186. Synthesis, Surface Activity and Micelle Formation of Novel Cyanine Dyes

by **Ermano Barni** and **Piero Savarino**
Istituto di Chimica Organica Industriale, Università di Torino
and **Ezio Pelizzetti**
Istituto di Chimica Analitica, Università di Torino
and **Guido Rothenberger**
Institut de Chimie Physique, Ecole Polytechnique Fédérale, Lausanne, Switzerland

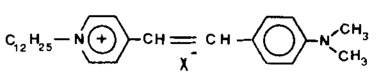
(20.V.81)

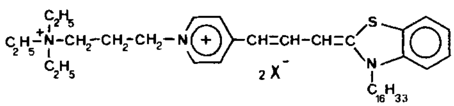
Summary

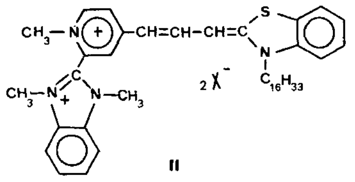
The synthesis, surface activity and micelle formation of three novel cyanine dyes with amphiphilic character is described. It is illustrated by combined surface tension and absorption measurements that in one case self-assembly is highly cooperative leading to aggregates with unique absorption properties.

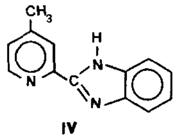
Introduction. - The unique light-absorbing properties [1] of cyanine dyes as well as their photoredox behaviour [2] make this class of chromophores viable candidates in a variety of light-induced processes, *i.e.* photography [3], where specific sensitizers are required. Our present efforts to develop micellar aggregates which could mimic the antenna function of chlorophyll in photosynthesis has brought three amphiphilic cyanine derivatives in the scope of our investigations.

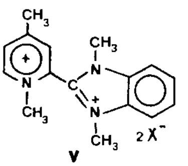
In a previous paper [4] 2-(4-methyl-2-pyridyl)benzimidazole (**IV**) was prepared together with isomeric and similar heterocyclic bases. The quaternisation of **IV** with dimethylsulfate leads to a bisquaternary salt **V** from which the unsymmetrical trimethine dye **II** is obtained; also, the preparation of **I** and **III** is described in the


I


III


II


IV


V

0018-019X/81/6/1943-06$01.00/0

present paper with an investigation of the surface activity and micelle formation of these dyes.

Experimental part. - a) *Apparatus.* Surface tension measurements were carried out with a *Krüss* tensiometer (model 84S1) using the ring method. Optical absorption spectra were obtained with a *Cary* UV. visible spectrophotometer. b) *Synthesis. 1-Dodecyl-4-a-[4'-(dimethylamino)styryl]pyridinium chloride* (**I**). 4-Methylpyridine (10^{-1} mol) was refluxed with 1-chlorododecane (1.3×10^{-1} mol) over a period of 12 h. On cooling diethyl ether was added, the product collected and repeatedly washed with diethyl ether. The quaternary salt (2×10^{-2} mol), *p*-dimethylaminobenzaldehyde (4×10^{-2} mol), abs. ethanol (20 ml) and piperidine (0.5 ml) were refluxed over a period of 1.5 h. The crude dye was twice crystallized from ethanol/water and gave a correct analysis, m.p. 231-233°. - UV. (EtOH): λ_{max} 482 nm, $\log\varepsilon$ 4.60.

1,3-Dimethyl-2-[2-(1,4-dimethylpyridinylio)]benzimidazolium diiodide (**V**, $X^- = I^-$). The free base **IV** (10^{-2} mol) was refluxed with dimethylsulfate (4×10^{-2} mol) in toluene over a period of 8 h. The solvent was separated, the residue was slurried with diethyl ether and subsequently added with a sat. aq. solution of KI. The crystalline product was collected, washed with a little water and crystallized from ethanol. The product gave a correct analysis, m.p. 308-310° - UV. (EtOH): λ_{max} 284 nm, $\log\varepsilon$ 4.03. - ^{1}H-NMR. (DMSO-d_6): 2.77 (3 H, $H_3C{-}C$ (pyridine)); 4.25 (3 H, $H_3C{-}\overset{+}{N}$ (pyridine)); 4.1 (6 H, 2 CH_3 (benzimidazole)).

1,3-Dimethyl-2-{1'-Methyl-4'-[3''-(3'''-hexadecyl-2'''-benzothiazolinylidene)-1''-propenyl]-2'-pyridylio}-benzimidazolium dinitrate (**II**, $X^- = NO_3^-$). 2-Methylbenzothiazole (1 mol) and 1-iodohexadecane (0.80 mol) were stirred 24 h at 170° and the isolated 2-methyl-3-hexadecylbenzothiazolium iodide (2×10^{-2} mol) was refluxed 30 min in acetic anhydride with *N,N*-diphenylformamidine (6×10^{-2} mol). After repeated treatments with ethyl ether, the crude 2-(β-acetylanilinovinyl-3-hexadecyl)benzothiazolium iodide (10^{-2} mol), dissolved in 25 ml of abs. ethanol, was treated with **V** (10^{-2} mol) and 2.5 ml of triethylamine. After refluxing 10 min the mixture was cooled, filtered and the residue washed with ethyl ether before crystallizing from ethanol. The diiodide was converted into dinitrate by treatment with $AgNO_3$ in ethanol. The dinitrate was crystallized from ethanol and gave a correct analysis, m.p. 200-202°. - UV. (EtOH, 6.8×10^{-6}M): λ_{max} 605 nm, $\log\varepsilon$ 5.12.

1-[3'-(Triethylammonio)propyl]-4-[3''-(3'''-hexadecyl-2'''-benzothiazolinylidene)-1-propenyl]pyridinium dinitrate (**III**). (3-Bromopropyl)triethylammonium bromide [5] (10^{-2} mol) and 4-methylpyridine (4×10^{-2} mol) were treated at 140° over a period of 2 h. The crude product was thrice slurried in hot acetone and crystallized from 1-butanol. The bisquaternary salt (10^{-2} mol) and 2-(β-acetanilinovinyl)-3-hexadecyl-benzothiazolium iodide (10^{-2} mol), dissolved in 30 ml of boiling abs. ethanol, were treated with 1.5 ml of triethylamine. After refluxing 1 h, the mixture was cooled, added of diethyl ether and the product collected. The dinitrate was obtained by mixing ethanolic solutions of the dye and $AgNO_3$, removing the silver halides and adding diethyl ether to the solution reduced to small volume. The crude product was crystallized from acetonitrile and gave a correct analysis, m.p. 196-198°. - UV. (EtOH): λ_{max} 566 nm, $\log\varepsilon$ 4.88.

Results and discussion. - The chromophore **I** is only weakly soluble in water, the saturation limit being around 4×10^{-4}M. The absorption spectrum displays a maximum around 458 nm with an extinction coefficient of 3.82×10^4M^{-1} cm^{-1}. It is noteworthy that its features do not change with concentration. This indicates that dimers or trimers are virtually absent, the main contribution to the spectrum arising from the monomeric form of the dye.

The surface tension decreases linearly with the logarithm of the dye concentration indicating that within the concentration range amenable to investigation no micellar aggregates are being formed. Using *Gibbs* equation:

$$\Gamma = -\frac{1}{mRT}\left(\frac{\partial \gamma}{\partial \ln c}\right)_T \qquad (1)$$

where γ is the surface tension and m a constant (m = 2 for compound **I** and 3 for compound **II** and **III**) one can evaluate the surface excess Γ. The reciprocal value of Γ represents the surface requirement per molecule. For compound **I** one obtains 90 Å^2/molecule.

The cyanine dye **II** is well soluble in water. In contrast to **I**, we note here significant changes in the absorption spectrum when the dye concentration is varied. Three examples are given in *Figure 1*. At 1.94×10^{-5}M concentration (a) the maximum of the absorption is located at 605 nm, the extinction coefficient being 9×10^4M^{-1} cm^{-1}. A shoulder appears also at 576 nm and another weak absorption peak around 280 nm. Further dilution does not change the shape of the spectrum indicating that it arises from the dye in its monomeric form.

At 7.73×10^{-5}M concentration (b, in *Fig. 1*), which is still well below the CMC (critical micelle concentration), one notices the appearance of an absorption in the wavelength region of 400-500 nm which is attributed to the presence of H-aggregates. The last concentration selected (2.48×10^{-3}M, (c)) is considerably above the CMC. The absorption maximum is here displaced to 576 nm with an apparent extinction coefficient of 5×10^4M^{-1} cm^{-1}. Such a shift is typical for the presence of dimer interaction.

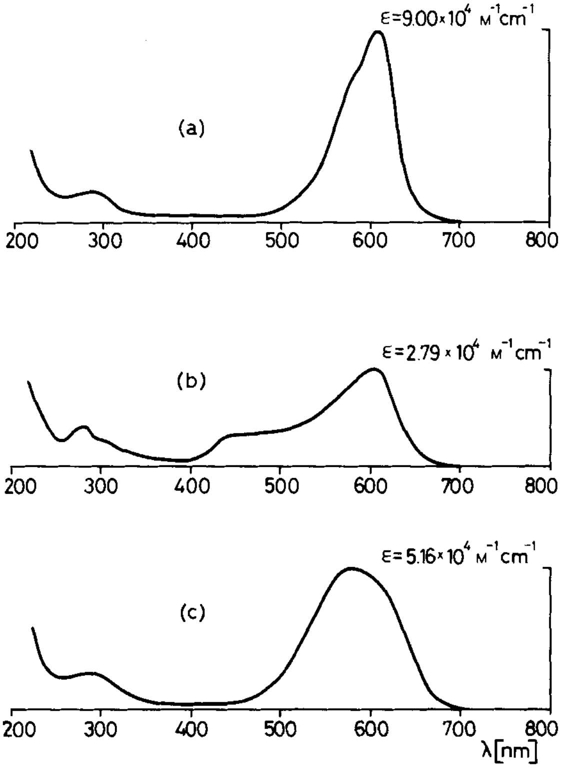


Fig. 1. *Influence of dye concentration on the absorption spectrum of cyanine* **II** *in water* (neutral solution, room temperature)

The surface tension concentration plot is displaced in *Figure 2.* A neat break point is obtained at 1.8×10^{-4} M concentration indicating the formation of micellar aggregates. From the slope of the line at lower concentrations, one obtains for the surface area per head group the requirement $1/\Gamma = 113$ Å^2/molecule. Evidently, the hydrophylic moiety of **II** is more bulky than that of **I** resulting in a larger value for the surface area occupied by one head group in the water-air interphase.

We conclude then that the main changes induced in the optical properties of **II** upon micelle formation is a broadening in the absorption towards the blue. This may indicate 'dimer'-type interactions of ajacent head groups in the aggregates. Interestingly, once micelles are formed, H-aggregates are no longer stable and are integrated in the micellar assemblies.

The absorption behaviour of dye **III** is displaced in *Figure 3.* Micelle formation is here accompanied by an abrupt change of the absorption features. A strong peak centered around 564 nm is observed in dilute solution while at higher concentrations a broad featureless band extending over the whole visible domain is obtained.

The surface tension *vs.* concentration plot in *Figure 4* exhibits a well defined break point at 8.4×10^{-5} M indicating micelle formation. Above the CMC., σ remains strictly constant over a concentration range of two orders of magnitude. This contrasts with the behaviour exhibited by the dye **II** where a slight decrease in σ is noted even above the CMC. value. Apparently the aggregation number of **II** continues to increase with concentration while that of **III** remains constant.

The optical results corroborate further this interpretation. While the absorption spectrum of **II** changes its shape continuously above the CMC. (ε is concentration dependant) that of **III** exhibits no changes over a wide concentration range once micelles dominate over monomers. This is shown in *Figure 5* where the apparent

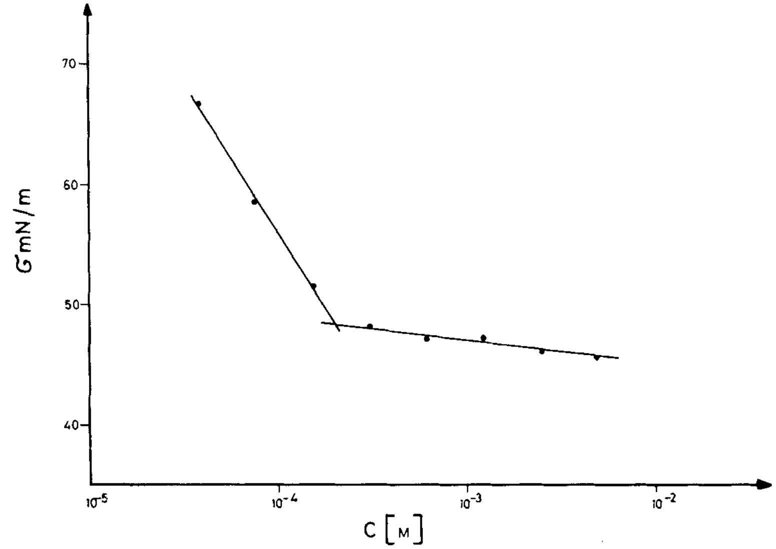


Fig. 2. *Surface tension-concentration plot for cyanine* **II**

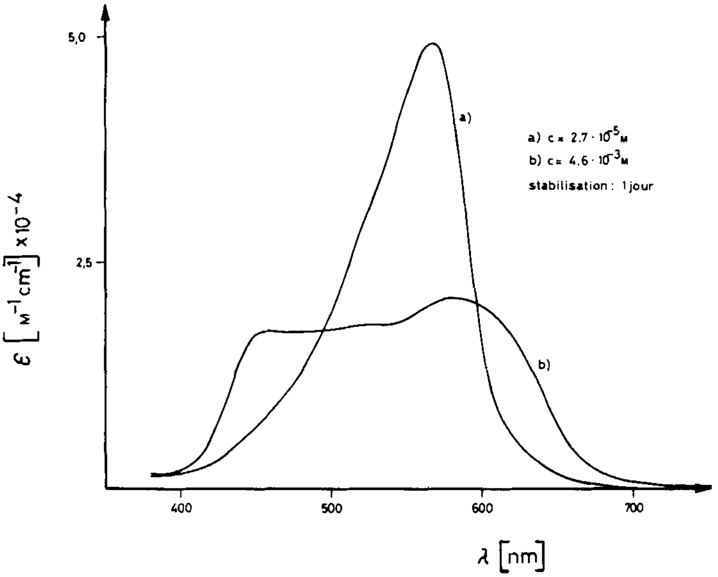


Fig. 3. *Absorption spectrum of cyanine* **III** *in water below and above the CMC.* (critical micelle concentration)

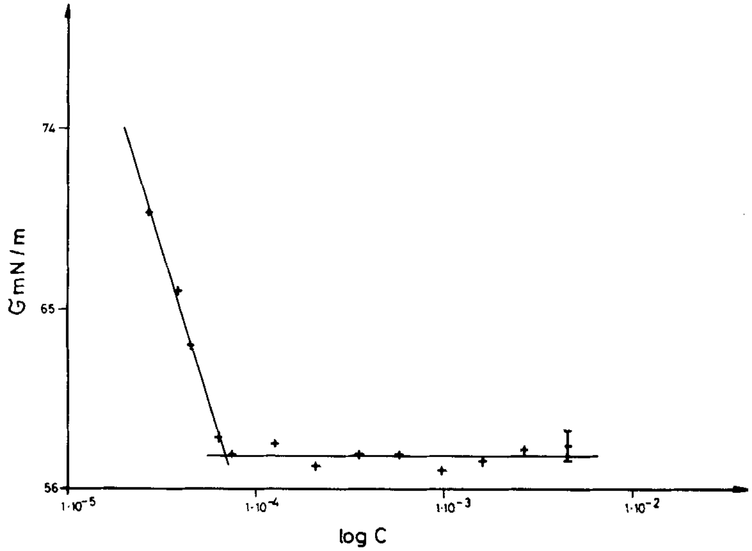


Fig. 4. *Surface tension-concentration plot for cyanine* **II** *in water at room temperature*

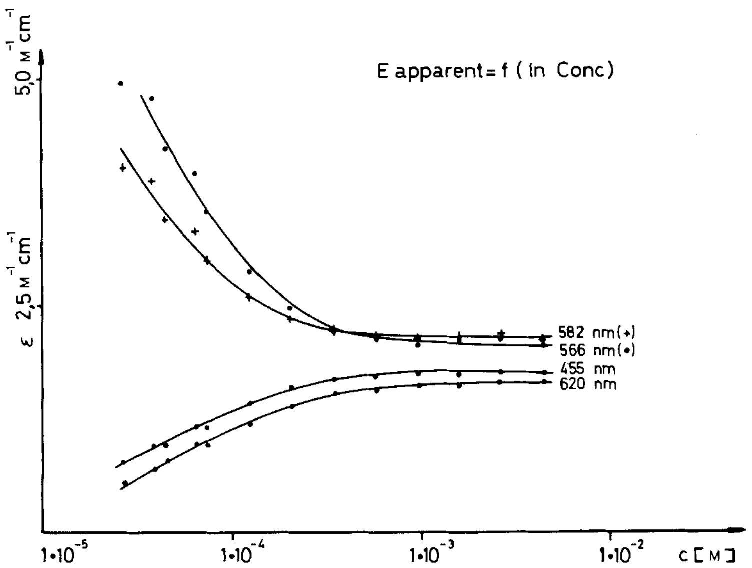


Fig. 5. *Apparent extinction coefficient of a solution of cyanine* **III** *as a function of concentration at different wavelengths*

extinction coefficient calculated from *Beers'* law and the total surfactant concentration is plotted against log c. In the domain of micelle formation the extinction of multimers grows at the expense of the monomer peak. However, no further changes are noted once micelles are the dominant species in solution. It appears then that with the cyanine dye **III** a compound has been found that assembles with a high degree of cooperativity. The ready formation of micelles of this type of cyanine dyes is encouraging for the search of materials, which in addition to their visible light absorption, display fluorescence in good quantum yield.

This work has been supported in part by *Ciba-Geigy AG* Corporation.

REFERENCES

[1] *A.H. Herz*, Photogr. Sci. Eng. *18*, 223 (1974); *A.H. Herz*, Advan. Colloid Interface Sci. *8*, 237 (1977).
[2] *H. Kuhn*, J. Photochem. *10*, 111 (1979).
[3] 'The Theory of the Photographic Process', 4th ed., T.H. James, McMillan, New York (1977).
[4] *E. Barni & P. Savarino*, J. Heterocyclic Chem. *14*, 937 (1977).
[5] *A.P. Gray, D.C. Schlieper, E.E. Spinner & C.J. Cavallito*, J. Am. Chem. Soc. *77*, 3648 (1955).