

THE DEPENDENCE OF ABSORPTION AND FLUORESCENCE OF DYE-DETERGENT MICELLE SYSTEMS ON THE DYE CONCENTRATION

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(Received June 1, 1971)

The shape of the absorption spectra is found to be changed by the increase of concentration of donor dye. At higher concentrations a band at 640 nm belonging to the form of higher dye-aggregates can be observed. In presence of detergent a new band at 465 nm appears, which can be attributed to the formation of water-insoluble complex salts. The local temperature of the excited molecules was found to decrease with increasing dye concentration.

Introduction

The migration of electron excitation energy from thionine (Th) to methylene blue (MB) in micelles was studied in [1]. It was shown, that the position of the main absorption bands of these dyes permits energy transfer from Th to MB, but not *vice versa*. The investigations reported in [2] showed that the yield of transfer is optimal at equivalent concentrations of Th and MB for the critical micelle concentration (c. m. c.) of the detergent. It was also shown that a very small amount of the detergent strongly bleaches the solution, i. e. decreases the value of $k(\lambda)_{\max}$, the maximum of the absorption coefficient.

From a study of the influence of temperature on the structure of dye-detergent systems [3] it was obtained that the efficiency of transfer from Th to MB is the highest at c. m. c. and at a temperature of 25°C. It was also found [4] that the increase of temperature shifts the c. m. c. towards higher detergent concentrations and promotes the dissociation of the water-insoluble complex salts and dimers. From these results we concluded that the solubilization of complex salts and dimers contributes to the increase of the effectivity of the energy migration in mixed dye solutions.

The influence of the temperature on the energy migration was studied also in [5]. It was shown that the effectivity of the energy migration is in a very close connection with the number of the micelles present in the system and with the structure of the dye-detergent system.

On the base of the examinations mentioned above, it seemed to be very interesting to study the influence of the change in dye concentration on the absorption and also on the luminescence properties of the dye-detergent systems. The aim of our present investigations was to establish the influence of the change in the donor dye (Th) concentration on the optical properties of the systems mentioned above.

Experimental results and discussion

The absorption and the luminescence properties of the Th solutions were studied at different detergent concentrations and at different dye concentrations. The experimental methods used are described in [2—5]. The detergent (sodiumlaurylsulphate; SLS) concentrations were between $2 \cdot 10^{-3}$ M/l, while the Th concentration were changed from $2 \cdot 10^{-6}$ M/l to $1 \cdot 10^{-4}$ M/l. The absorption and the luminescence of the examined systems seemed to be influenced both by the detergent and the dye concentration.

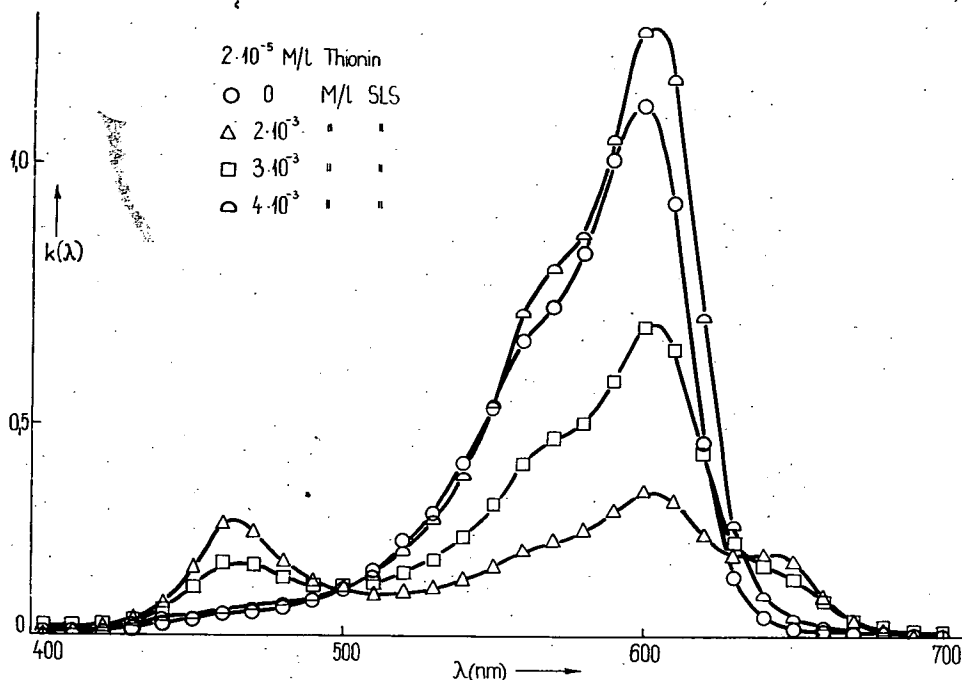


Fig. 1. Absorption spectra of $2 \cdot 10^{-5}$ M/l solutions of thionin different detergent concentrations

Fig. 1 shows the absorption spectra of the solutions of $2 \cdot 10^{-5}$ M/l of Th at different detergent concentrations. The maximum of the main absorption band (α -maximum) of aqueous solution is at 600 nm, that of the solutions containing different amounts of detergent is at about 605 nm. The addition of detergent to the system shifts the location of maximum towards the longer waves by 3—5 nm, in a good accordance with the results of [1].

Fig. 1 also shows that in solutions containing detergent — in addition to the α -maximum — three satellite maxima can be observed: the first is the so-called γ -band at 465 nm, the second is the β -band at 565 nm (due to dimer forms of the dye) and the third is the δ -band at 640 nm.

The curves belonging to different concentration of SLS have an isosbestic point at 500 nm, near to the γ -band, probably due to an equilibrium of monomer and

dimer forms of the dye present in the solutions at low dye concentrations. With increasing dye concentration higher associates can be formed [6], therefore this point disappears at higher concentrations. This explanation seems to be corroborated by the appearance of the δ -band at 640 nm possibly due to the absorption of higher aggregates.

Table I

The maxima of absorption coefficients, $k(\lambda)_{\max}$, for the α -bands at different dye concentrations and at different amounts of detergent

$C_{\text{SLS}} \cdot 10^3$ (M/l)	C_{Th} (M/l)					
	$2 \cdot 10^{-6}$	$5 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$1 \cdot 10^{-4}$
0	0.25	0.41	0.86	1.90	4.95	11.42
2	0.05	0.06	0.12	0.26	0.58	2.09
2.5	0.08	0.11	0.17	0.31	0.65	2.20
3	0.14	0.18	0.25	0.38	0.78	2.33
3.5	0.22	0.26	0.34	0.56	1.02	2.49
4	0.26	0.44	0.75	1.18	2.15	3.64
6	0.28	0.73	1.45	2.69	6.04	13.15
8	0.29	0.73	1.47	2.90	6.40	15.00

The maximum absorption coefficients for the α -bands determined at different dye concentrations are listed in Table I. It can be seen that $k(\lambda)_{\max}$ for a solution containing $5 \cdot 10^{-6}$ M/l Th, decreases from 0.409 to 0.068 on addition of $2 \cdot 10^{-3}$ M/l detergent to the solution. These results are in a good accordance with the data of MUKARJEE and MYSELS [7] and can be interpreted by the formation of highly water-insoluble complex salts of the detergent anion and the dye cation.

The formation of this kind of complex salts was studied in [7] and in [4], too. It was shown that the γ -band originating from the absorption of complex salts has a maximum at $2 \cdot 10^{-3}$ M/l detergent content, above this concentration it decreases up to the c. m. c. and remains constant or disappears at higher detergent concentrations. The disappearance of the γ -band is due to the solubilization of dye-detergent complex salts.

In Fig. 2 $k(\lambda)_{\max}$ is plotted for different concentrations of Th versus detergent concentration. This figure shows that around and above the c. m. c. $k(\lambda)_{\max}$ increases with increasing concentration of SLS and reaches an almost constant value at a concentration of $6 \cdot 10^{-3}$ M/l of detergent. Also this phenomenon is due to the solubilization of the dye-detergent complex salts, i. e. incorporation of dye into the micelles. The spectroscopical evidence suggests that the micelles carry mainly monomeric dye cations, with a certain proportion of dimers [1].

It is to be noted, however, that at higher detergent concentrations $k(\lambda)_{\max}$, in most cases, exceeds the value measured in aqueous solution. This results, probably, can be interpreted by the presence of non-absorbing dye-aggregates in aqueous solution containing higher dye concentrations [3]. The solubilization of these non-absorbing dye-aggregates results the „recolarization” of the system observed with increasing detergent concentration.

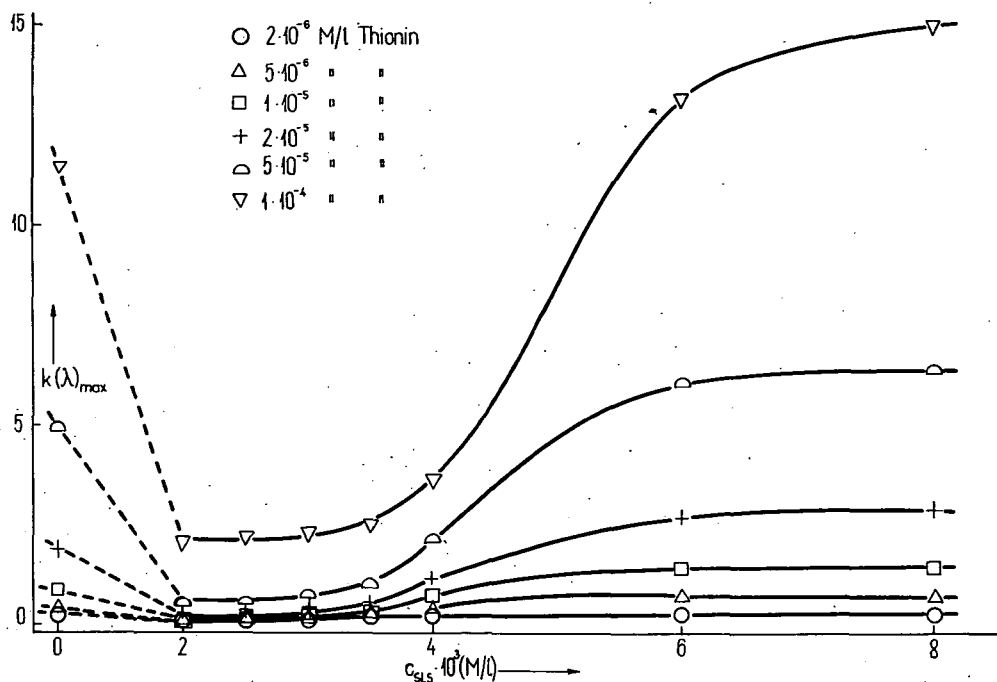


Fig. 2. Absorption coefficients of thionin solutions with different dye concentrations versus detergent concentration

The fluorescence spectra of the systems show a similar change with the concentrations of dye and detergent. In Table II the maxima of the fluorescence intensity, $f_q(\lambda)_{\max}$, measured in solutions of different Th concentrations containing different amounts of detergent, are entered. The fluorescence is almost completely quenched at very low concentrations of the detergent. As it was shown in [1], this is due to the formation of neutral molecules. After the solubilization of these molecules by the detergent anions, the fluorescence is restored. Our data clearly show that the solubilization depends both on the concentration of dye and of detergent.

It can also be observed that $f_q(\lambda)_{\max}$ — similarly to $k(\lambda)_{\max}$ mentioned above — from $4 \cdot 10^{-3}$ M/l detergent concentrations exceeds the values measured in aqueous solutions. The higher values of $f_q(\lambda)_{\max}$ can be attributed to the solubilization of the dye-aggregates present in aqueous solutions. This leads to the interesting observation that in solutions with high detergent concentrations no quenching of fluorescence appears [8—9], but — instead of quenching — an increase of fluorescence occurs with increasing dye concentration. This is in good accordance with results given in [1] for Th at detergent concentrations near to the c. m. c.

Between the absorption and the fluorescence spectra an universal relation was given by STEPANOV [10]:

$$\frac{f_q(\bar{v})}{k(\bar{v})} = D(T) \bar{v}^3 \exp(-h\bar{v}/kT), \quad (1)$$

Table II

The maxima of fluorescence intensity, $f_q(\lambda)_{\max}$, solutions of different thionin concentrations and at different amounts of detergent

$C_{SLS} \cdot 10^3$ (M/l)	C_{Th} (M/l)					
	$2 \cdot 10^{-6}$	$5 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$1 \cdot 10^{-4}$
0	19.68	28.92	40.19	98.22	271.70	525.30
2	2.05	1.88	1.13	1.77	3.69	4.59
2.5	4.32	3.04	1.80	3.12	3.24	4.73
3	8.06	4.49	3.01	5.17	3.73	4.82
3.5	15.16	8.76	4.85	7.34	5.54	5.88
4	19.49	23.44	19.65	24.14	46.81	17.09
6	26.12	43.54	54.32	140.40	215.30	289.10
8	30.40	43.31	57.32	163.70	321.50	642.10

where $f_q(\bar{\nu})$ and $k(\bar{\nu})$ denote the fluorescence and the absorption spectra, respectively, $D(T)$ is a constant independent of $\bar{\nu}$, T is the absolute temperature, h and k are Planck's and Boltzmann's constants.

In order to check the validity of this equation it should be re-written in the form [11]:

$$F(\bar{\nu}) \equiv \frac{h}{kT} \bar{\nu} =$$

$$= 3 \log \bar{\nu} - \log [f_q(\bar{\nu})/k(\bar{\nu})]. \quad (2)$$

According to this function $F(\bar{\nu})$ has to be linear and from the slope of the straight line the temperature, T , can be obtained. Experimentally $F(\bar{\nu})$ was found to be linear, but the temperature calculated from the slope, T^* , was in most cases higher than the macroscopical (experimental) temperature ($T^* \cong T$). It was interpreted by many authors (see e. g. in [12]) that the local temperature of the excited molecules in the instant of fluorescence is higher than the macroscopical temperature of the system.

The validity of Eq. (1) and Eq. (2) for dye-detergent systems was checked by BÁLINT *et al.* [13]. They found a minimum local temperature near to the c. m. c.

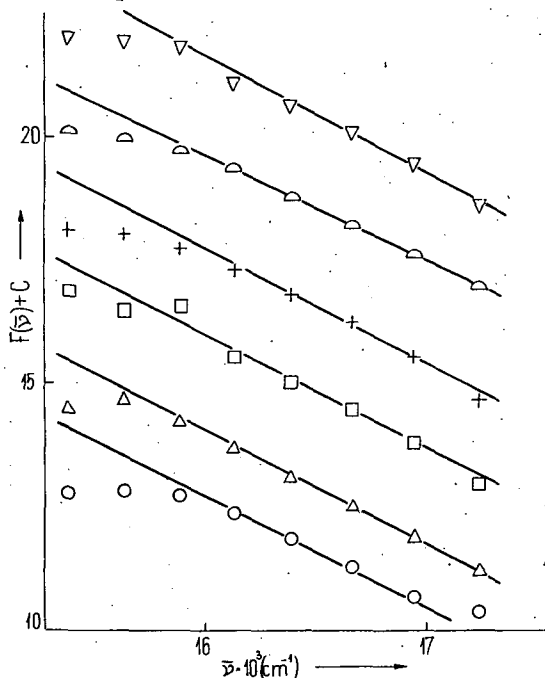


Fig. 3. $F(\bar{\nu})$ functions for solutions with different thionin concentrations; \circ - $2 \cdot 10^{-6}$ M/l, Δ - $5 \cdot 10^{-6}$ M/l, \square - $1 \cdot 10^{-5}$ M/l, $+$ - $2 \cdot 10^{-5}$ M/l, \times - $5 \cdot 10^{-5}$ M/l and ∇ - $1 \cdot 10^{-4}$ M/l.

in all cases investigated. A correlation between the local temperature and the fluorescence yield was also obtained in [13].

For our aqueous systems $F(\bar{\nu})$ is plotted in Fig. 3. The linearity of $F(\bar{\nu})$ is well fulfilled in all cases, the slopes of the straight lines are different for solutions of different dye concentration. The local temperature, T^* , calculated for aqueous solutions and for solutions containing $6 \cdot 10^{-3}$ M/l detergent are given in Table III. T^* decreases in both cases with the increase of dye concentration.

Table III

The local temperatures, T^* (°K), calculated for aqueous solutions of thionin and for thionin solutions containing detergent with concentration of $6 \cdot 10^{-3}$ M/l

C_{Th} (M/l)	T^* (°K)	
	$C_{SLS}=0$	$C_{SLS}=6 \cdot 10^{-3}$ (M/l)
$2 \cdot 10^{-6}$	329.1	373.7
$5 \cdot 10^{-6}$	312.6	357.9
$1 \cdot 10^{-5}$	303.5	346.6
$2 \cdot 10^{-5}$	296.3	336.1
$5 \cdot 10^{-5}$	288.8	324.9
$1 \cdot 10^{-4}$	285.4	320.3

decreases in both cases with the increase of dye concentration. For the first sight this seems to be in a contradiction to the results of [14], where an increase of T^* was found on increasing the dye concentration. This contradiction can be solved by taking into consideration the fact mentioned above that in detergent solutions the concentration quenching of fluorescence can not be observed. In this case the lifetime of excited state is longer, a larger fraction of the excess energy is dissipated by the instant of emission and this results in a lower T^* , i. e. the local temperature of the excited molecules decreases.

There is no clear explanation, however, for the higher values of T^* in solutions containing detergent with concentration of $6 \cdot 10^{-3}$ M/l. A trivial source of this

phenomenon is revealed by comparison of $k(\lambda)_{max}$ and $f_q(\lambda)_{max}$ for the solutions containing equal amounts of dye and different amounts of detergent. In the case of solutions with $1 \cdot 10^{-4}$ M/l concentration of Th, at detergent concentration of $6 \cdot 10^{-3}$ M/l, the increase in $k(\lambda)_{max}$ is 15,1% and for the $f_q(\lambda)_{max}$ a decrease can be obtained. Why the spectra behave in this manner it is still not understood.

It has to be noted that the local temperatures of the excited molecules obtained for solutions of Th with concentrations of $5 \cdot 10^{-6}$ M/l are in a good accordance with the values given in [13], where $T^* = 345.4$ °K was found for aqueous solution of Th, and $T^* = 367.7$ °K for solution containing SLS with concentration of $6 \cdot 10^{-3}$ M/l. The latter is very near to our result ($T^* = 357.3$ °K), but the difference between the values of T^* obtained for aqueous solutions is found to be significant. Let be mentioned, however, that looking at Fig. 2 given in [13], $T^* = 355.4$ °K seems to be too high.

The authors are indebted to Professor Dr. L. SZALAY, Director of Institute, for helpful discussions and valuable advices during the preparation of the text.

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ЗАВИСИМОСТЬ АБСОРБЦИОННЫХ И ФЛУОРЕСЦЕНТНЫХ
СВОЙСТВ КРАСИТЕЛЬ-ДЕТЕРГЕНТ СИСТЕМЫ ОТ КОНЦЕНТРАЦИИ
КРАСИТЕЛЯ

Я. Хевеши и Ж. Розжа

Экспериментальные результаты показывают, что ход спектра поглощения изменяется при повышении концентрации детергента. При более высокой концентрации красителя при 640 нм появляется полоса поглощения, которая относится к агрегатам красителя высшего порядка. При наличии детергента в растворе наблюдается и полоса поглощения при 465 нм возникающая из-за нерастворимых в воде солей. Между локальной температурой возбужденных молекул и изменением концентрации красителя наблюдается обратное отношение.