Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Simaltaneous Measurement of Guest and Host Ordering in a Nematic Lyophase via Fluorescence Spectroscopy

J. P. McClymer [a] & M. M. Labes [b]

[a] Department of Physics and Astronomy, University of Maine, Orono, ME, 04469

[b] Department of Chemistry, Temple University, Philadelphia, PA, 19722

Version of record first published: 24 Sep 2006.

To cite this article: J. P. McClymer & M. M. Labes (1991): Simaltaneous Measurement of Guest and Host Ordering in a Nematic Lyophase via Fluorescence Spectroscopy, Molecular Crystals and Liquid Crystals, 195:1, 39-44

To link to this article: http://dx.doi.org/10.1080/00268949108030888

Mol. Cryst. Liq. Cryst., 1991, Vol. 195, pp. 39–44
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Simultaneous Measurement of Guest and Host Ordering in a Nematic Lyophase via Fluorescence Spectroscopy

J. P. MCCLYMER

Department of Physics and Astronomy, University of Maine, Orono, ME 04469

and

M. M. LABES

Department of Chemistry, Temple University, Philadelphia, PA 19122

(*Received April, 1990; in final form July 12, 1990*)

The temperature dependence of the order parameters $P_2(\cos\theta)$ have been determined via fluorescence emission measurements for both a guest dye (3.3'diethylthiacarbocyanine iodide) and the lyotropic nematic host disodium cromoglycate. The guest is found to have a significantly lower order parameter than the host while both show the same temperature dependence. The angle between the absorption and emission moments of the dye is found to be approximately 64°. The higher moment of the order parameter, $P_4(\cos\theta)$, can also be determined, but because of its sensitivity to this angle a quantitative measurement is not possible.

Keywords: order parameter, lyotropic, nematic, fluorescence

INTRODUCTION

It is rather common to use guest molecules as probes of nematic order in thermotropic systems. Fewer studies have been conducted in lyotropic systems.[1–5] The ability of the guest to quantitatively trace the host's order is not straightforward in lyophases. Frequently the guest is solubilized to some extent within the hydrophobic core of these extended micellar structures, and the guest's polarity is of great importance in determining the nature of the interaction at the surface. As a consequence, studies of guest-host interactions in lyotropic media require measurement of both guest and host order parameters.

Disodium cromoglycate (DSCG) forms a nematic phase in the concentration range 13% to 17% by weight in water, with a temperature range from 15 to about 40 degrees, where a transition to an isotropic phase occurs.[6] X-ray diffraction studies[6] indicate that the nematic phase consists of cylindrical aggregates of DSCG molecules. These aggregates align perpendicular to a magnetic field, indicating that the system has negative diamagnetic anisotropy.[6,7]

In addition to X-ray diffraction investigations, the phase transitions have been studied using optical microscopy,[6,7] differential scanning calorimetry,[7] NMR,[8] FT-IR,[9] and UV-VIS absorption[10] measurements. The nematic undergoes a first order phase transition to the isotropic state, and the phases are separated by a coexistence region.

Studies of guest dyes in the nematic, performed using UV-Vis absorption spectroscopy, find that most dyes whose length is comparable to the width of a DSCG micelle insert themselves perpendicular to the cylindrical axis while longer dyes align along the cylindrical axis, either within or without the micelle.[10] The dye 3.3′diethylthiacarbocyanine iodide (DESCI) has been found to be a member of the first class of dyes as indicated by a negative order parameter with respect to the director. In this work, because of the very different emission wavelengths of guest and host in a fluorescence experiment, simultaneous measurements of both guest and host ordering is performed.

EXPERIMENTAL

DSCG was kindly provided by Fisons Inc. and was used without further purification. A small amount of DESCI was mixed with a deoxygenated buffer solution consisting of 0.01 M sodium phosphate, 0.2 M sodium chloride, and 0.3 M sodium acetate and then added to the DSCG to form a 15% by weight nematic phase. The well mixed solution was then transferred to flat capillary cells (.02 × 4 × 30 mm) and flame sealed. The flat glass capillary was obtained from Vitro Dynamics Inc. The extremely low turbidity and low ($\Delta n \approx 10^{-3}$) birefringence allow the use of such relatively thick samples.

A sample was placed in a 2 Tesla field until uniform alignment of the director along the long axis of the cell was achieved. It was then transferred to a temperature controlled housing containing two rare earth permanent magnets which produced a field of 0.1 T, constraining the director to remain along the cell's long axis which is vertical. The sample stood at room temperature allowing the order to decay to an equilibrium value which, according to Reference 5, should take a number of hours. We actually waited many weeks for a singularity which developed in the center of the sample to relax away. The sample does not appear to undergo any large changes over this time span as the transition to the two phase ($N + I$) region occurs slightly above 32.9°C and the sample is fully isotropic by 37°C, which is consistent with the published phase diagram.[6]

The polarized fluorescence was monitored on a Perkin Elmer MPF-66 spectrometer using a sheet polarizer. A 90° scattering geometry was used with the sample cell 45° with respect to the incident light so that specular reflections were not directed toward the detector. The absorption/emission wavelengths for the DSCG were 385/485 nm and 500/585 for the guest dye. The nematic host exhibited very weak emission. Two minute scans were made for the following polarization states of the exciting and emission beams respectively, where the orientation is with respect to the director: perpendicular-perpendicular (HH), parallel-parallel (VV), perpendicular-parallel (HV), all using two polarizers and with a parallel (V) and

perpendicular (H) after the exciting beam. In addition the fluorescence of the dye was studied in glycerol as a function of temperature.

DISCUSSION

Determination of the order parameter from the fluorescence data requires information on the geometrical arrangement.[11-16] Following Chapoy and Dupre,[11] Figure 1 defines the appropriate angles. In particular, the absorption (α) and emission (ϵ) moments generally are not parallel to each other. Thus, the intramolecular energy transfer angle δ, defined as $\cos\delta = (\alpha) \cdot \epsilon$, is a fixed structural property of the molecule. Assuming cylindrical symmetry and that the absorption moment is along the molecular axis which is itself perpendicular to the director, the scattering elements for the dye are[11]:

$$
\begin{aligned}
Iv &= I_v \langle\cos^2(\theta)\rangle \\
Ih &= I_h\ 1/2\ (1 - \langle\cos^2(\theta)\rangle) \\
Ivv &= I_{vv}\ (3/8\ \sin^2(\epsilon)^*[1 - 2\ \langle\cos^2(\theta)\rangle + \langle\cos^4(\theta)\rangle] \\
&\quad + 1/2\ \cos^2(\epsilon)^*[\langle\cos^2(\theta)\rangle - \langle\cos^4(\theta)\rangle]) \\
Ihh &= I_{hh}\ (3/64\ \sin^2(\epsilon)^*[1 + 2\ \langle\cos^2(\theta)\rangle + \langle\cos^4(\theta)\rangle] \\
&\quad + 1/16\ \cos^2(\epsilon)^*[3 - 2\ \langle\cos^2(\theta)\rangle - \langle\cos^4(\theta)\rangle]) \\
Ihv &= I_{hv}\ (1/16\ \sin^2(\epsilon)^*[1 + 2\ \langle\cos^2(\theta)\rangle - 3\ \langle\cos^4(\theta)\rangle] \\
&\quad + 1/4\ \cos^2(\epsilon)^*[\langle\cos^2(\theta)\rangle + \langle\cos^4(\theta)\rangle]).
\end{aligned}
\tag{1}
$$

The $\langle . . . \rangle$ indicates an appropriate statistical average. The angle θ is the angle between the director, which has been previously defined by cell geometry and the external field to be along the vertical axis, and the long axis of the micelle. The method of calculating Equation 1 already takes into account the negative sign of the order parameter of the dye as well as the position of the amphiphilic molecules themselves which, except for the end caps, are perpendicular to the long axis of the micelle. The net result is that the order parameter calculated using these equations is expressed as a positive quantity. Not taking into account the actual placement of the dye molecule gives incorrect expressions for the fluorescence intensity.

The prefactor in each expression contains information on the instrumental wavelength dependent polarization bias. The prefactor must be either eliminated or corrected before useful information can be extracted. For this particular instrument most of the polarization bias results from uneven polarization distribution in the exciting beam. This effect could be seen qualitatively by illuminating a PIN pho-

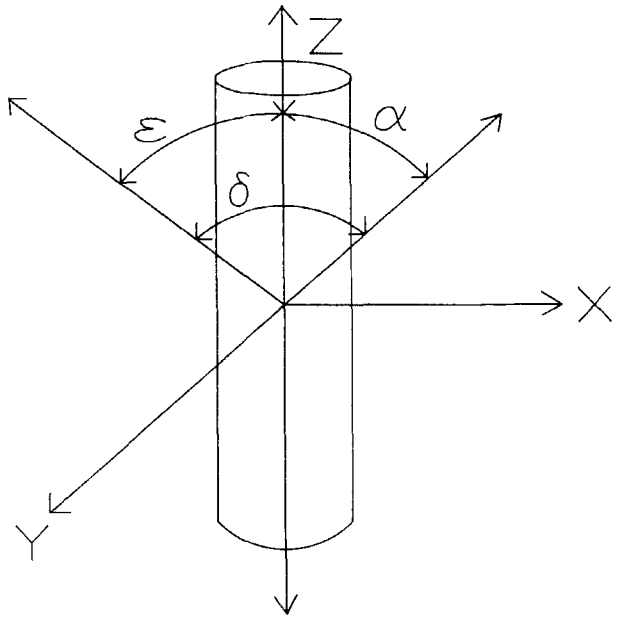

FIGURE 1 The geometrical arrangement of the absorption moment and emission moments and their angles to the molecular axis Z. α = absorption angle; ϵ = emission angle; δ = angle between absorption and emission moments. Note that the optic axis (not shown) need not be coincident with the molecular axis; the angle between them we refer to as θ.

todiode with the exciting beam as a polarizer in the light path was rotated. Quantitative corrections were made using a quartz wedge supplied by the manufacturer.

The need for the general expression given by Equation set 1 can be determined by measuring the degree of polarization,[11,13] which is defined as

$$P = (Ivv - Ivh)/(Ivv + Ivh) \tag{2}$$

In an isotropic phase $P = 0.5$ if both the absorption and emission moments remain collinear during the fluorescence lifetime. If this condition is not satisfied then the fluorescence is reduced to

$$(3\cos(\delta)^2 - 1)/(3 + \cos(\delta)^2) \tag{3}$$

where δ is again the intramolecular energy transfer angle between the two moments.

According to Chapoy and DuPre,[11] the measured value of this angle is the effective thermal average of a fixed, structural property that may depend on the lifetime of the excitation. We determine this angle, averaged over different lifetimes, by measuring the polarization ratio of the dye in glycerin at a number of temperatures. These measurements give P as a function of viscosity which is related to the fluorescent lifetime. The relative flatness of the data from about 400 to 1600

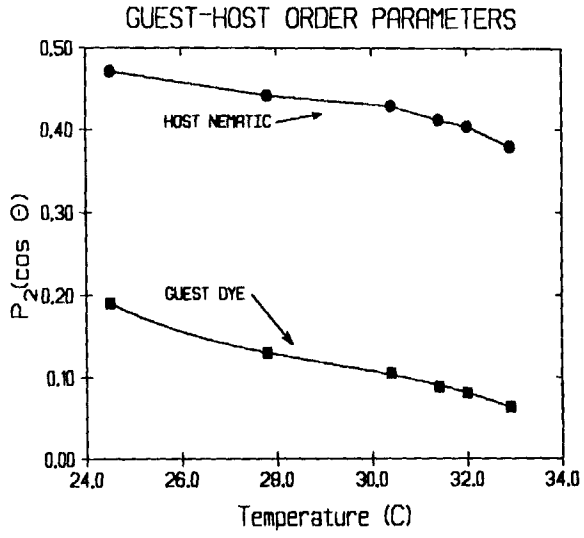

FIGURE 2 Temperature dependence of the order parameter for the host nematic and guest dye.

centipoise indicates that the lifetime of the fluorescent state is sufficiently short so that rotational correction terms to Equation 1 are not needed. This conclusion is supported by measurements in other solvents, where the lifetime is found to be less than the experimental resolution of 4 nanoseconds.[17] The degree of polarization is 0.38 which means that the angle between the absorption and emission moments is about 24 ± 2°, making ϵ about 66°.

The calculation of $P_2\langle\cos^2\theta\rangle = \langle 3/2\cos^2\theta - 1/2\rangle$ is made using the two single polarizer measurements (Iv and Ih) for both the dye and DSCG and the results are shown in Figure 2. These values are much lower than those reported in References 7 and 8 in which a much larger magnetic field was applied. Similar values were found in a study of the 5CB-dye system[18] that did not utilize large fields.

Calculation of $\langle\cos^4\theta\rangle$ from the ratio Ihh/Ihv is extremely sensitive to the value of ϵ. This fact precluded us from determining P_4 in this experiment. In the 5CB/dye study, it was also not possible to determine P_4 accurately.[18]

The P_2 order parameter of both the nematic host and the guest show the same temperature dependence. As might be expected, guest order is considerably lower than that of the nematic host. For the guest dye, determination of P_4 turns out to be sensitive to details of the molecular structure which are not sufficiently well known.

Acknowledgment

This work was supported by a grant from the National Science Foundation-Solid State Chemistry under Grant No. DMR 84-04009.

References

1. M. Kuzma, V. Skarda and M. M. Labes, *J. Chem. Phys.*, **81**, 2925 (1984).
2. V. Skarda and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, **126**, 187 (1985).
3. L. B. Johansson, O. Soderman, K. Fontell and G. Lindblom, *J. Phys. Chem.*, **85**, 3694 (1981).
4. L. B. A. Johansson and G. Lindblom, *Q. Rev. Biophys.*, **13**, 63 (1980).
5. R. Weber and H. Hoffman, *Liq. Cryst.*, **3**, 203 (1988).
6. N. H. Hartshorne and G. D. Woodard, *Mol. Cryst. Liq. Cryst.*, **23**, 343 (1973).
7. H. Lee and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, **84**, 137 (1982) and **91**, 53 (1983).
8. D. Goldfarb, Z. Luz, N. Spielberg and H. Zimmermann, *Mol. Cryst. Liq. Cryst.*, **126**, 225 (1985).
9. Y. W. Hui and M. M. Labes, *J. Phys. Chem.*, **90**, 4064 (1986).
10. B. D. Bostwick and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, **147**, 179 (1986).
11. L. L. Chapoy and D. B. DuPre, *Methods of Experimental Physics: Polymer Physics*, ed. R. A. Fava, (Academic Press, New York, 1980).
12. L. L. Chapoy and D. B. DuPre, *J. Chem. Phys.*, **69**, 519 (1978).
13. L. L. Chapoy and D. B. DuPre, *J. Chem. Phys.*, **70**, 2550 (1979).
14. D. I. Bower, *J. Poly. Sci. Poly. Phys. Ed.*, **10**, 2135 (1972).
15. D. I. Bower, *Structure and Properties of Oriented Polymers*, ed. I. M. Ward, Applied Science Publ. Ltd., London (1975).
16. I. Kimura, M. Kagiyama, S. Nomura and H. Kawai, *J. Polym. Sci. A-2*, **8**, 383 (1970).
17. T. M. Kelley and D. F. O'Brian, *Photog. Sci. Eng.*, **18**, 68 (1974).
18. H. Yoshida, S. Kobinata and S. Maeda, *Mol. Cryst. Liq. Cryst.*, **131**, 209 (1985).