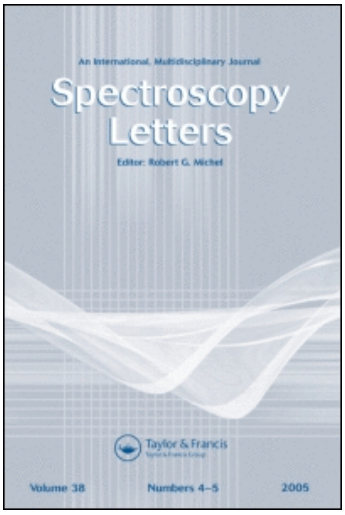

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ORIENTATION STUDIES OF PROBE MOLECULES IN LAMELLAR LIQUID CRYSTALLINE LIPID SYSTEMS BY LINEAR DICHROISM

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The LD-method of inclined incidence was found useful in the study of the orientations of probe chromophores (carotene, anthracene) solubilized in lamellar mesophases of the systems sodium octanoate/decanol/water and sodium di-2-ethylhexylsulphosuccinate/water, respectively. The results suggest the existence of two competing molecular orientation mechanisms aligning the longest axis of the probe molecule either parallel with the lamellar surface or perpendicular to it.

Ordinary LD spectroscopy is not applicable at normal incidence on thin layers containing chromophores which are uniaxially oriented along an axis perpendicular to the layer plane. However, it has recently been shown[1], that the orientation of a chromophore may be revealed by studying an aligned lamellar sample at inclined incidence. If $A_{\perp}$ denotes the absorption when the electric vector of light oscillates parallel to the "hinge axis", around which the sample is tilted, and $A_{\parallel}$ denotes the absorption when the electric vector is perpendicular to this axis the ratio $(A_{\parallel} - A_{\perp})/A = LD/A$ (A is the absorption of a random sample, LD is supposed to have been corrected for polarised reflection) is given by

$$\frac{LD}{A} = \frac{3}{2}\left(3 < \cos^2\theta > - 1\right) \cos^2\omega / \sqrt{1 - \left(\cos\omega/n\right)^2} \qquad (1)$$

The angle ω is that between the plane of the sample and the direction of light propagation, n is the average refractive index of the sample, θ denotes the angle between the molecular transition moment responsible for the absorption and the normal to the plane of the sample (FIG. 1).

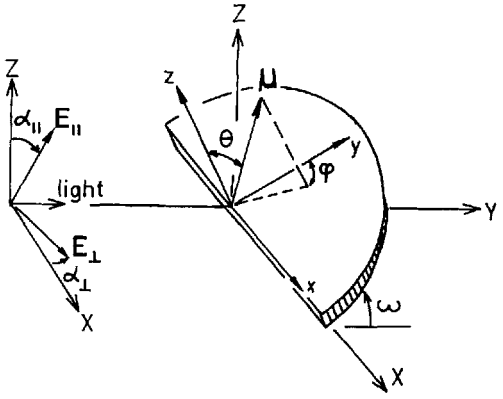

FIG. 1

Schematic picture of a macroscopically aligned membrane at inclined (ω) incidence in the elliptically conical (α) light pencil in a linear dichroism spectrometer. The orientation angles, θ and ϕ, of the transition dipole moment of the probe chromophore in the membrane coordinate system (x y z) and the membrane alignement in the laboratory coordinate system (X Y Z), respectively.

If the transition moment is along a symmetry axis, say x, in the molecule, the order parameter $f_x = (3 < \cos^2\theta_x > - 1)/2$ obtained from eq. (1) may be used as a measure of the average orientation of this axis with respect to the optical axis of the sample.

We have doped with chromophoric probe molecules samples from two lamellar liquid crystalline lipid systems; viz. the lamellar phase of the system sodium n-octanoate/n-decanol/water (System I) and the lamellar phase of the system sodium di-2-ethylhexylsulphosuccinate/water (System II).

Macroscopic alignment was obtained by heating the sample, placed as a thin layer between two glass plates, to 100°C and then cooling it down to room temperature. LD was found to follow the dependence on ω ($90^o \leq \omega \leq 30^o$) predicted by eq. (1), FIG. 2. That the orientation was uniaxial was proved by a zero LD at $\omega = 90$.

Depending on the size and shape of the chromophore molecule and on the type of the liquid crystalline "solvent" the chromophore molecules were found to orient themselves in two ways inside of the hydrophobic

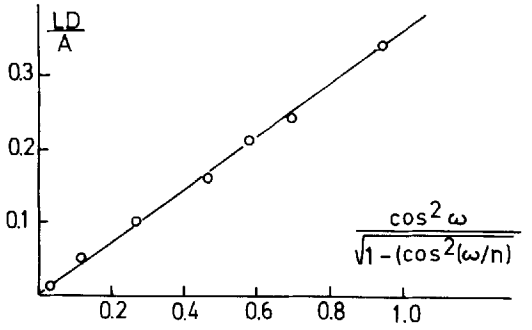

FIG. 2

LD (corrected for reflection) plot according to eq. (1) for the band A of carotene in the system I.

region. The longest dimension of the molecule was either parallel or perpendicular to the optical axis (the normal to the surface of the lipid lamellae). In System I short rod-like molecules (such as diphenylethyne, anthracene etc.) were oriented parallel, whereas a long molecule, such as β-carotene, was perpendicularly oriented. In System II all molecules were perpendicularly oriented.

The order parameter f (θ) was reproducible for corresponding samples as long as the total layer thickness was the same. The degree of orientation could be decreased by raising the temperature but it regained its initial value upon returning to the original temperature. However, a small mutual displacement of the glass plates caused a completely irreversible randomisation.

A monotonic decrease in f (θ) with increasing total sample layer thickness was generally the rule, see e.g. TABLE 1. This phenomenon is of course caused by incomplete macroscopic orientation at large distances from the glass plate.

With the aim of estimating to what extent the dimensions of the amphiphile and water lamellae influence the solute orientation we have also made some preliminary studies on samples of different composition.

FIG. 3 shows the orientation of trans-β-carotene and anthracene, respectively, in System II as function of weight composition. In both cases f (θ) obviously goes through a maximum.

TABLE 1

Obtained orden parameters of anthracene dissolved in a system of 18.2% sodium n-octanoate, 35.5% n-decanol and 46.3% water

Sample thickness /μm	253 nm (z-polarized)				377 nm (y-polarized)			
	LD_{45}	A	$(\frac{LD}{A})_{45}$	f_z	$LD_{45} \times 10^2$	A	$(\frac{LD}{A})_{45}$	f_y
10*	0.055	0.29	0.19	0.11	- 0.18	0.021	- 0.08	- 0.05
28*	0.12	1.31	0.09	0.05	- 0.26	0.058	- 0.04	- 0.03
50*	(0.18)	2.22	0.08	0.05	- 0.53	0.105	- 0.05	- 0.03
120	(0.36)	5.28*	0.07	0.04	- 0.85	0.250	- 0.03	- 0.02

* calculated from A at 377 nm.

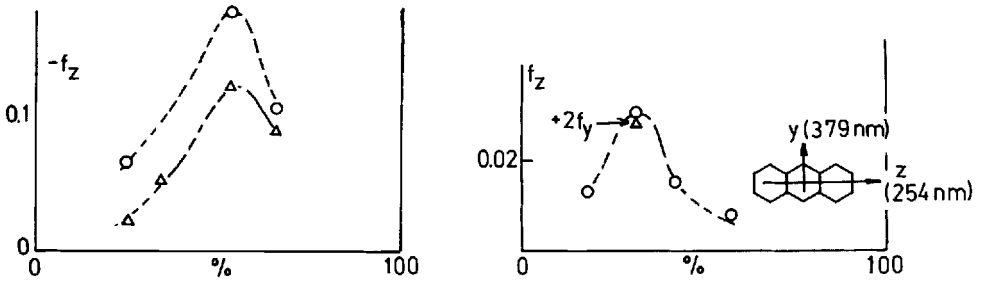

FIG. 3

System II, orientation of β-carotene (band A) (left) and of anthracene (right) and dependence on lipid composition. (Sample thickness 20 μm ○ , 40 μm Δ).

A similar behaviour has also preliminarily been found in some cases of System I, see e.g. TABLE 2.

It is easy to understand the observation of an orientation of short rod-like molecules (anthracene, diphenylethyne) parallel to the long-chain hydrocarbons of the lipid lamellae of System I, i.e. parallel to the optical axis. On the other hand, the trans-β-carotene, whose molecule has a length of 2.2 nm, can hardly adopt such a parallel orientation along the chains inside the thin amphiphile layers (lipid layer thickness is about 2.4 nm)[3].

In the case of System II the branched hydrocarbon implies a less regular order inside the amphiphilic lamellae and the interaction between probe molecule and hydrocarbon chains can hardly be expected to yield any effective net probe orientation (FIG. 4).

TABLE 2

Obtained long-axis order parameter (f_z) and order parameter obtained from band B (f_B) of β-carotene "dope" (less than 0.1%) in System I.

% NaC_B	% decanol	% H_2O	Sample thickness μm	$(\frac{LD}{A})_A$	f_z	$(\frac{LD}{A})_C$	f_z	$(\frac{LD}{A})_B$	f_B
40.2	34.7	25.1	40	- 0.21	- 0.12	- 0.18	- 0.11	0.17	0.10
			25	- 0.25	- 0.14	- 0.21	- 0.12	0.17	0.10
18.2	35.5	46.3	40	- 0.22	- 0.12	- 0.24	- 0.14	0.79	0.46
			24	- 0.28	- 0.16	- 0.34	- 0.20	0.81	0.46
12.1	27.9	60.0	40	- 0.14	- 0.08	- 0.21	- 0.12	0.24	0.14

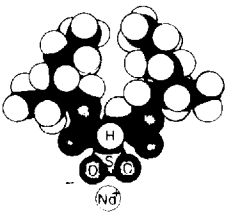

FIG. 4

The molecular configuration of sodium di-2-ethyl-hexylsulphosuccinate

Thus the predominant perpendicular orientation toward the optical axis obtained suggests an independent orientation mechanism favouring in-plane orientation. This idea of two different orientation mechanisms is also supported by the orientation of trans-β-carotene in the samples of System I. Furthermore, according to Eckert and Kuhn[2] (and also following an analysis of the results presented in our earlier report[1]) only two of the observed absorption bands (A and C in FIG. 5) derive from trans-β--carotene while the third band (B) is due to the cis-isomer; the latter band is assigned to be polarised along the C_2 axis of this now planar molecule. The positive sign of the f_B values (TABLE 2) thus indicate that this direction is aligned parallel to the amphiphile hydrocarbon chains. The poor correlation for different compositions between f_Z (which is believed to reflect the long-axis orientation of mainly trans - carotene) and f_B may be caused by a varying degree of isomerization.

Finally we want to comment on the possibility of using anthracene in order to measure the average orientations of the molecular axes, f_z and f_y. Since $\Sigma f = 0$ we are able to determine all three order para-

meters and for the highest orientation we obtain $f_z = 0.11$ $f_y = -0.05$ and $f_x = -0.06$ (see TABLE 1). As deduced from other studies anthracene behaves not as an ideal disc ($f_z = f_y$) but rather as a rod, viz. $f_y = f_x$.

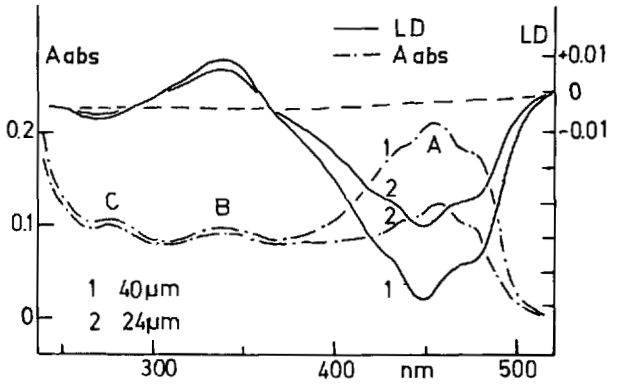

FIG. 5

A_{abs} and LD spectra of β-carotene in System I at $\omega = 45^0$ (two sample thicknesses)

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