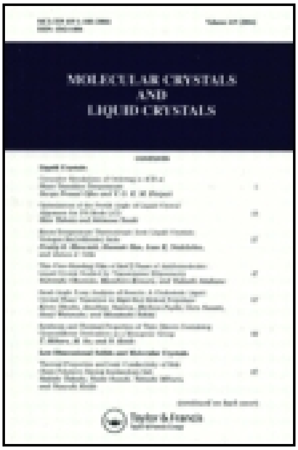

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The Nematic Lyophases N_C+, N_C-, N_D+ and N_D- as Hosts for Orange-red and Phaeophytin a in Model Systems

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THE NEMATIC LYOPHASES N_C+ , N_C - , N_D+ AND N_D- AS HOSTS FOR ORANGE-RED AND PHAEOPHYTIN A IN MODEL SYSTEMS.

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Abstract Two probe molecules, Orange-red (OR) and the photosensitive pigment phaeophytin a (Pha) have been studied in micellar nematic lyophases of different aggregate shapes and magnetic properties representing the N_C+, N_C- , N_D+ and N_D- classes. Good order have been obtained when the results from linear dichroism measurement were related to theoretical calculations. The results allow to select the host probe alignment and also to determine the phase class. A photochemical reaction has been studied using Pha as sensitizer in nematic solution. The reaction was followed through spectral absorption of the reaction product reduced methylviologen . Two situations have been compared in oriented systems of N_D+ micelles : the excitation beam was polarized parallel or perpendicular to the field direction. The quantum yield was twice as high in the first case which is a clear proof of effect from orientation.

INTRODUCTION

Many new nematic lyophases of amphiphilic aggregates have been reported in the literature since the survey of Forrest [1] at the beginning of 1981 and our own table presented at the Sunapee meeting the same year. The solutions have been divided into four classes: N_C + , N_C - , N_D + and N_D - according to aggregate shape, N_C for cylinders and N_D for disks, and to their magnetic orientation mode, + and - for the aggregate axes parallel and perpendicular to the field direction. [2]

The anisotropic order in these solutions can be transmitted to solute molecules as in thermotropic systems, a fact that introduces complementary properties to solute molecules in micelles.

Convenient solutions representing the four nematic lyophase classes have been selected from the literature. Laurent and Samori have shown that one can play with aggregate shape and field direction in order to optimize the desired position of a solute molecule [3] . The authors have calculated the solute order parameters using the values of linear dichroism for Orange-red (OR).

We have shown that another probe molecule, phaeophytin a (Pha) can be successfully ordered in these nematic solutions. Pha was chosen as a representative for the photosynthetic pigments in order to build a model system of the tylakoid membrane. Some examples of dye molecule orientation in nematic lyophases have also been reported in the literature [4].

As a complement to the determination of solute ordering which results from the anisotropic aggregate properties, we have further made an estimation of the solute implantation in the micelles of the host solution [5]. This has been expressed through the values of local polarity obtained from spectral absorption data which were related to Kosower's Z values and Taft's $\pi*$ parameters for probes in organic solvents.

The utility of such probe organization has further been shown for a chemical reaction where the efficiency of Pha as a photosensitizer has been investigated when dissolved in a nematic lyophase oriented in the magnetic field.

EXPERIMENTAL PART

4. Dimethylamino - 4' - nitroazobenzene (OR) was prepared by diazocoupling of 4 - nitroaniline and 4 - dimethylaniline . The product was recrystallized from ethanol and ethanol /benzene, m.p. 230 - 232°C.

Phaeophytin a (Pha) was obtained from pure chlorophyll a with oxalic acid in acetone / water solution. The pigment, purified by chromatography , had the required Soret over Red band ratio $r_{QB} = 1.99$ in ethylether.

The soaps were prepared and purified as follows : sodium decylsulfate (SdS) from decanol and "fuming" sulfuric acid, the product was neutralized with sodium hydroxide and recrystallized from absolute ethanol; potassium laurate (KL), potassium hexyloxybenzoate (KHxOB) and potassium heptyloxybenzoate (KHpOB) by exact neutralization of lauric acid (Aldrich "Gold Label"), hexyloxy- and heptyloxybenzoic acids (Frinton) with alcoholic potassium hydroxide. KL was recrystallized twice from absolute ethanol, KHxOB from ethanol/water and methanol and KHpOB from ethanol/water and ethanol/ethylacetate. The soaps were dried at 120°C under reduced pressure and stored protected from moisture.

Decanol (dOH) and heavy water were Merck products,light water was purified through a Millipore R/Q ion exchange unit. Sodium sulfate and potassium chloride were analytical grade compounds.

The phases of composition according to Table I were prepared by mixing the exact weighed compounds using vibration and ultrasound. They were stored at 24°C and used after about one week when appropriate textures had developed as observed by the polarizing microscope.

Dye solutions were prepared from accurate stock solutions in acetone. The stock solvent was evaporated and replaced by the nematic solutions. The dyes were completely dissolved ,using vibration and ultrasound. The concentrations were 2.2×10^{-4} moles.kg^{-1} (2.5×10^{-4}M) for OR and 1.2×10^{-4}moles.kg^{-1} (1.3×10^{-4}M) for Pha. They were suitable for spectroscopic measurements in the cells used, of 1 mm's path.

Ethylenediaminetetraacetic disodium salt (EDTA) was provided by Janssen and methylviologen (MV^{2+}) by Aldrich. The solute concentration of the nematic reaction-mixtures were : EDTA : 2×10^{-3} M.kg^{-1}, MV : 5.8×10^{-3} M.kg^{-1} and Ph a :

0.9 x 10^{-4} M.kg^{-1}. The reagents were incorporated in the solution one after the other,under light protection. The oxygen was eliminated by agitation under a stream of He bubbled through a heavy water trap. The cells were also filled under flush of He.

The dichroic measurements in the magnetic field were done with the described experimental device[14]. The field was 1.2 Tesla and the temperature control ± 0.05°C.

The absorption spectra of Pha and the photochemical reactions were recorded on a Beckman Acta C III spectrophotometer with polarizers inserted in front of the sample cells. The irradiation was done in the 670 nm band of Pha using a halogen lamp with filters selectioning a band of about 10 nm. The irradiation power was measured with a Tektronix photometer about 90 w/m^2 (3.10^{20} photons s^{-1}. m^{-2}). A beam polarizer was used for the experiment in the oriented system.

The transition temperature and texture observations were made with a Leitz Dialux Pol MF microscope on which a heating-cooling device had been adapted.

RESULTS AND DISCUSSION.

SELECTION OF GOOD REPRESENTATIVES OF THE FOUR NEMATIC CLASSES

The systems chosen for our experiments representing the N_C+, N_C-, N_D+ and N_D- are presented in Table I. Most of them are well known,their phase domains are close to room temperature and they dissolve our probe molecules. They have been named after the abrevations used for the soap amphiphiles followed by a number in brackets according to our classification [15].

Such systems are very sensitive to compound quality and handling and we have therefore reported the transition temperatures observed on our samples although the solutions are most of the time known from the literature. We have also added the pH values and physical data that we have measured on some of our samples.

DICHROIC MEASUREMENTS, ORDER AND IMPLANTATION SITES OF PROBES IN NEMATIC SOLUTIONS ORIENTED BY A MAGNETIC FIELD

We have used the theoretical results recently developed[3] and we have summarized the results of linear dichroism and order for the rod-like probe OR. The molecule has a long dimension close to the amphiphilic chain length. This water insoluble molecule was assumed to be equally distributed within the aggregate including caps or rim.

We have used these data in order to compare them with what was found for Pha in the same nematic lyophases. The results are given in table II.

The general formula for linear dichroism of a probe molecule in the micellar aggregate is $LD = \frac{3\ Sa \times Sm}{2} (2 - \sin^2 \beta)$. Sa : aggregate order parameter with respect to field direction, S_m : probe molecule order parameter with respect to the aggregate axis and β : transition moment angle for the probe with the main molecular axis.

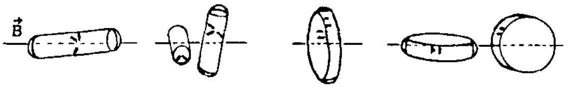
N_C^+	N_C^-	N_D^+	N_D^-
KL(2)[7]	KL(2) / KHpOB[10]	KL(4) / KHpOB[12]	KL(4)[13]
KL D_2O KCl	KL D_2O KHpOB KCl	KL D_2O KHpOB dOH KCl	KL D_2O dOH KCl
33 64,8 2,2	26,1 64,2 7,5 2,2	17,5 62,6 12,4 5,3 2,2	30 60 6 4
20°C < N_C^+ < 45°C	20°C < N_C^- < 34°C	20°C < N_D^+ < 48°C	20°C < N_D^- < 70°C
pH d	pH	pH	pH d Δn
9,5 1,129	10	11	11 1,114 $7,4.10^{-3}$
KL(3)[8]	KHxOB(3)[11]	KHxOB(4)[11]	KL(3)[8]
KL D_2O dOH	KHxOB D_2O dOH	KHxOB D_2O dOH Na_2SO_4	KL D_2O dOH
26 67,8 6,2	36,5 55,9 7,6	39,1 48,9 5,8 6,2	26 67,8 6,2
18°C < N_C^+ < 42°C	27°C < N_C^- < 40°C	20°C < N_D^+ < 70°C	10°C < N_D^- < 15°C
pH d $\eta_{30°}$	pH	pH	pH d $\eta_{30°}$
11 1,117 160	9	9	11 1,117 160
SDS(3)[9]			SDS(3)[9]
SDS D_2O dOH			SDS D_2O dOH
35,9 56,9 7,2			35,9 56,9 7,2
28°C < N_C^+ < 42°C			20°C < N_D^- < 24°C
pH d Δn $\eta_{35°}$			pH d $\eta_{22°}$
5,5 1,113 $-1,97\ 10^{-3}$ 300			5,5 1,113 640

KL = Potassium Laurate ; KHxOB = Potassium Hexyloxybenzoate ; KHpOB = Potassium Heptyloxybenzoate ; SdS = Sodium decylsulfate ; dOH = decyl alcohol .

d = density ; η = capillarity flow viscosity (cP).

TABLE I

The experimental data for the solutions representing the four classes of nematic lyophases: their compositions are given in percentage by weight. KL = potassium laurate, KHxOB = potassium hexyloxybenzoate, KHpOB = potassium heptyloxybenzoate, SdS = sodium decylsulfate, dOH = decanol.
The temperature domains of the phases are indicated as well as the pH and some values of density = d, capillary flow viscosity = η and birefringence = Δn.



$$\text{L.D.} = 3/2\ S_aS_m\ (2 - \sin^2\beta) \qquad \text{For } \beta = 0 \quad \text{L.D.} = 3\ S_aS_m$$

	N_{C^+}	N_{C^-}	N_{D^+}	N_{D^-}
S_a (dir. = $\vec{B}$)	1	-1/2	1	-1/2
S_m(aggr. axis)	-1/2	-1/2	1	1
$S_a\,S_m$	-1/2	1/4	1	-1/2
L.D.max = 3 $S_a\,S_m$ (perfect order)	-1,5	0,75	3	-1,5

	KL(2)	SdS(3) t >28°	KL(3) t >18°	KHxOB(3)	KHxOB(4)	KL(4)/ KHpOB	KL(4)	SdS(3) t<24°	KL(3) t<15°
C = Correction factor for half-spheres or rim.	0,427	0,567	0,427	0,427	0,425	0,425	0,425	0,434	0,425
L.D._{max} corr. = C∗L.D._{max}	-0,641	-0,851	-0,641	0,320	1,275	1,275	-0,638	-0,651	-0,638
O.R. β=0 (490 nm)									
L.D. exp.	-0,275	-0,377	-0,285	0,281	0,750	0,527	-0,253	-0,383	-0,297
$\text{TaTm} = \dfrac{\text{L.D.exp.}}{\text{L.D.}_{max}\ \text{corr.}}$	0,43	0,44	0,43	0,88	0,59	0,41	0,55	0,59	0,47
Ph a (670 nm)									
L.D. exp.			-0,66	0,50		1,05			-0,69
TaTm			1,03	1,56		0,82			1,08
$\text{TaTm}' = \dfrac{\text{L.D.exp.}}{\text{L.D.}_{max}}$			0,44	0,67		0,35			0,46

TABLE II

The theoretical values of LD for perfect order[3]: S_a = aggregate axis order with respect to the field, S_m = molecular axis order with respect to the aggregate, leading to LD_{max} and LD_{max} corr. when the values are corrected for effect from caps or rim. The experimental values of LD: for OR where $\beta_{490nm} = 0$ (β = angle between the transition moment and the molecular long axis) and for Pha at the 670nm transition Q_y situated in the tetrapyrrole plane. The LD_{exp} values have been obtained from spectral absorbances in polarized light as indicated in the text. The rates of order in the systems are expressed as $T_a \times T_m$.

The first two lines in table II give the ideal order parameters in the four micellar situations and, the third line, their combination $S_a S_m$ leading to the values LD $_{max}$ when the order is perfect.

These values neglect end-effects from the two half spheres in the case of cylinders and from the rim in the case of disks. The end-effects are important, however and variations appear for the same type of aggregates due to different dimensions when they are not built up from the same amphiphiles. A "correction" factor C is thus introduced leading to LD $_{max}$ corr. (about half of the incorrected values).

The measured values of LD have been obtained from : $LD_{exp} = \frac{A_{\parallel} - A_{\perp}}{1/3\ (A_{\parallel} + 2A_{\perp})}$.

$A_{\parallel}$ and $A_{\perp}$: optical density of the absorption band, in parallel and perpendicular plane of light polarization with respect to the field direction.

The order of the systems, $T_a T_m$ has been expressed as a rate between the experimental and the calculated maximum value of linear dichroism.

This order ratio has reasonably good and consistent values for OR in almost all situations : the sign of LD $_{exp}$ for OR correspond to $\beta = o$, thus to the long molecular axis perpendicular to the interface. The $T_a T_m$values for Pha are too high (> 1). This could be explained from the important dimensions of the pigment molecule. We have therefore assumed that this probe is absent in the aggregate extremities and thus calculated a $T_a T_m'$ using the non corrected value of LD $_{max}$. These results fall in the same range as those for OR.

In the N_C- situation, the $T_a T_m$values are high for both probes compared with the orther classes. We can explain this from wall effects where the situation of the cylinder axis parallel to the cell windows is privileged, leading higher values of $A_{\parallel}$

The sign and value of LD at 670 nm for Pha indicate a red Qy transition moment perpendicular to the interface as they are comparable to those of OR. Imprecise values are obtained for the Qx band at 540 nm, but with opposite sign which confirms this transition parallel to the interface.

From $T_a T_m$ about 0.5, a probe order parameter of 0.7 is obtained using the aggregate order parameter 0.7 reported in the literature.

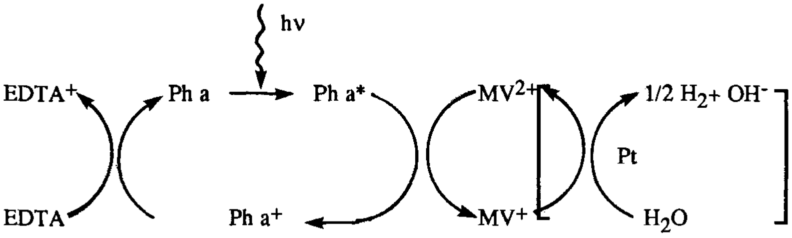
The expermiments show that probe molecules can be oriented in lyotropic as well as thermotropic guest/host systems. The theoretical considerations show that the N_D + is above all the best situation for well defined alignment and N_C- the poorest.

Informations from LD of known probe molecules can , on the other hand, be used for identification of the nematic classes; the sign of LD for both probe molecules, Pha as well as OR, distinguishes two groups : + for N_C- and N_D+, - for N_C+ and N_D-. The magnitude of LD will indicate whether the phase is N_C- or N_D + since the values for N_D $^+$ are considerably higher. The N_C and N_D can usually be well distinguished by their planar or homeotropic textures. This is applicable to both groups.

A complementary study has been made of implantation sites of OR and Pha within the micellar aggregates studied [5]. The results are consistent with a site in polar regions near the interface for OR. Pha is, on the contrary, likely located in the non polar micellar core. This could be in agreement with a perpendicular implantation of the tetrapyrrole plane containing the deduced perpendicular Q_y transition moment, between the limits of the amphiphilic bilayer.

APPLICATION OF NEMATIC LYOPHASES AS SOLVENTS FOR A PHOTOCHEMICAL REACTION

We have chosen the following reaction where phototransfer of electrons is involved



Similar reaction systems have been investigated in the literature in ordinary micellar solutions [16,17,18].

These offer advantages of radical trapping and charge separation due to the hydrophobic and hydrophilic compartments and to the charged interface.

Our purpose was to see if the nematic state could be maintained after dissolution of the different reagents, if the electronic transfer was possible in our systems and if orientation of the photosensitive molecule, Pha, favoured the capture of incoming light. We have used ethylenediaminetetraaceticacid disodium salt EDTA as electron donor and 1,1'- dimethyl - 4-4'- bipyridinium dichloride MV^{2+} as electron acceptor, both soluble in the aqueous phase.

The nematic textures were maintained in the degassed solutions after incorporation of the reagents as seen from texture observations.

The reaction, which could be observed as the solution became colored in blue due to MV^{+}, was followed through the changes in the absorption spectrum.

Our experiments did not include the part in brackets in the reaction scheme, but the water reduction can be done when MV^{2+} is reduced in presence of a catalyst according to the literature [19,20].

Figure 1 shows two series of experiences when the reaction was carried out in non oriented KL(3) solution. The figure depicts the evolution with time of irradiation. The

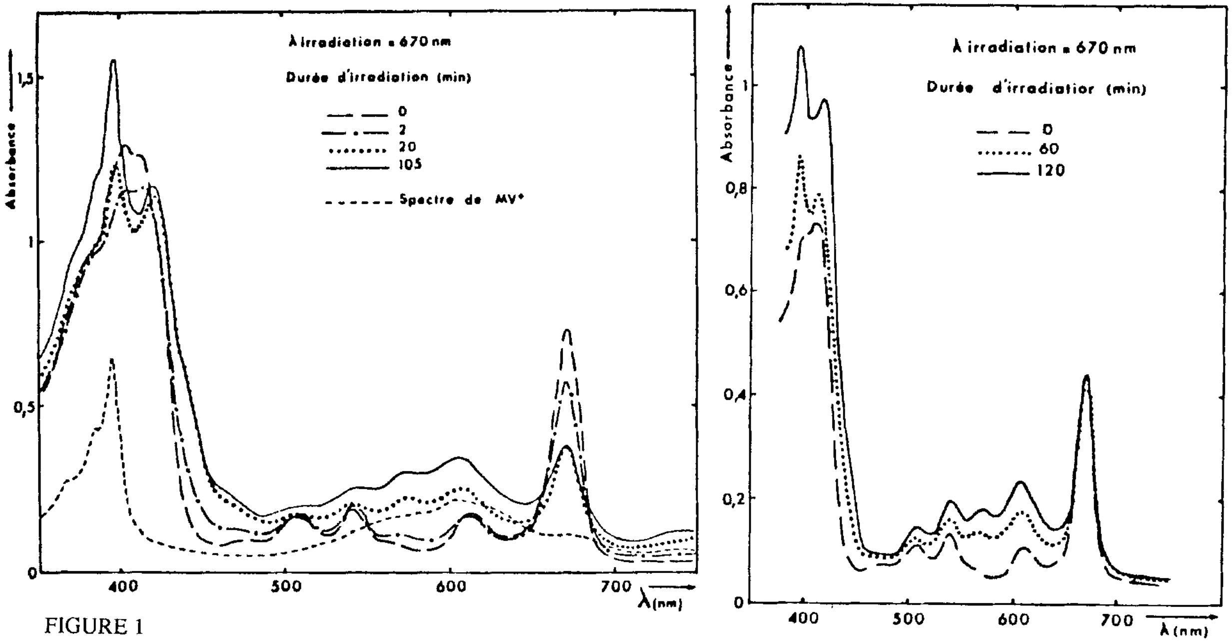


FIGURE 1

Absorbance of the system: Pha = 0.9 x 10^{-4} M. kg^{-1}, MV^{2+} = 5.8 x 10^{-3} M. kg^{-1}, EDTA = 2 x 10^{-3} M. kg^{-1} in KL(3) when the irradiation time was varied. Two experiences are shown. The absorption spectrum of MV^{+} is given.

spectrum of MV^+ is given for comparison purposes [21].

The quantum yield of the reaction is given by the following expression :

$$\Phi = k \frac{\text{Abs } MV^+}{\varepsilon \times \text{Power} \times T \left(1 - 10^{-\text{Abs Pha}}\right)}$$

k = numerical factor including filter effect.
Power = lamp power per unit area
T = irradiation time
ε = molecular absorbance coefficient of MV^+ ($1.4 \times 10^{-4}\ M^{-1}\ cm^{-1}$) [21]

Table III gives the quantum yield for two different series of experiences in KL(3) :

Table III

Experience 1		Experience 2	
T	Φ	T	Φ
600 s	0.014	120 s	0.014
1 800 s	0.015	300 s	0.014
		1 200 s	0.012

They are likely miminum values because of MV^+ bleaching due to recombination reactions.

We have further examined the orientation effect on the reaction. The influence of magnetic alignment on the photosensitive probe molecule Pha in N_D+ (KL(4)/ KHpOB) and N_D- (KL(4)) is shown in figure 2.

The N_D phase was chosen for our experiment where two identically oriented cells were compared when irradiated with light parallel or perpendicular to the field direction. The result is shown in figure 3. The increases in absorbance at 580 nm from MV^+ production after 50 minutes of irradiation correspond to quantum yields of 0.031 for parallel light and 0.017 for perpendicular light.

The unambiguous orientation effect is thus evident. The study should be pursued for other chromophores in other phases.

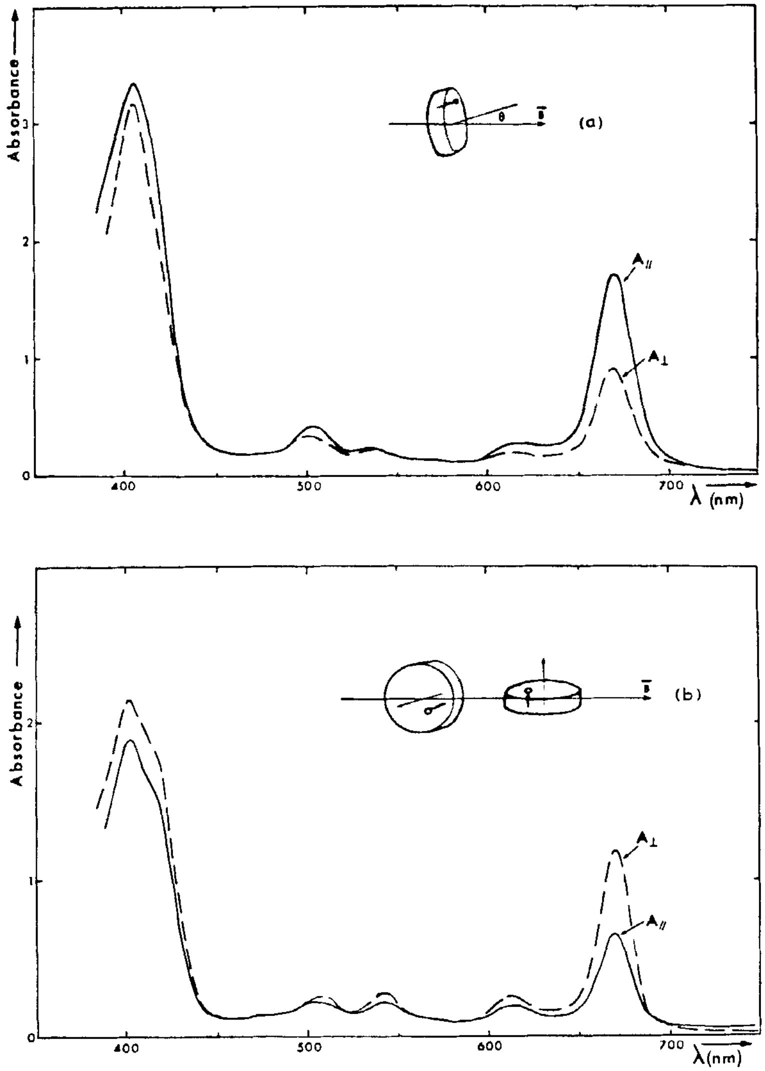


FIGURE 2

Absorbance of Pha = 1.2 x 10^{-4} M. kg^{-1} in KL(4)/KHpOB, N_D+ and in KL(4), N_D- oriented in the magnetic field (polarized light).

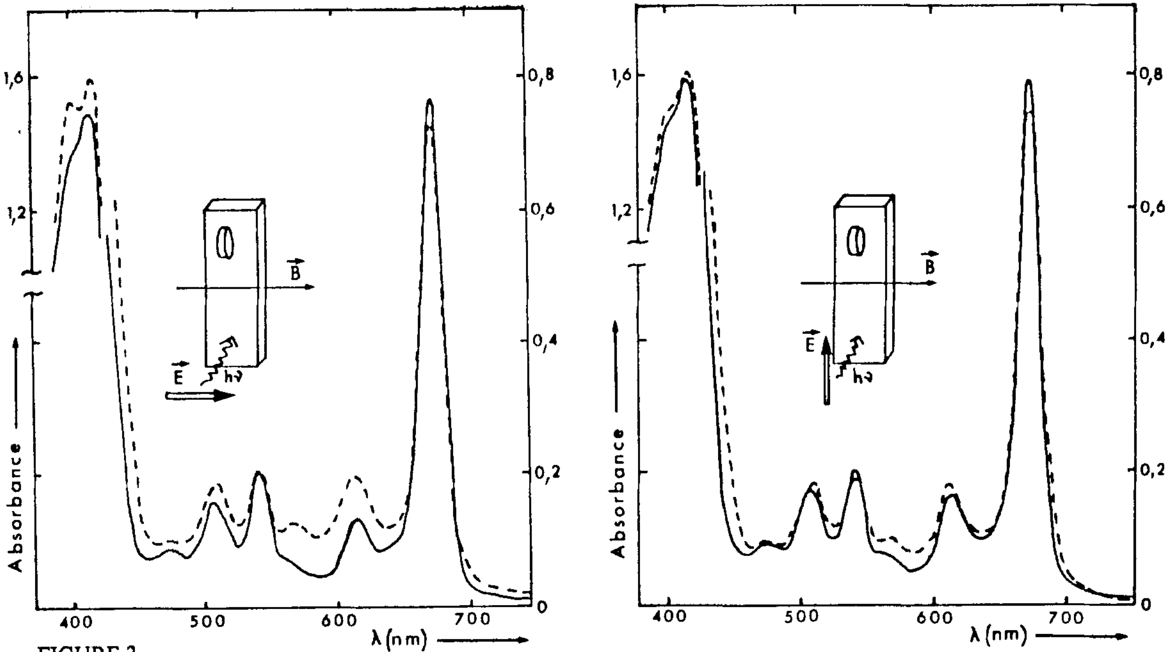


FIGURE 3

Absorbance of the system: Pha = 0.9 x 10^{-4} M. kg^{-1}, MV^{2+} = 5.8 x 10^{-3} M. kg^{-1}, EDTA = 2 x 10^{-3} M. kg^{-1} in KL(4)/KHpOB, N_D+ oriented in the magnetic field, ——— initial spectrum, - - - - - - after irradiation as illustrated during 50 min with a polarized beam.

CONCLUSIONS

The nematic lyophases are useful solute hosts. They provide selective solubility in hydrophobic and hydrophilic regions where reagents can be approached or separated due to charges at the interface. These general micellar properties are combined with anisotropic orientation effects arising from aggregate shape and magnetic properties.

We have shown that these combined micellar effects on solutes can be applied to improve a chemical reaction. They can also provide a tool for phase class identification.

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