

SPECTRAL PROPERTIES OF CHLOROPHYLL-*a* IN LIQUID CRYSTAL

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Chlorophyll *a* molecules dissolved in liquid crystals are oriented to a high degree at low electric fields. The observed spectral effects, obtained from absorption and emission anisotropy measurements, can be interpreted by solvent-pigment and pigment-pigment interactions. It seems, that the former exceeds the latter even at high ($1 \cdot 10^{-3}$ M) chlorophyll concentration.

Chlorophyll *a* (Chl *a*) dissolved in liquid crystal LC seems to be an interesting subject of investigation because of its fluid-oriented structure simulating a lamellar system of photosynthetic organisms [1, 2]. By such an anisotropic model information is provided on the orientation of transition moments with respect to the skeleton of

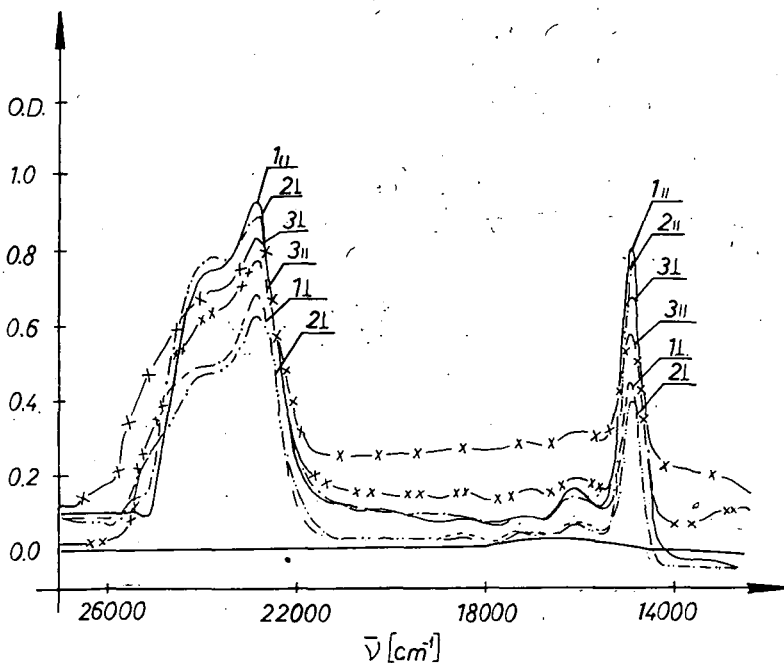


Fig. 1. Absorptions of parallel (\parallel) and perpendicular (\perp) components of polarized light of Chl *a* in LC (curve 1 — 0 V; X — 5 V; 3 — 20 V)

the molecule, as well as on the eventual influence of pigment orientation on the intermolecular interaction. Both these information are of value in the studies on the excitation energy migration in the photosynthetic apparatus [3].

The solution of chromatographically purified Chl *a* in EBBA×MBBA (p-ethoxybenzylidene p'-butylaniline + p-methoxybenzylidene p'-butylaniline) mixture was located in the measuring cell with windows of conducting glass. The thickness of the pigmented LC layers was of order 10^{-2} mm. The reference cell was filled with pure LC. In the results of the special preparation of windows, even without electric field, some homogeneous (planar) orientation of LC molecules is found. The investigated sample behaves as uniaxial crystal with an optical axis lying in the plane of windows. Various potentials from 0 to 20 V were applied across a cell. The spectrum of Chl *a* in LC is shifted towards longer wavelength with respect to the spectrum in ethyl ether. This shift is about 10 nm and is practically independent of the voltage applied.

Fig. 1. shows the polarized components of absorptions A_{\parallel} and A_{\perp} . In all measurements polarizers axes in measuring and reference beams were parallel. A_{\parallel} was obtained at horizontal orientation of LC axis, whereas A_{\perp} by the change in position of both measuring and reference cells. The shapes A_{\parallel} and A_{\perp} components of absorption are different and are changing with the electric potential applied to

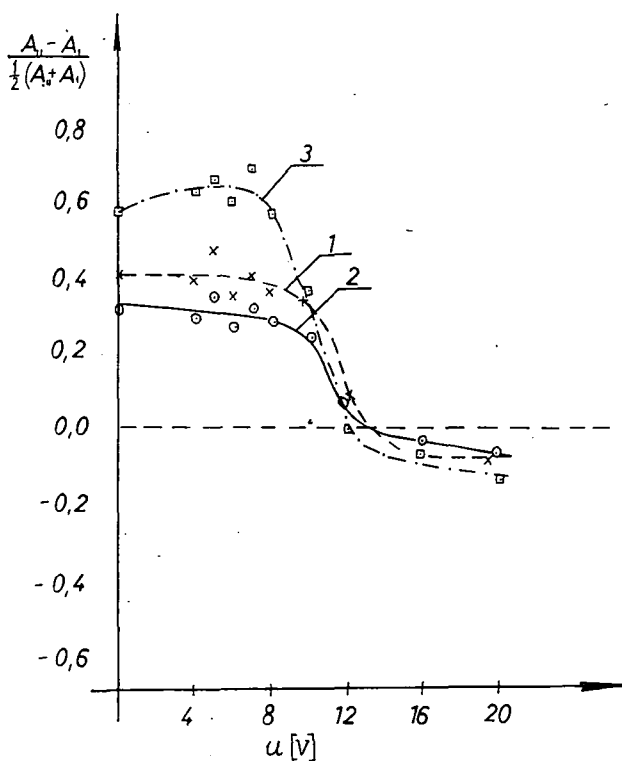


Fig. 2. Dichroism of Chl *a* in LC vs. voltage for various absorption maxima: 1 — 420 nm; 2 — 347 nm 3 — 671 nm

the cells. Fig. 1 presents three types of effects; at 0 V Chl *a* array is caused by electrode rubbing; at 5 V Chl is oriented by an electric field in maximum degree, whereas at 20 V the effect of the so-called "dynamic scattering" [4] appears because some ionic currents are formed between electrodes. In this case anisotropy of absorption is negative.

Fig. 2 shows a linear dichroism of absorption as a function of electric potential for various maxima of absorption spectrum. At low potential the highest anisotropy is exhibited by the red-band, the lowest band the main Soret band. This suggests that at low potential, the red-band transition moment forms a low angle with the orientation direction of LC. At low voltage, the dichroism of absorption is positive. The increase in voltage causes a change in the regular LC and Chl *a* arrangements.

The attenuation of light by scattering on LC is compensated by a reference cell but the light beam is in some degree depolarized and the paths of light may be different in both positions of the sample. Though these secondary effects diminish

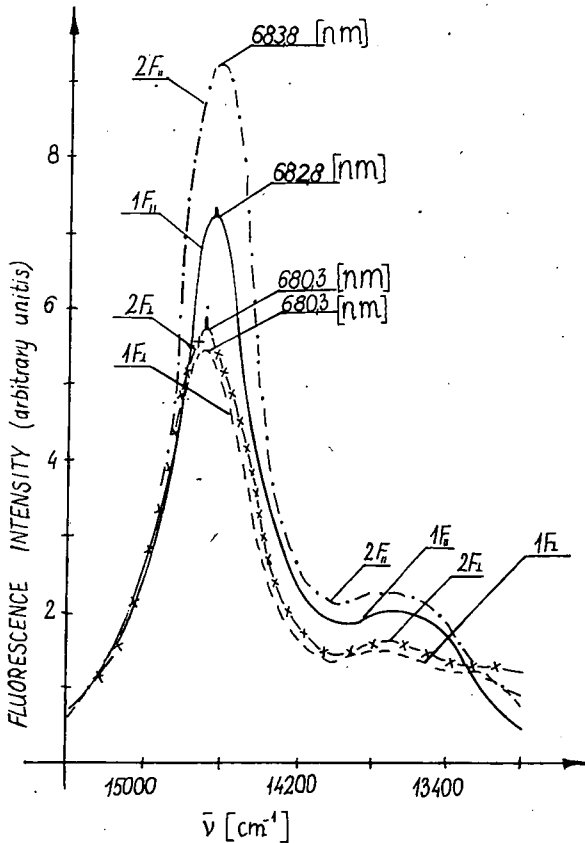


Fig. 3. Spectra of polarized components of fluorescence excited with natural light 1 — 0 V; 2 — 4 V
 $\lambda_{exc} = 437 \text{ nm}$

the dichroism, the change in sign of dichroism as well as the fluorescence data, suggest that, in this case, almost a perpendicular orientation of Chl *a* molecules is reached related to that observed at low potential. Polarized components of fluorescence spectra F_{\parallel} and F_{\perp} (Fig. 3) were done in two perpendicular positions of a sample. From the spontaneous polarization of fluorescence, obtained by excitation with natural light, the degree of Chl *a* orientation was calculated. It was highest at 4 V — equal to about 20 per cent. The lifetime of fluorescence, in both positions of the sample, was equal to 5.0 ± 0.2 ns. Obtained from the absorption the spectro-oscillator strength of Chl *a* in LC is similar to that of Chl *a* in ether ($f_{LC} = 0.24$, $f_{eth} = 0.23$ [5]).

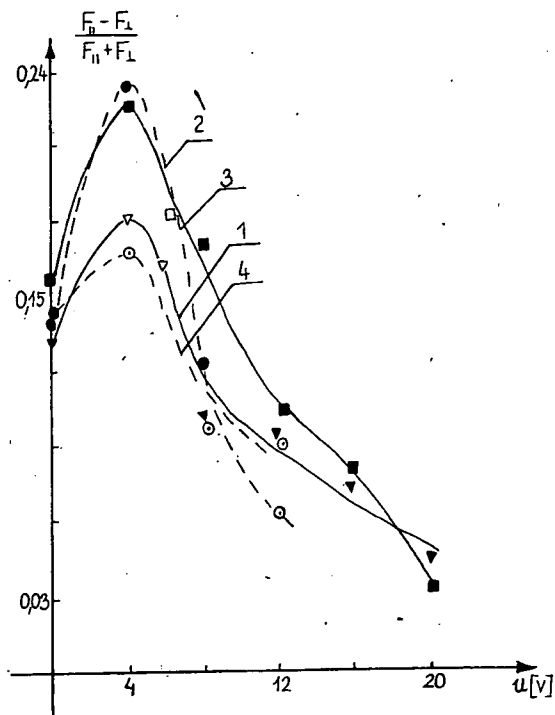


Fig. 4. The dependence of fluorescence polarization degree on voltage applied.

- 1;2 — at 683 nm (main band),
- 3;4 — at 735 nm (satellite band),
- 1;3 — excitation with polarized light,
- 2;4 — excitation with natural light

Fig. 4 shows the change in degree of fluorescence polarization *vs.* electric potential applied to the main fluorescence band and fluorescence shoulder. In all cases, the maximum of the fluorescence anisotropy occurs at 4 V. The position and half-widths of the maxima occurring in parallel (F_{\parallel}) and perpendicular (F_{\perp}) components are different and are changing with the voltage. All F_{\parallel} components are shifted towards longer wavelengths; the largest shift is observed at 4 V (Table I). The positions of

Table I
Spectral parameters of emission maxima Chl a in LC

Voltage (V)	excitation with natural light				excitation with polarized light			
	position of maximum λ (nm)		half-width δ (cm^{-1})		λ		δ	
	F_{\parallel}	F_{\perp}	F_{\parallel}	F_{\perp}	F_{\parallel}	F_{\perp}	F_{\parallel}	F_{\perp}
0	682.8	680.3	569.2	607.7	683.2	681.7	569.7	569.2
4	683.8	680.3	561.5	638.5	684.2	681.7	538.5	576.9
6	—	—	—	—	684.2	681.7	546.1	576.9
8	682.1	680.3	584.6	630.8	683.4	682.5	561.5	576.9
12	682.5	680.3	592.3	630.8	683.4	681.7	561.5	584.6
16	—	—	—	—	683.2	681.7	596.2	584.6
20	—	—	—	—	683.2	681.7	584.6	584.6

the F_{\perp} maximum do not vary with the potential applied; this means that it is independent of the degree of Chl orientation. The changes in fluorescence spectra as a result of Chl orientation, are larger than those in absorption. It seems, therefore that as a result of orientation Chl in excited state is perturbed stronger than Chl in normal state. Two possible sources of this perturbation were discussed:

1) the influence of the Chl interaction with solvent and 2) increase in interaction between pigment molecules as a result of Chl regular orientation.

In the first case in LC two types of chlorophylls were supposed to appear: to the first group belong some molecules attached to LC interacting strongly with LC and subjected to reorientation by an electric field together with LC molecules. The second type of molecules is weakly interacting with solvent and is insensitive to the voltage applied. The emission spectrum of the first type of molecules is strongly perturbed. It follows from comparing our results to those given by SEELY and JENSEN [6] that the spectral shifts observed as well as the changes in shape of spectra, are to be compared to those due to interaction with various isotropic solvents.

NORDEN and DAVIDSSON [7] had measured the linear dichroism of porphyrin in various anisotropic media and found that the matrix can perturb the porphyrin electronic spectra by simulating some vibronic transition and attenuating others. It is possible that, as a result of a strong interaction between the pigment excited and the LC molecule attached for long to it, the vibronic transition, polarized parallel to the long LC axis, is enhanced whereas the perpendicular one decreases. In consequence, the half-width of the band decreases and the band is shifted. It is suggested by the different spontaneous fluorescence polarizations of the main fluorescence band and of the fluorescence shoulder that more than one type of emitting centres appear.

Taking into account a second possibility, in order to establish whether the exciton model can be responsible for the effect observed, we calculate the distances between the interacting molecules on the basis of HOCHSTRASSER and KASHA'S [8] formula. It was supposed that an observed spectral shift appeared as a result of the pigment-pigment interaction. Red shift can only appear if angle α between the direction of

the interacting transition moments and the line connecting the molecular centres is ranging from 0° to 55° .

Taking $\alpha=55^\circ$ the distance typical of the resonance interaction for large Chl aggregates, as well as for dimers, was obtained for example $R=50 \text{ \AA}$ was obtained from an experimental shift in the fluorescence spectra observed as a result of the increase in degree of Chl orientation. The results reported lead to the following conclusions:

1. Chlorophyll molecules in LC at low electric fields are oriented to a high degree. At higher voltages, the orientation of the pigment molecules is not same as at low and zero potentials.
2. The red band transition moment is oriented almost parallel to the direction of LC orientation.
3. The observation of pigment absorption and emission anisotropy provides some information about the reorientation of LC molecules.
4. At this stage of our work it is not possible to distinguish univocally between two mechanisms which could be responsible for the effects observed. It seems that interaction between solvent and pigment molecules exceeds interaction between chlorophyll molecules even at a high 10^{-3} M chlorophyll concentration.

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СПЕКТРАЛЬНЫЕ СВОЙСТВА ХЛОРОФИЛЛА-а В ЖИДКОМ КРИСТАЛЕ

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Хлорофилл-а, растворенный в жидком кристалле при низком значении электрического поля в высокой степени находится в ориентированном состоянии. Наблюдаемые спектральные изменения спектров поглощения и анизотропии люминесценции объясняются взаимодействием между растворителем и хлорофиллом-а, и пигментами. Установили, что значение взаимодействия растворитель-пигмент до $1 \cdot 10^{-3} \text{ M}$ концентрации хлорофила-а превышает значение взаимодействия пигмент-пигмент.