This article was downloaded by:
On: *26 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Degree of order of aromatic and *N*-heterocyclic probes embedded in sodium lauril sulphate lyomesophases

Ourides Santin Fo[a]; Mário José Politi[a]; José Atílio Vanin[a]; Paulo Celso Isolani[a]
[a] Instituto de Quimica, Universidade de São Paulo, CEP, Brasil

To cite this Article Fo, Ourides Santin , Politi, Mário José , Vanin, José Atílio and Isolani, Paulo Celso(1992) 'Degree of order of aromatic and *N*-heterocyclic probes embedded in sodium lauril sulphate lyomesophases', Liquid Crystals, 11: 1, 15 — 23

To link to this Article: DOI: 10.1080/02678299208028965

URL: http://dx.doi.org/10.1080/02678299208028965

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 1992, VOL. 11, NO. 1, 15–23

Degree of order of aromatic and *N*-heterocyclic probes embedded in sodium lauril sulphate lyomesophases

by OURIDES SANTIN Fo.*, MÁRIO JOSÉ POLITI,
JOSÉ ATÍLIO VANIN and PAULO CELSO ISOLANI

Instituto de Química, Universidade de São Paulo,
P.O. Box 20780, São Paulo CEP 01498, Brasil

(*Received 16 May 1991; accepted 8 July 1991*)

Linear dichroism, time-resolved and steady-state anisotropy emission fluorescence were applied to the study of chromophores embedded in aligned and non-aligned lyotropic nematic phases. The phases are composed of sodium dodecyl sulphate, 1-decanol and water and contain long rod-like aggregates, which align their long axis parallel to an applied magnetic field. Pyrene, *p*-terphenyl, 9,10-diazaphenanthrene and carbazole were dissolved in these aggregates. The dichroic ratio results obtained for these probes in aligned mesophase show two main trends: firstly the hydrocarbons (pyrene and *p*-terphenyl) exhibit a dichroic ratio (ratio between absorption intensities of two perpendicular polarized beams of light) higher than unity for their in-plane long axis polarized band and a dichroic ratio near unity for their in-plane short axis polarized band. In this case the plane of the molecule tends to be oriented perpendicular to the symmetry axis (C_∞ axis) of the aggregates; and secondly for the *N*-heterocyclic molecules (9,10-diazaphenanthrene and carbazole) the situation is reversed, and these two probes tend to align the molecular plane nearly parallel to the symmetry axis of the aggregates.

The steady-state and time-resolved anisotropy values obtained for pyrene are typically 0·060 and 0·080 for non-aligned and aligned lyomesophases, respectively. In the first case the anisotropy is caused by a photoselective excitation of pyrene molecules embedded in a viscous environment and in the second, besides the photoselection, there is the effect of alignment by the applied magnetic field.

1. Introduction

The original discovery of the formation of nematic lyotropic liquid-crystalline phases, made by Lawson and Flautt [1], with sodium decyl sulphate (SDS), opened a wide area of investigation. Since then, many other systems forming nematic cylindrical (N_c) phases (i.e. systems composed of rod-like aggregates, whose director or optical axis align parallel to an applied magnetic field) have been described and studied. N_c systems obtained from SDS and potassium laurate (KL) are among the most investigated [2–5].

Recently [6], a N_c lyomesophase has been obtained with sodium dodecyl (lauril) sulphate (SLS). Subsequently, many investigations with the SLS/1-decanol/water N_c lyotropic phase have been performed in order to fully understand these systems. These studies include the description of the nematic domain in the ternary phase diagram [7], a characterization of the structure of the nematics contained in cylindrical capillaries by optical microscopy [8] and X-ray diffraction [9]; the first order N_c–N_d transition by optical microscopy [10], and the viscoelastic properties [11] of the N_c phase.

---

* Author for correspondence.

To date, no SLS N_c phase has been studied with the techniques of linear dichroism or polarized fluorescence. These techniques, which are useful for investigating the orientation of guest molecules, have been applied to sodium decyl sulphate [12] and potassium laurate [13, 14] N_c lyomesophases.

Here, we have used dichroic ratios for the determination of the order parameter of pyrene, *p*-terphenyl, 9,10-diazaphenanthrene and carbazole to obtain information about their orientation in aligned and non-aligned N_c SLS nematic phases, and results were compared with those reported for SDS [12, 13] and KL [14].

2. Theoretical

2.1. *Dichroic ratio*

The interaction of plane polarized light with a chromophore embedded in an oriented medium can lead to several results, depicted schematically in figure 1. If the light beam propagates along the x direction (laboratory frame) and the transition moment of the molecule is defined in the molecular frame, the extent of absorption of $I_{\parallel}$ and $I_{\perp}$ will be determined by the averaged orientation of the directions of the absorption transition moment with respect to the polarization planes of the incident light (see figure 1). If the molecular orientation in the sample is known, the direction of the transition moment within the molecular frame can be easily obtained. Conversely, if the averaged transition moment direction is known, information about the preferred molecular orientation is accessible.

The ratio of absorptances for the two polarizations considered ($A_{\parallel}$ and $A_{\perp}$), defined as the dichroic ratio, can be related to Saupe's order parameter by [15]

$$D=\frac{A_{\parallel}}{A_{\perp}}=\frac{1+2S}{1-S}. \tag{1}$$

This ratio contains information about the averaged distribution of the absorption dipole moment of the chromophore.

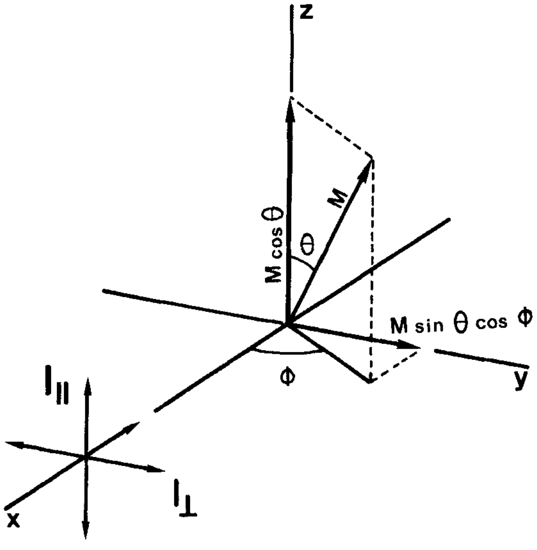


Figure 1. Transition dipole moment M and its projections in relation to the two plane polarized beams of incident light.

2.2. *Polarized fluorescence*

In an isotropic solution, fluorophores are oriented randomly. Upon excitation with polarized light, molecules with absorption transition dipoles parallel to the electric vector of the excitation are preferentially excited. This selective excitation results in a partially polarized fluorescence emission.

To obtain information about molecular orientation and motion from static and time-resolved fluorescence anisotropy measurements, the emission anisotropy, r or $r(t)$, respectively, is usually recorded. These functions are defined as [16]

$$r=\frac{F_v-F_h}{F_v+2\cdot F_h}, \tag{2}$$

and

$$r(t)=\frac{F_v(t)-F_h(t)}{F_v(t)+2\cdot F_h(t)}, \tag{3}$$

where $F_{(v,h)}$ are the fluorescence emission intensities of the vertical and horizontal polarizations respectively, when the sample is excited with vertically polarized light, with respect to the laboratory frame axes.

The time-resolved and steady-state anisotropy measurements can be related to the average angular displacement of the fluorophore which occurs between absorption and subsequent emission of light. This displacement depends on the rate and extent of rotational diffusion during the lifetime of the excited state, which, in turn, depends on the viscosity of the solvent, the size and shape of the molecule and its rotational motion.

Considering a Dirac function excitation pulse, the decays of fluorescence intensity and anisotropy can be described, respectively, by

$$F(t)=F_0\exp(-t/\tau), \tag{4}$$

and

$$r(t)=r_0\exp(-t/\varphi), \tag{5}$$

where τ is the fluorescence lifetime and φ is the rotational correlation time of the fluorophore. Assuming that the only processes involved, in the time-scale of the experiment, is the emission of fluorescence and the reorientation of the fluorophore, $r(t)$ will depend on the relation between τ and φ. Thus, if $\tau \ll \varphi$, a constant $r(t)$ value will be observed. When $\tau \gg \varphi$, the redistribution of the dipole moments will be completed before the emission occurs. In this latter case, only an equilibrium value will be observed for the anisotropy [17].

The equilibrium value is a function of the microviscosity of the environment, being zero for low viscosity and higher for more viscous media such as liquid crystals. The intermediate cases, when $\tau \approx \varphi$, $r(t)$ provides information about the tumbling motion of the molecule.

Here we investigate the behaviour of $r(t)$ for pyrene, a long-lived fluorophore, included in a SLS nematic N_c lyomesophase and compare the results with reported values for KL/N_c systems.

3. Experimental

Sodium dodecyl sulphate (Riedel de Häen) was recrystallized three times from absolute ethanol. Water and 1-decanol were triply distilled in an all glass apparatus. Pyrene [18], *p*-terphenyl [19], 9,10-diazaphenanthrene [20] and carbazole [21] (see figure 2), all from Eastman Kodak were used without further purification.

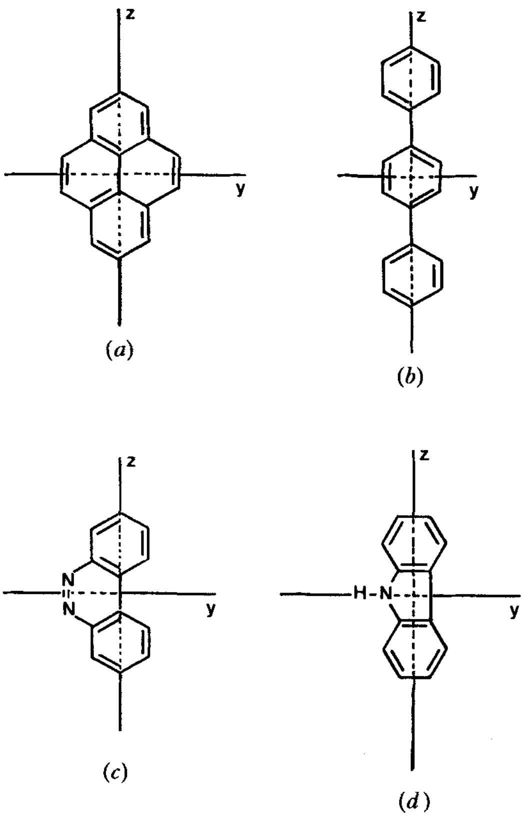


Figure 2. Molecular structures of the probes (*a*) pyrene, (*b*) *p*-terphenyl, (*c*) 9,10-diazaphenanthrene and (*d*) carbazole, with their respective molecular frames. For the orientations of the transition dipole moments of each molecule see [17–20].

The mesophases were prepared with the following composition: 25·00/4·47/70·53 wt.% of SLS, 1-decanol and water, respectively. The formation of a cylindrical N_c type phase, was checked by visual inspection of the sample texture between crossed polarizers [6]. The mesophases were doped with the probes by dissolving them in the decanol used to prepare the samples. Final probe concentration was always kept lower than 10^{-4} mol l^{-1}, in order to avoid inner filter effects, dimer formation or self-quenching. The lyomesophases were prepared and homogenized in test-tubes ($\phi = 1{\cdot}0$ cm) and transferred to 0·100 cm optical path absorption cuvettes. Doped and reference samples were macroscopically aligned by placing in the same geometry in a 2·3 T magnetic field for at least 24 h. The samples retained their orientation for several hours after removal from the field, as verified by their texture between crossed polarizers. The absorption spectra with polarized light were obtained in a Beckman DU-7 Spectrophotometer, equipped with an adjustable polarizer. The steady-state fluorescence and anisotropy spectra were obtained in a Perkin–Elmer LS-5 spectrofluorimeter equipped with polarization accessory (90° geometry). Time-resolved fluorescence and anisotropy decays were obtained with a PTI LS-1 (Canada) time-resolved spectrofluorimeter, using in both cases 0·500 cm optical path fluorescence cuvettes and a PTI supplied polarization accessory. The absorption and fluorescence experiments were carried out with the alignment in two directions, as

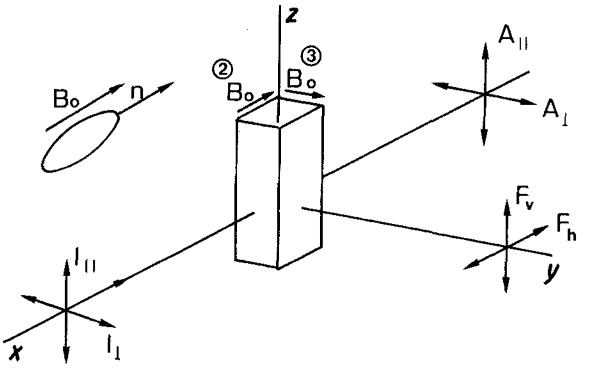


Figure 3. Geometric arrangement and orientation of the micelles of the lyomesophase in relation to the plane of polarization of the incident light beam and fluorescence emission. B_0 is the applied field. The director of the phase (n) defines the optical axis of the sample. Condition 2: incidence of light parallel to the applied field and condition 3: incidence of light perpendicular to the applied field.

illustrated in figure 3, and with unaligned samples as well. The overall conditions of the experiments are described below:

(1) Sample freshly prepared and transferred to the cuvette without action of the magnetic field;
(2) Sample aligned by the magnetic field with director parallel to the direction of the incident light (cf. figure 3);
(3) Sample aligned by the magnetic field with director perpendicular to the direction of the incident light (cf. figure 3).

4. Results and discussion

4.1. *Dichroic ratios*

The values of the dichroic ratio D are summarized in table 1.

The data presents a distinct trend, depending on the experimental set up. Under condition 1 (freshly prepared sample without alignment), D values scatter about unity with a standard deviation (σ) of *c.* 0·035. This trend is observed even for the $-y$ or $-z$

Table 1. Dichroic ratio† (D) for pyrene, *p*-terphenyl, 9,10-diazaphenanthrene and carbazole in conditions 1, 2 and 3.

Probe	$\lambda(i)$‡/nm	D for condition 1	D for condition 2	D for condition 3
Pyrene	233·0(z)	1·029	1·005	1·236
	274·0(y)	1·014	0·990	1·019
	337·0(z)	0·976	0·985	1·300
p-Terphenyl	211·5(y)	1·056	0·997	1·015
	283·5(z)	1·093	0·995	1·447
9,10-Diazaphenanthrene	311·0(z)	1·015	1·010	0·939
	358·0(y)	1·042	1·017	1·053
Carbazole	294·0(z)	0·998	0·996	0·950
	337·0(y)	1·000	0·991	1·403

† Each dichroic ratio value is the standard mean of at least three independent determinations.
‡ i is the axis of polarization of the band in the molecular frame.

polarized bands. Under condition 2 the scattering about unit was reduced, whatever the polarization of the band and σ decreased to 0·010. In condition 3 two different behaviours can be distinguished:

(i) for pyrene and *p*-terphenyl, D values for the $-z$ polarized bands are greater than unity, while those for the $-y$ band are very near unity;
(ii) for the *N*-heterocycles the situation is reversed, D values for $-z$ bands being lower and those for $-y$ bands greater than unity.

Samples recently transferred to capillaries, (condition 1), contain microdomains of ordered micelles [22]. Thus, the interaction of the polarized light with the chromophore in each domain can, in principle, cause differential absorption of the vertical and horizontal components of the light. The micelles in each microdomain are ordered, but randomly distributed in the bulk of the phase [21]. Therefore, one should expect a D value dispersed about unity. In condition 2, the dispersion of the D value about unity is reduced. This suggests the existence of an isotropic distribution of the $-z$ and $-y$ dipole moments of the molecules with respect to the polarization of the incident light, which results in a dichroic ratio approximately equal to one. Supposing that, in this condition the direction of propagation of light is perpendicular to the plane of the aromatic rings of the probes (provided that the degree of non-planarity of the phenyl rings of *p*-terphenyl is low when confined in these systems [23, 24]), then these planes are isotropically distributed around the direction of propagation (which is the same as the symmetry axis of the micelles), leading to $A_{\parallel}/A_{\perp} \approx 1$.

In condition 3, if the plane of the aromatic rings of pyrene and *p*-terphenyl lies perpendicular to the symmetry axis of the micelle and contains the propagation axis, then vertically polarized light will be absorbed more intensely than horizontal, leading to a ratio $A_{\parallel}/A_{\perp}$ higher than unity for the in-plane $-z$ polarized bands. In the case of the short-axis in-plane ($-y$) polarized bands of these two molecules, the D value is very near to unity. This effect can be explained by the strong dispersion of the symmetry axis of the micelles around the direction of the applied field.

The situation for the *N*-heterocycles is strikingly different. The D values for the in-plane short axis ($-y$) absorption bands are higher than unity, while the D values for the long axis in-plane ($-z$) absorption bands are somewhat lower than unity. These results suggest that the *N*-heterocycles lie their $-z$ long axis nearly parallel to the symmetry axis of the micelles, with their in-plane ($-y$) short axis radially distributed around this symmetry axis and their polar *N*-groups directed toward the interface of the micelle. This conclusion agrees with the data of Samori and Mattivi [13].

4.2. *Fluorescence*

The steady-state fluorescence anisotropy of pyrene in liquid-crystalline lyomesophase systems is presented in figure 4, as a function of wavelength emission. The fluorescence anisotropy is lower for a non-aligned mesophase than for an aligned mesophase, with the excitation parallel to the external applied magnetic field (see figure 3).

The $r(t)$ decay curves for aligned and non-aligned lyomesophases are displayed in figure 5. As can be seen, $r(t)$ rapidly reaches a limiting non-zero constant value for both systems. This can be interpreted by the fact that the time dependence of anisotropy ceases within a very short time compared to the lifetime of fluorescence (147 ns), as already pointed out by Johansson and Lindblöm [14].

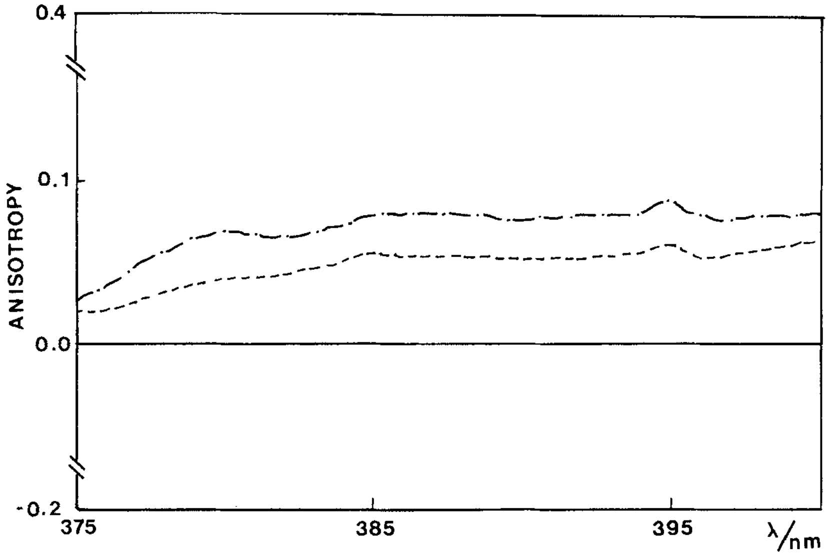


Figure 4. Fluorescence emission anisotropy of pyrene in: (– – –) non-aligned phase and (— · — · —) aligned phase with excitation parallel to the field. $\lambda_{exc} = 337$ nm.

Table 2. Steady-state and time-resolved emission anisotropies of pyrene in some systems ($\lambda_{exc} = 337$ nm; $\lambda_{obs} = 385$ nm).

Sample	r	$r(\infty)$
Liquid crystal with EXC ∥ B_0	0·087	0·082
Liquid crystal without B_0	0·061	0·062

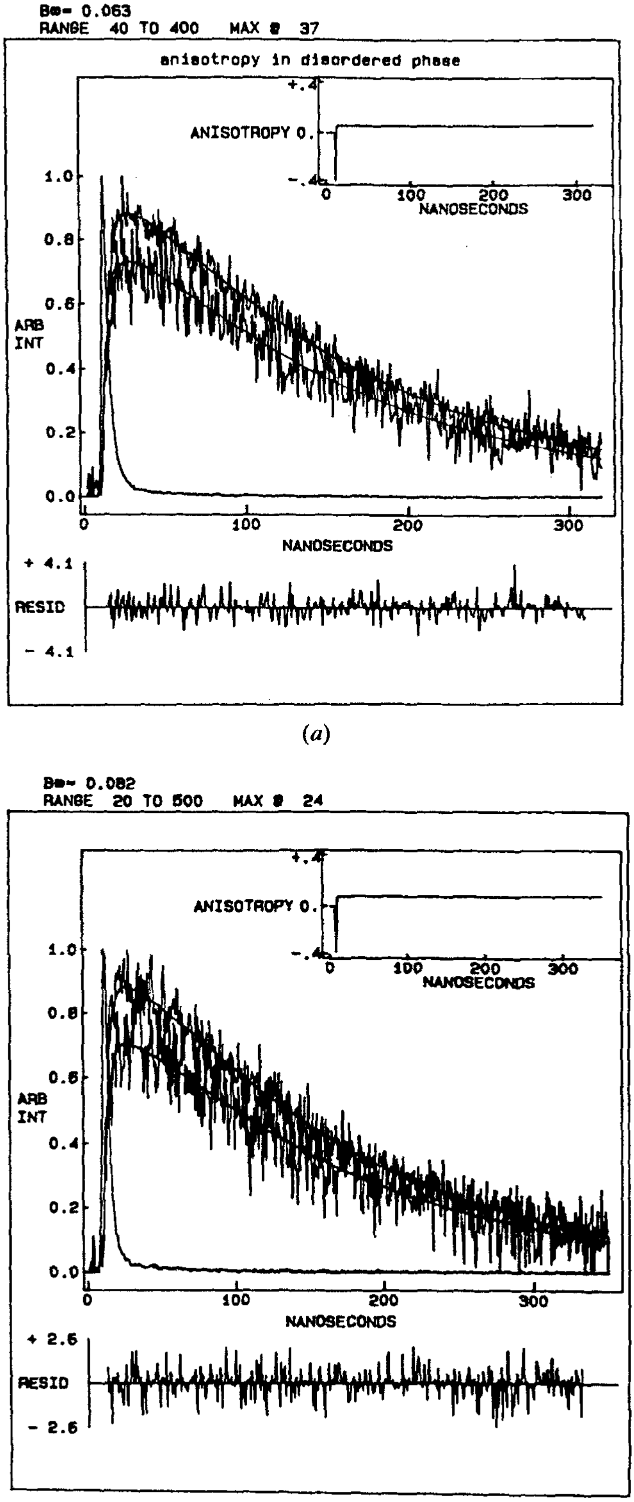
In table 2, values of r measured at $\lambda_{exc} = 337$ nm and $\lambda_{em} = 385$ nm and the corresponding limiting $r(t)$ values are listed. The values of r and $r(t)$ are quite similar and present the same trend as observed in figure 4.

The residual anisotropy after the absorption and emission of light in the case of a disordered phase can be attributed to the photoselective absorption and emission of the isotropically distributed probes embedded in a relatively viscous environment. For the ordered systems, besides the photoselection, there is a positional ordering of the fluorophores, which leads to an increase in the residual anisotropy.

The agreement of our results from steady-state and time-resolved anisotropy for a disordered liquid crystal with those reported by Johansson and Lindblöm (working with a KL phase) shows that there is no relation between the rigidity of the pyrene molecule included into the micelle and the chain length or head-group of the monomer and hence, the viscosity of the environment can be considered nearly the same. In addition, the difference between the anisotropy of the aligned and non-aligned lyomesophases shows the strong influence of the magnetic alignment over these systems.

5. Conclusions

The results presented here show that aromatic hydrocarbons tend to align radially within the host micelle. However, nitrogen heterocycles are strongly affected by



(*a*)

(*b*)

Figure 5. $r(\infty)$ values and anisotropies for (*a*) non-aligned and (*b*) aligned lyomesophases.

alignment of the *N*-polar groups by the polar micellar surface. The behaviour of the guest molecules embedded in SLS lyomesophases is similar to that in KL systems, despite the differences in composition and the monomer structures of the two systems.

We acknowledge financial support from CNPq and FAPESP, thanks to Hernán Chaimovich for useful discussion and Frank Herbert Quina for revision and to Eduardo H. Horikawa for the drawings.

References

[1] LAWSON, K. D., and FLAUTT, T. J., 1967, *J. Am. chem. Soc.*, **89**, 5489.
[2] RADLEY, K., REEVES, L. W., and TRACEY, A. S., 1976, *J. phys. Chem.*, **80**, 174.
[3] FUJIWARA, F. Y., and REEVES, L. W., 1978, *Can. J. Chem.*, **56**, 2178.
[4] FUJIWARA, F. Y., and REEVES, L. W., 1980, *J. phys. Chem.*, **84**, 653.
[5] HENDRIKX, Y., CHARVOLIN, J., RAWISO, M., LIEBÉRT, L., and HOLMES, M. C., 1983, *J. phys. Chem.*, **87**, 3991.
[6] AMARAL, L. Q., MARCONDES-HELENE, M. E., BITTENCOURT, D. R., and ITRI, R., 1987, *J. phys. Chem.*, **91**, 5949.
[7] AMARAL, L. Q., and MARCONDES-HELENE, M. E., 1988, *J. phys. Chem.*, **92**, 6094.
[8] BITTENCOURT, D. R. S., and AMARAL, L. Q., 1989, *Liq. Crystals*, **4**, 283.
[9] AMARAL, L. Q., 1989, *J. appl. Cryst.*, **22**, 519.
[10] AMARAL, L. Q., 1990, *Liq. Crystals*, **7**, 877.
[11] PINTO, A. V. A., and AMARAL, L. Q., 1990, *J. phys. Chem.*, **94**, 3186.
[12] SÖDERMAN, O., LINDBLÖM, G., JOHANSSON, L. B. A., and FONTELL, K., 1980, *Molec. Crystals, liq. Crystals*, **59**, 121.
[13] SAMORI, B., and MATTIVI, F., 1986, *J. Am. chem. Soc.*, **108**, 1679.
[14] JOHANSSON, L. B. A., and LINDBLÖM, G., 1986, *Liq. Crystals*, **1**, 53.
[15] JOHANSSON, L. B. A., SÖDERMAN, O., FONTELL, K., and LINDBLÖM, G., 1981, *J. phys. Chem.*, **85**, 3694.
[16] LAKOWICZS, J. R., 1983, *Principles of Fluorescence Spectroscopy* (Plenum Press), chap. 6.
[17] ZANNONI, C., 1979, *Molec. Phys.*, **38**, 1813.
[18] HOIJTINK, G. J., VELTHORST, N. H., and ZANDSTRA, P. J., 1960, *Molec. Phys.*, **3**, 533.
[19] THULSTRUP, E. W., SPANGET-LARSEN, J., and GLEITER, R., 1979, *Molec. Phys.*, **37**, 1381.
[20] GOTTARELLI, G., SAMORI, B., and PEACOCK, R. D., 1977, *J. chem. Soc. Perkin 2*, 1208.
[21] PINKHAM, C. A., and WAIT, S. C., 1968, *J. molec. Spectrosc.*, **27**, 326.
[22] ISOLANI, P. C., REEVES, L. W., and VANIN, J. A., 1979, *Can. J. Chem.*, **57**, 1108.
[23] SUZUKI, M., 1960, *Bull. chem. Soc. Japan*, **33**, 109.
[24] GUPTA, S. P., and KRISHNA, B., 1972, *J. Am. chem. Soc.*, **94**, 57.