye molecules in lyophases.[2–4] The purpose is two-fold: to establish the relative orientation of a dye molecule to the extended micellar aggregates, and to determine the degree of ordering. The variation in these parameters with the size and shape of the solute and with the nature of the aggregate should allow one to understand the structural aspects of lyophases and the nature of their microenvironment in more detail.

In this study, the focus is on the lyotropic nematic phase prepared by dissolving disodium cromoglycate (DSCG) in water. Approximately 15% DSCG in water forms a stable nematic phase in the temperature range 9–27°C.[5–8] Although several models exist for the structure of this lyophase,[5–11] we favor a picture consisting of cylinders of 20 Å cross-sectional diameter and 200 Å length; V-shaped DSCG dianions with their charges pointing outward to the walls of the cylinder are assembled in the cross-section,[11,12] as indicated in Figure 1. The study consists of dissolving guest dyes in the lyophase, aligning such samples in a magnetic field, and recording their polarized absorption spectra.

EXPERIMENTAL

DSCG was kindly provided by Fisons, Inc. Both cationic and anionic dyes were employed: Methyl Red (Mallinckrodt); Thiazine Red, Nu-

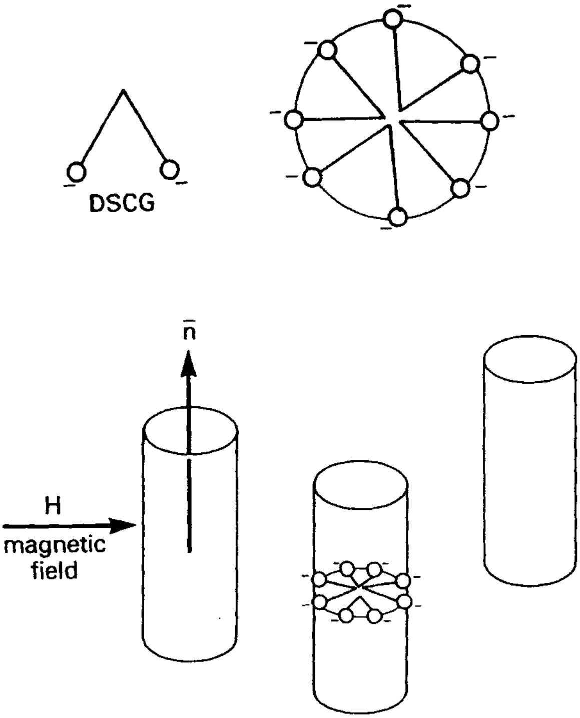

FIGURE 1 Cross section of cylindrical extended micelle of DSCG-H_2O, and definition of the director n with respect to an applied magnetic field H.

clear Fast Red, Indigo Carmine (Fluka); Malachite Green, Eosin Y (Eastman Organic Chemicals); Ethidium Bromide, Ethyl Orange, Safranine 0, 1,1'-Diethyl-4,4'-Carbocyanine Iodide, Direct Blue 71 (Aldrich); 3,3'-Diethylthiacarbocyanine Iodide (Molecular Probes); Direct Red 80, Naphthol Blue Black, Mordant Brown 33 (Atlantic Chemical Co.). Dyes were recrystallized until their extinction coefficients remained constant upon further crystallization. Direct Blue 71 contained only 20% dye, but we were unsuccessful in recrystallizing, and the dye was employed without further purification.

Dye solutions were prepared in deionized water. Spectra of all dyes in absolute ethanol (with the exception of Direct Red 80 and Direct Blue 71, which were insoluble) were also obtained for the purpose of characterizing dye behavior in a less polar environment. All spectra were recorded on a Perkin Elmer 330 UV-VIS spectrophotometer. Buffer solutions were prepared in deionized water using sodium phosphate, both monobasic and dibasic forms, having ionic strengths, μ, of 0.1 – 0.9.

The components were stirred in screw capped centrifuge tubes for at least 18 hours to ensure homogeneity of the phase. The liquid crystal solution was then transferred to rectangular profile glass capillaries of 0.02 cm thickness (Vitro Dynamics Inc.), and sealed with a torch. Capillaries were then aligned in a magnetic field of 20 kG overnight. The DSCG lyophase has negative diamagnetic anisotropy,[6] i.e. the plane of the DSCG molecule aligns parallel to a magnetic field, whereas the cylindrical axis of the aggregate (the nematic director n) aligns perpendicular to the magnetic field. Samples were placed in the magnet so that n is oriented parallel to the capillary long axis. This sample geometry is pictured in Figure 1.

Polarized absorption spectra of the aligned thermostated samples were collected using two sets of polarizers, one set each in the reference and sample compartments. The absorbance, A, was recorded with light polarized parallel ($A_\parallel$) and perpendicular ($A_\perp$) to the liquid crystal director, n. Because DSCG absorbs strongly below 400 nm, one is restricted to the observation of visible bands only. From the measurement of $A_\parallel$ and $A_\perp$, the order parameter S is calculated from the following equation:[2]

$$S = (A_\parallel - A_\perp)/(A_\parallel + 2A_\perp) = 1/2\langle 3\cos^2\beta - 1\rangle$$

Here $A_\parallel$ and $A_\perp$ are the measured absorbances at the wavelength of maximum absorption. β is the angle between the transition moment vector of the probe dye and the nematic director n, the bracketed portion of the equation indicating a thermal average of molecular motions.

RESULTS AND DISCUSSION

Table I gives the order parameter S of a group of water soluble dyes in the DSCG lyophase at room temperature, and also lists the approximate dimensions of the dye molecules (estimated from bond lengths), as well as the variations induced in the phase transition temperature nematic to nematic + isotropic (N → N + I) determined via optical microscopy. It is clear that the magnitude and sign of S depend on molecular geometry and charge distribution of the dye.

TABLE I

Order parameter (25°C) for water soluble dyes in the 15% DSCG-water nematic lyophase

Dye name(a)	Size, Å(b)	S	Dye concentration $M \times 10^3$	$T_{n \rightarrow n+i}$,°C
Indigo Carmine	12	−.029±.002	2.0	27.8
Thiazine Red	18	−.040±.002	2.3	28.7
Nuclear Fast Red	5 × 7	−.100±.008	3.4	28.5
Naphthol Blue Black	20	−.020±.002	1.1	28.6
Mordant Brown 33	12	−.048±.002	3.4	29.8
Methyl Red	12	−.071±.002	2.5	28.0
1,1′-Diethyl-4,4′-carbocyanine iodide	15	−.092±.002	0.46	28.3
Direct Blue 71	28	−.005±.002	0.58	28.8
Ethyl Orange	16	+.009±.003	0.79	28.6
Direct Red 80	46	+.190±.020	0.50	29.2
3,3′-Diethylthia-carbocyanine iodide	15	−.088±.002	1.3	28.8
Malachite Green	7 × 7	−.032±.002	0.52	28.7
Ethidium bromide	9 × 9	−.198±.020	8.0	26.6
Safranine O	7 × 7	−.080±.002	0.74	28.3
Eosin Y	7 × 7	−.014±.002	0.61	28.7

[a] The structures of these dyes are readily available; for reasons of space, only their names and the approximate molecular dimensions are given.

[b] If the molecule is rod-like, only the length is given; if the molecule is disc-like, length and width are listed in that order.

TABLE II

Wavelength of maximum absorption (nm) of dyes in water, ethanol, and the DSCG-water lyophase

Dye	Wavelength in nm in respective solvent		
	Water	Ethanol	Lyophase
Methyl Red	518	498	536
Malachite Green	615	619	626
Indigo Carmine	608	599	622
Thiazine Red	508	509	520
Nuclear Fast Red	516	515	531
Naphthol Blue Black	596	616	635
Mordant Brown 33	458	460	450
3,3′-Diethylthia-carbocyanine Iodide	548	557	565
Ethidium Bromide	482	532	508
Safranine O	498	531	539
Eosin Y	515	524	522
1,1′-Diethyl-4,4′-carbocyanine Iodine	622	707	722
Direct Blue 71	591	a	588
Ethyl Orange	472	424	481
Direct Red 80	540	a	556

a = insoluble in ethanol

Small dye molecules tend to be solubilized and orient perpendicular to the director n, irrespective of whether they are rod or disc shaped. The very large molecule Direct Red 80 orients parallel to n, presumably because the molecule is much larger than the diameter of the extended micelle. Only one other dye, ethyl orange, has a (very small) positive S value, meaning it is essentially disordered. One also observes that those dyes having several charged groups within their structure tend to have lower S values than those having a single ionic charge.

Band shifts in absorption of some dye molecules correlate well with the polarity of the microenvironment.[12] In Table II, the wavelength of maximum absorption of the dyes studied are presented in water, ethanol, and the DSCG-water lyophase. For those dyes in which there is a red shift (bathochromic) as one proceeds from the less polar ethanol to the more polar water, it is interesting to note that the DSCG lyophase shows even a further red shift, indicating that the polarity of the environment is even greater than that of water.

To study this latter problem thoroughly, an independent investigation of the spectrum of methyl orange, a well-known polarity probe, was undertaken in a group of lyophases.[12] The conclusion of that study is that DSCG indeed consists of a highly polar microenvironment, presumably because of "internal" hydrogen-bonded water within the extended micellar interior. The secondary hydroxyl group in the glyceryl bridge of the DSCG molecule is also involved in this hydrogen bonding.[11]

It is interesting to examine the effects of changes in ionic strength and temperature on the order parameter of guest dyes, and a detailed study was conducted utilizing ethidium bromide, because of its high S value. For all of the data reported in Figure 2, the dye concentration was held constant at 5.4 ± 0.1×10^{-3}M and a phosphate buffer was added at the ionic strength indicated. S decreases with increasing temperature and increases with ionic strength. Adding electrolyte to a lyotropic liquid crystal effectively screens the coulombic repulsion between polar head groups on the surface of the nematic rods, re-

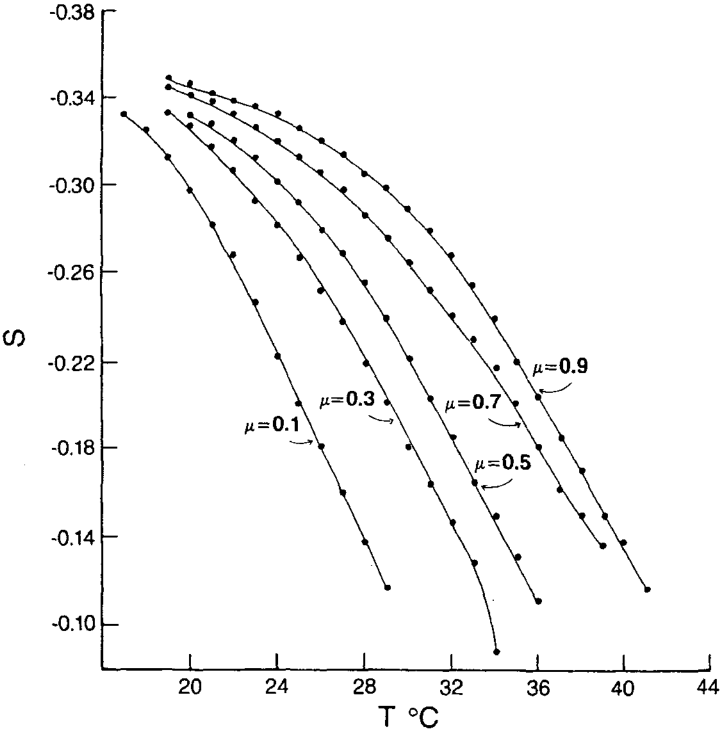

FIGURE 2 Order parameter S of ethidium bromide (5.4×10^{-3}M) in the DSCG lyophase as a function of temperature at various ionic strengths (phosphate buffer).

TABLE III

Effect of ionic strength on the order parameters of Ethidium Bromide in DSCG lyophase at 24°C and on the transition temperature of the phase

Increase in ionic strength, μ	S	$T_{n\rightarrow n+i}$(°C)
0.0	−0.198	26.6
0.1	−0.235	29.1
0.3	−0.282	34.1
0.5	−0.307	37.0
0.7	−0.314	39.4
0.9	−0.331	41.3

sulting in stiffer rods.[13] Decreasing temperature is also expected to lead to more ordering of a lyotropic.[14] Both of these effects on the host structure cause a concomitant change in the S value of the guest dye.

Adding electrolyte to DSCG is known to also affect the phase transition temperature drastically. Table III gives data on the change in both S and $T_{N\rightarrow N+I}$ with increasing ionic strength, and it is clear that the change in S value is a combined effect of added electrolyte and increase in phase stability.

The host order parameter has been determined by NMR spectroscopy[15] and by infrared spectroscopy[11] to have values of −0.26 and −0.14 respectively. DSCG has an absorption band of relatively high extinction coefficient at 325 nm, but by employing very thin cells (~12 μm) it is possible to measure S for DSCG itself. A value of −0.20 was obtained, which is consistent with that obtained by other methods, and lends credence to the absorption spectroscopic methodology as a valid mode of assessing orientational order of both guest and host species.

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