

THE LIGHT ABSORPTION OF SOME CYANINE DYES ADSORBED ON CELLOPHANE

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(Received June 5, 1956)

On the basis of experimental data the shifts of the bands toward the longer wave lengths caused by the adsorption could be stated. It means the diminution of excitation energy in consequence of adsorption. The energy values of the shifts as compared with each other prove that the shift is caused not only by processes like polymerizations, but also by the release of the energy of adsorption.

It was stated, especially in the case of V compounds, that polymerization may occur in solution. So the longer wave length side band appears even in solution.

In this laboratory a series of investigations has been started aiming to establish the relation between the adsorption and light absorption mechanism of dyes. The present paper contains the first part of these examinations. These investigations involved some cyanine dyes adsorbed on cellophane. For these studies: 1./ the absorption spectra of dyes were determined in alcoholic solution 2./ one or more cellophane lamellae adsorbed were set between two quartz plates depending on the measure of the adsorption and the spectra were determined again as compared to the same number of cellophane lamellae unadsorbed.

1. Experimental results

The absorption spectra of cyanine dyes of different type are shown in the figures to compare the spectra of the solutions with those of adsorbed dyes. The investigations were made with the following dyes: 4-(2-ethyl-1-benzoxazylidene-ethylidene)-3-methyl-rhodanine (I), 3-methyl-5-(2-ethyl-1-benzoxazylidene-ethylidene)-2-thio-2,4(3,5)-oxazoldione (II), 1,1'-ethyl- β -naphthoxazolo-carbocyanine Iodide (III), 1,2-diethyl-benzoxo-carbocianine Iodide (IV), 4-(2-ethyl-1-benzthiazolidene-ethylidene)-3-methyl-1-phenyl-5-pyrazolone (V), 3-methyl-(2-ethyl-1-benzthiazolidene-ethylidene)-2-thio-2,4(3,5)-oxazol-dione (VI.)

A band of high intensity was found in the spectra of the solutions in the visible range, while bands of strikingly lower intensity in the u. v. range. The cyanine dyes themselves are flat molecules containing two heterocyclic nuclei which are bound with polymethyne chain in coplanar arrangement [1]. The shifting of the bands toward the longer wave lengths and the increase of extinction were stated by HAUSSER et al. [2] with the enhancement of poly-

methyne chain. If chromophores are on the end of the chain, the bands of double bonds are superposed on those of chromophores. In addition the band arisen in the visible range, the appearance of a weaker band was demonstrated by BLOUT and FIELDS [3] at the shorter wave lengths. In SCHEIBE's opinion [4] the cause both of the colour of the dye and of the appearance of the first band is the excitation of the electrons of the chromophores conjugated

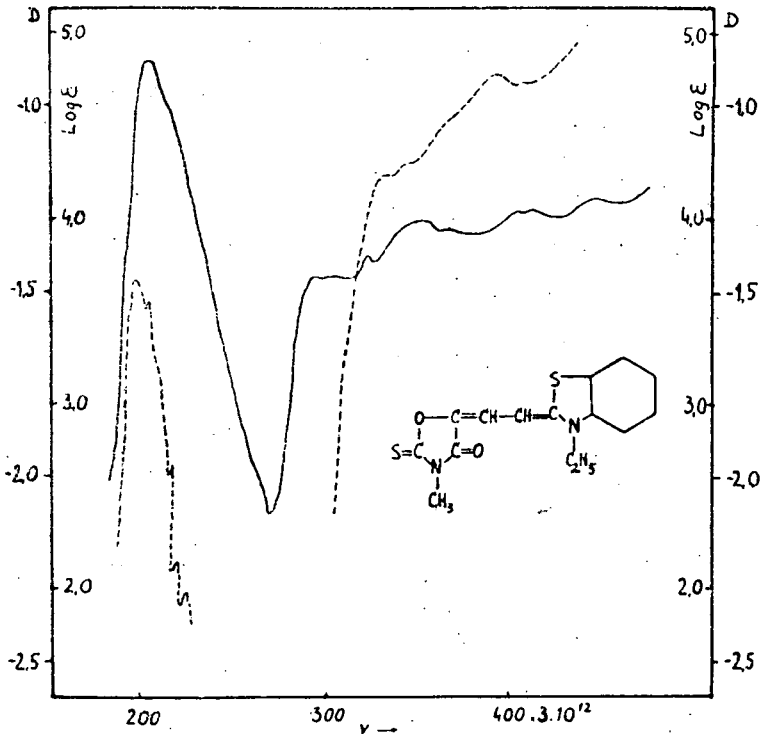


Fig. 1. — The ultraviolet absorption spectra of 5-(2-ethyl-1-benzoxazolidene-ethylidene)-3-methyl-rhodanine.
soln. ———; ads. - - - - -

in the mesomeric state. This is proved by the effect of planarity or non-planarity of the molecule exerted on the light absorption. The extent of conjugation depends on planarity or non-planarity, respectively.

According to KORTUM and DREESEN [5] the spectrum due to the excitation of the chromophores disappears in consequence of the uniform conjugation connecting the chromophores with polyenic chain, when the molecule behaves like a uniform chromophore. By an earlier statement [6] it was supported that the longer the polyenic carbon chain is the less the difference of the energy between the ground and excited state. Further BROOKER et al. [7] proved that the place and intensity of the first band depend on the basicity of nuclei, i. e. on the oscillation of the charge among the nuclei.

In the present paper the shift of the visible spectrum toward the longer wave lengths due to the influence of adsorption on cellophane surface was stated for the above cyanine dyes. Moreover, a shift to the same direction for the bands in the u. v. range was also observed. It was accounted for the value of energy corresponding to the band shift. This was done taking the difference between the value of the energy of the first band of the solution and that of

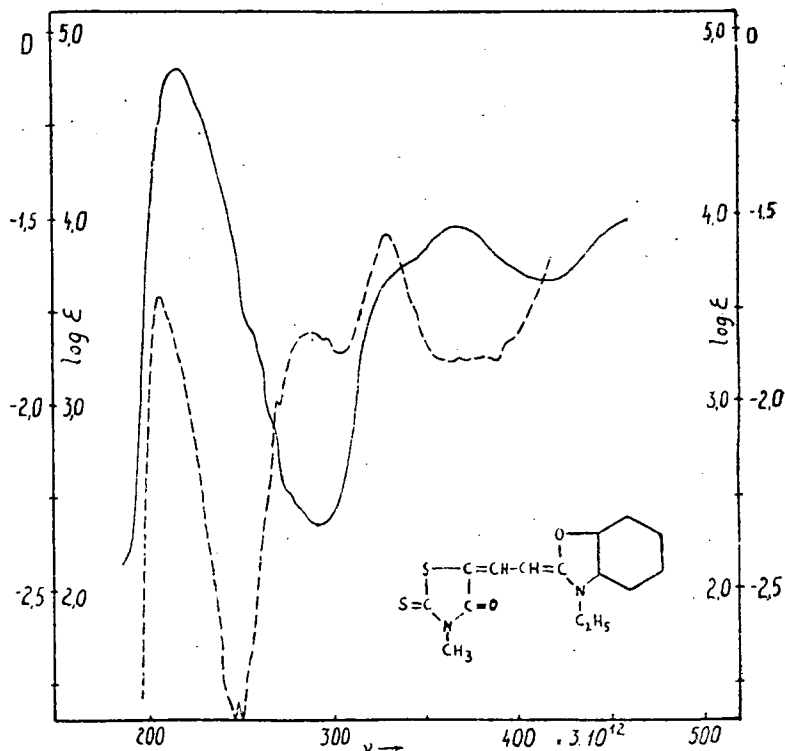


Fig. 2. — The ultraviolet absorption spectra of 3-methyl-5-(2-ethyl-1-benzoxazylidene)-2-thio-2,4(3,5)-oxazoldione, soln. —; ads. —

the adsorbed layer. In consequence of the adsorption the change of the relative intensity of the bands appearing in the visible and u. v. range is striking, if compared with each other, as after the adsorption the difference in intensity between the bands diminished. Besides, a sharp additional peak appeared at the side of the longer wave length of the first band.

2. Discussion

In one of his papers [8] JELLEY has published that many dye suspensions in liquid show a very narrow light absorption band at the longer wave lengths, with accompanying fluorescence too and that this band disappears in crystalline

state. In his opinion a transition from the dissociated state to the crystalline state through an intermediate molecular state occurred in a true solution showing a characteristic absorption and fluorescence. SCHEIBE et al. [9] observed a change of absorption with the concentration in aqueous solution for such saltlike compounds as polymethyne dyes, and moreover, they noted the appearance of a new band at higher concentrations. This band was attributed to

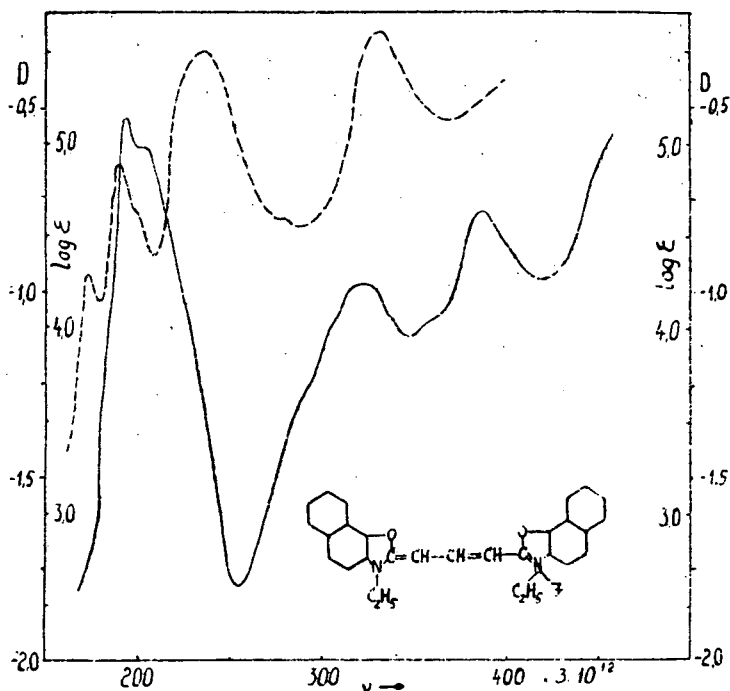


Fig. 3. — The ultraviolet absorption spectra of 1,1'-ethyl- β -naphthoxazolo-carbocyanine iodide.
soln. —————; ads. - - - - -

polymerization. This polymerization was observed especially for isocyanine where the electron-jump is so screened that an extremely narrow and intense band accompanied by noticeable fluorescence band appears. The polymerization, however, turns out to be reversible owing to the disappearance of the narrow band on influence of heating or dilution. Their statement was supported by a strong adsorption of the polymer form on different surfaces, which shifts the bands perceptibly. Besides, they stated that the freshly cut fluorite and the polystyrol do not adsorb. The latter was interpreted by the reduced possibility of the conjunction of the negative ions of dyes owing to the negative charges on the surface. On the other hand the adsorption of the CH-radicals on the surface of polystyrol hinders the polymerization resulting in non-appearance of the characteristic sharp band. Consequently, SCHEIBE stated that the band was not due to the molecular state as assumed by JELLEY, but to polymeriza-

tion, though according to JELLEY's further examinations [10] a polymerization rather than nematic aggregates arose.

As to the adsorption of cyanine dyes on an anisotropic surface like cellophane a reference concerning the fact that the molecules have edge-on orientation, could be found only in the literature. SHEPPARD et al. [11] examining the adsorption on silverhalide grain observed the adsorption to take place ac-

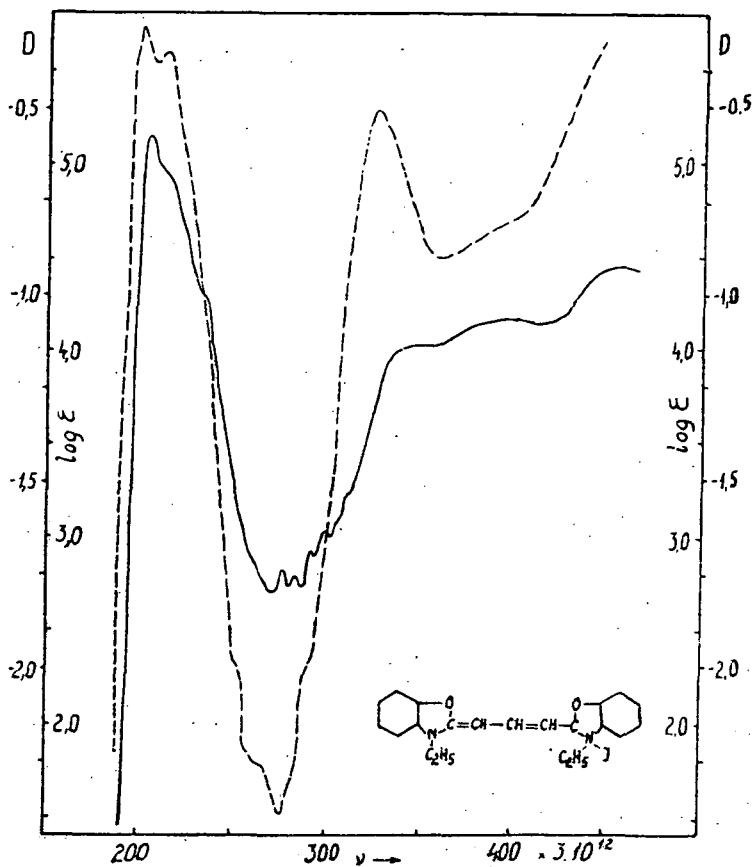


Fig. 4. — The ultraviolet absorption spectra of 1,2-diethyl-benzoxo-carbocyanine Iodide, soln. ———; ads. - - - -

ording to the LANGMUIR's isotherm. Consequently the edge-on monomolecular layer of dye cations comes into being. The adsorption of cyanine dyes was also thoroughly studied by WEST et al. [12] on photographic emulsion. Besides, the less adsorbing dyes show often discontinuity; isolated molecules and so called »coöperative« phases arise with varying spectral characteristics. Adsorption of several layers has also been supposed and it was stated that the merocyanines, which are not considered as dye-cations, obey the LANGMUIR's

isotherm. Further, the weaker adsorption of the non-planar than that of planar dyes was observed, and in their opinion the adsorption bonds are caused by electrostatic and VAN DER WAALS forces. Particularly strong VAN DER WAALS forces occur for cyanine dyes caused by the unlocalized electrons of conjugated chain and by the amplitude of the movement of the charge through the conjugated chain [13].

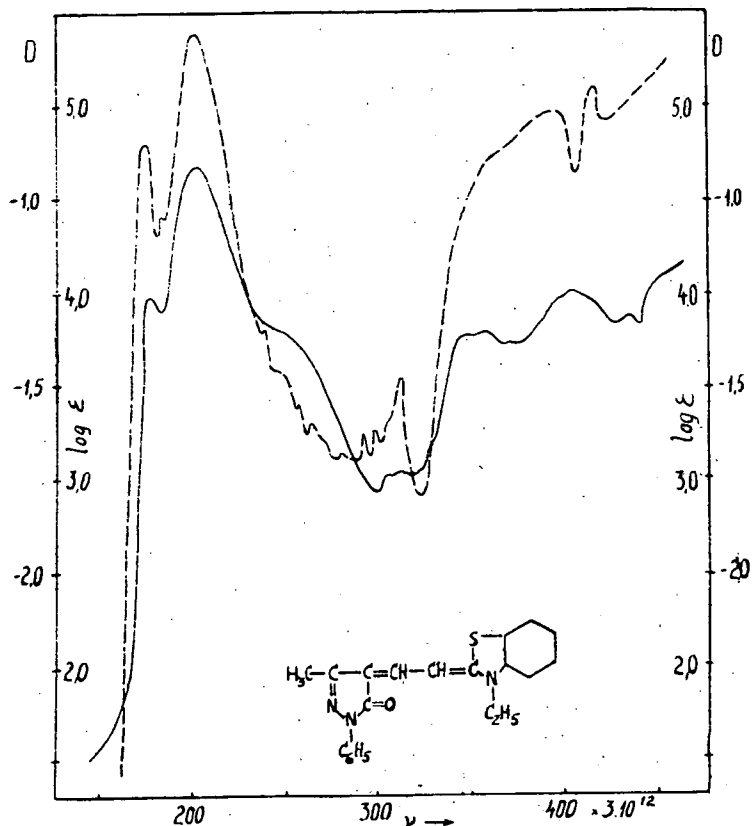


Fig. 5. — 4-(2-ethyl-1-benzthiazolidine-ethylidene)-3-methyl-1-phenyl-5-pyrazolone, soln. ———; ads. - - - -

The light absorption of the adsorbed layer on silverhalide was also studied by WEST et al. They observed the change of the absorption with both the increasing covering of the surface (with increasing adsorption) and increasing concentration in solution. By an adsorption of a very slight degree the spectrum shifted toward the shorter wave lengths as compared to that of aqueous solution. This shift was attributed to the isolated adsorbed molecules of dye, the electron levels of which was affected rather by the surface of adsorbent than by other molecules. On adsorption of higher degree the hypsochromic shift was observed to be analogous to the dimeric or polymeric bands in more concentrated aqueous solutions. In the case of some dyes the appearance of a re-

lative sharp band was found on the adsorption of a still higher degree at longer wave lengths. This was attributed by JELLEY and SCHEIBE to the rise of thread-shaped aggregates. On the basis of the investigation of LEERMAKERS et al. [14] many dyes, from which alcoholic or aqueous solutions of higher concentration can not be prepared, show this sharp band in an adsorbed state.

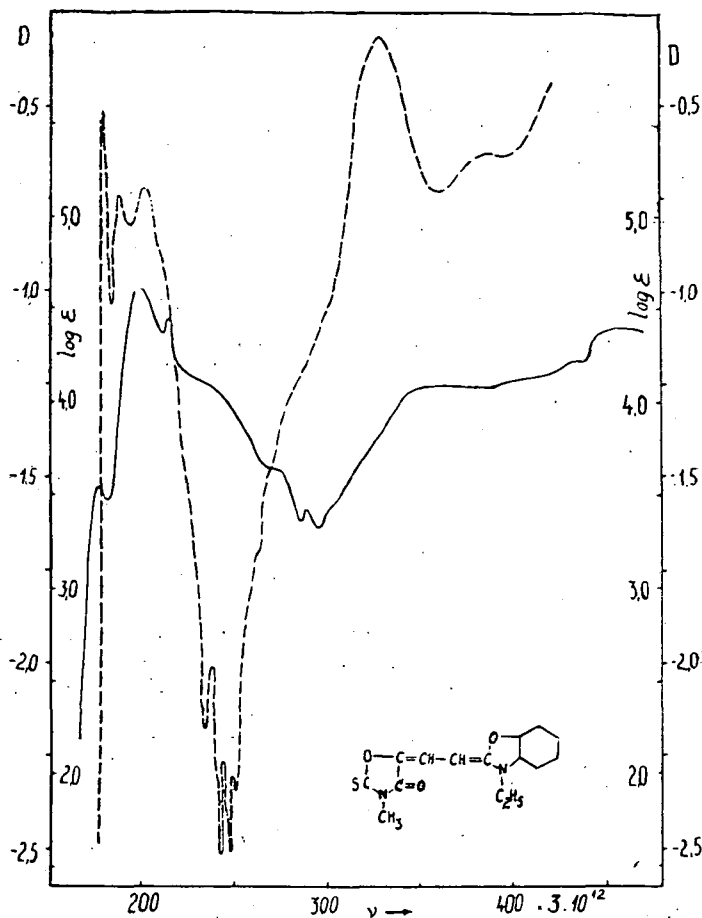


Fig. 6. — The ultraviolet absorption spectra of 3-methyl-(2-ethyl-1-benzthiazolidine-ethylidene)-2-thio-2,4(3,5)-oxazolidene, soln. ———; ads. ———

Bearing in mind the above mentioned facts the process of adsorption would bring about such changes of the spectra as the dimerization or polymerization do in solution of higher concentration. This is supported by the sharp, intensive band appearing at the longer wave length side for III, V, and VI compounds. The shift toward the longer wave lengths proves the di-

minution of excitation energy. The shift occurred in the following order: VI > I = III > II > IV > V. Owing to the slight shift its reason was supposed to be not completely the processes like dimerization or polymerization but only partly. Nevertheless, the appearance of the longer wave length band would prove to play a greater part of polymerization in consequence of adsorption for the VI and III compounds, where the shift is the largest. On the other hand, for the V compound, where the shift is the slightest, the longer wave length band appeared already in the solution which showed the occurrence of polymerization in spite of dilute solution.

It is known, however, that the adsorption involves the release of energy [15]. Thus an other energy is required to excite the free than the adsorbed molecules. This difference of the energy corresponds to the adsorption energy. If greater energy is absorbed in the adsorbed state than in the free one, then the spectrum shifts to the shorter wave lengths. In this case the adsorption energy is less in the excited than in the ground state, and vice-versa.

Hence the differences of energy obtained by the experiments are proportional partly to the adsorption energy. This value is the lowest for the V compounds, showed in the table, where a stronger polymerization may be assumed even in the solution on the basis of the appearance of the longer wave length side band. These data verify LONDON's statement cited above. On the basis of the diminution of the relative differences of heights among the bands in the visible and the u. v. range, however, can be concluded, that the adsorption diminishes the probability of transitions. Again this means the adsorption induced by electrostatic forces diminishes the probability of charge-oscillation among the nuclei.

Table

Compds.	Solution		Adsorbed layer		
	ν_{\max} cm ⁻¹ x 3 · 10 ¹²	ΔE_s in Kcal	ν_{\max} cm ⁻¹ x 3 · 10 ¹²	ΔE_a in Kcal.	$\Delta E_s - \Delta a$ Kcal
I	204	58,28	197	56,28	2
II	213	60,85	206	58,99	1,86
III	104	55,43	187	53,43	2
IV	207	59,14	202	57,71	1,43
V	204	58,28	202	57,71	0,57
VI	198	56,57	180	51,43	5,14

3. Experimental

The adsorption of the lamellae of cellophane run in the following way. A glass of 200 ml closely tied with wet cellophane — on having been dried — was put in a Petri dish filled with an alcoholic solution of the dye, so as to have a layer of a solution of 0,5 cm over and under the cellophane. Having the pattern adsorbed it was washed thoroughly to eliminate the crystals of the dye deposited on the surface. The lamellae were cut in dry condition.

The absorption curves were determined using a BECKMAN Model DU Photoelectric Quartz Spectrophotometer in the interval of 3 m μ . On the absorption curves of the solutions the molar extinction coefficients were plotted against the wave lengths, while in the case of the adsorbed layers the optical density ($\log I_0/I$). The values of energy were computed by the usual formula: $E = h \cdot \nu \cdot N$.

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I wish to extend my thanks to prof. A. KISS for calling my attention to the problem and for his appreciable suggestion.

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