

# MIGRATION OF THE ELECTRON EXCITATION ENERGY IN SYSTEMS OF ORDERED STRUCTURE

## I. Absorption properties

By

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An aqueous detergent (sodium-lauryl-sulphate) solution containing three luminescent dyes in equimolar concentration was applied as *in vitro* photosynthetic model system. Experiments were made for studying the changes in the absorption properties of dyes due to the increase in dye and detergent concentration. It was found that with increasing dye-concentration different kinds of complexes of the dyes and of dyes and detergent come into being, which will be solubilized by increasing detergent concentration. The solubilization contributes to the increase in effectivity of the energy migration in these mixed solutions. This can be demonstrated by the fluorescence properties of the investigated system.

### Introduction

It is well known that photosynthesis begins with a photochemical process subsequent to the absorption of light energy. The absorbed energy is transferred from the absorbing pigment molecules to those actually taking part in the photosynthesis, to the so-called reaction centrum.

Investigations of the energy migration in *in vivo* systems are very difficult owing to the fact that these systems are very sensitive to light, to heat, to experimental conditions and, in most cases, the composition of the pigment present in the system is not known. These difficulties can be partly eliminated by performing the investigations in model systems which approximate the structure of the photosynthesizing system.

Models used for this purpose are often solutions containing micelles [1]. The lamellar structure of the detergent (sodium lauryl sulphate) system applied imitates, at least to some extent, the structure of the chloroplasts in the photosynthesizing *in vivo* systems.

The migration of electron excitation energy from thionin (Th) to methylene blue (MB) in systems containing these dyes in an aqueous solution of sodium lauryl sulphate (SLS) was studied by SINGHAL *et al.* [2], HEVESI and co-workers [3], [4] and RÓZSA [5]. The model applied by BÁLINT *et al.* [6] and LEHOCZKI *et al.* [7] consisted of aqueous solution of SLS, containing rhodamine 6G (Rh6G) and thionin. The results of these experiments showed that the efficiency of the energy

transfer from Rh6G to Th or from Th to MB is the highest at the critical micelle concentration of the detergent (c.m.c.) and at room temperature. It was also shown [8] that the effectivity of the energy migration is very closely connected with the number of the micelles present in the system, and therefore with the structure of the dye-detergent solutions.

To extend these earlier investigations performed in aqueous SLS solutions containing rhodamine 6G and thionin or Th and methylene blue, respectively, a system consisting of the above three luminescent dyes in detergent solutions was investigated. This system represents a better approach to the *in vivo* system, where usually more than two kinds of pigment are present in the chloroplast.

The aim of the present paper is to study the influence of the change in concentration of the dye and the detergent on the effectivity of the transfer of excitation energy. These changes can be demonstrated by the changes in luminescence intensity of the dyes applied. Therefore, the properties of the absorption and fluorescence in three-component micellar systems were measured.

#### *Composition of the systems. Experimental methods*

Sodium lauryl sulphate was used as detergent, rhodamine 6G, thionin and methylene blue were applied as luminescent dyes. Mixed solutions containing equimolar quantities of these dyes were studied, the concentration of the dyes was varied from  $2 \cdot 10^{-6}$  M to  $1 \cdot 10^{-4}$  M. The detergent concentration changed from 0 to  $8 \cdot 10^{-3}$  M. For preparing the solutions, first the required volumes of stock solutions of the dyes were pipetted into the flask, then the detergent was added to the solution, and finally the mixture made up to the mark with water distilled in a three-stages quartz distillation apparatus. Each set of the measurements was completed within 48 hours after the preparation of the solutions. The experiments were repeated several times, and the mean values of the results were used for drawing the conclusions.

The absorption spectra of the systems were recorded on an Optica Milano Type CF—4DR spectrophotometer, the recording unit was a compensograph Type Specdomax C. The fluorescence spectra were measured on a spectrophotometer DFS—12 (Leningrad). The light source was a low-pressure mercury lamp HBO 500. The sample was contained in a 1 cm cell. The wavelength of exciting light was 436 nm and 494 nm, respectively. The fluorescence spectra were corrected for reabsorption [9] and for spectral response of the photomultiplier. The experimental temperatures were kept constant within  $\pm 1$  °C in an adequate sample holder with the aid of an U—10 type Höppler ultrathermostat.

#### *Results and discussion*

The absorption and luminescence properties of mixed solutions containing three luminescent dyes and detergent were investigated. The measured characteristics seemed to be influenced both by detergent and dye concentration. The absorption spectra of the systems are not additive; the absorption spectra of mixed solutions cannot be built up from the absorption spectra of the one-component systems. This indicates

the presence of chemical interactions among the investigated dyes and between the dyes and the detergent used. This is supported by the deformation of the absorption spectra of mixed solutions containing detergent, compared with the absorption spectra of the corresponding aqueous solutions.

Figs. 1 and 2 show the absorption spectra of the solutions of  $2 \cdot 10^{-6}$  and  $5 \cdot 10^{-5}$  M dye concentration at different SLS concentrations. The figures show, that the addition of a small amount of detergent to the solutions shifts the maxima

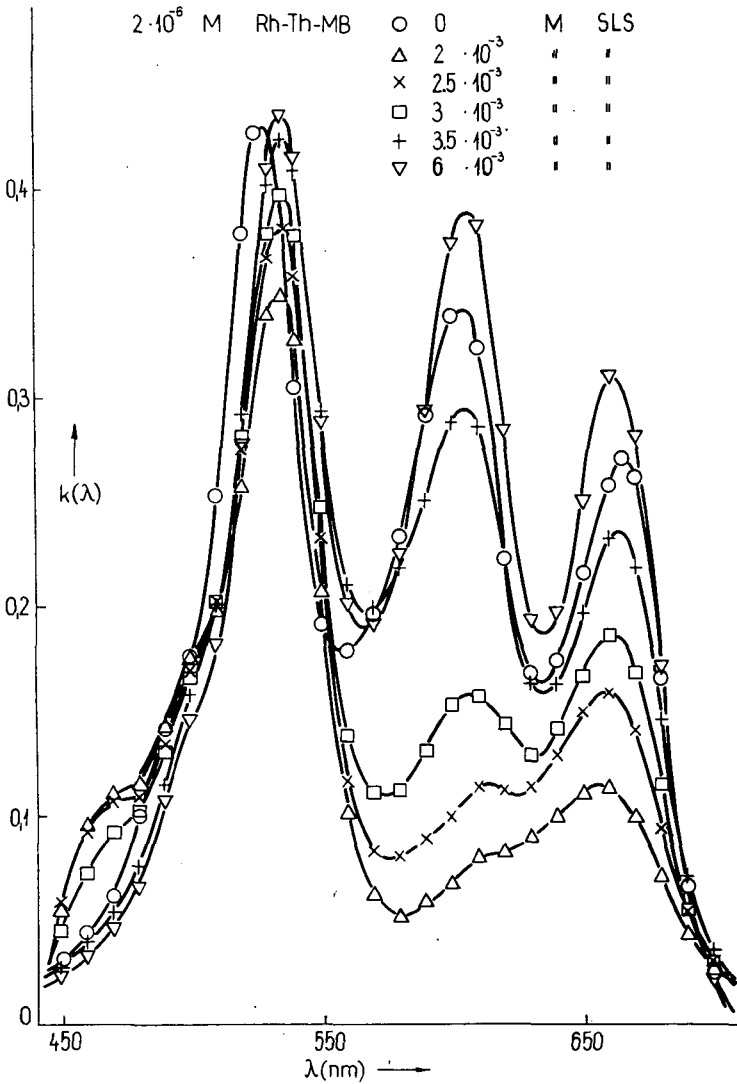


Fig. 1

of the absorption spectra toward longer wavelengths, but further increases in detergent concentration have no essential effect on the position of the maxima. The extent of these shifts in mixed solutions is in good accordance with the results measured in one-component systems [2, 5—7, 10, 11]. An exception is the behaviour of the  $\alpha$ -band of MB, which is at 665 nm in aqueous solutions. Adding detergent to the aqueous mixed solution this peak shifts toward shorter wavelengths and the extent of the shift depends on the detergent concentration. This phenomenon can be explained by the circumstance that the  $\alpha$ -band of MB is partly overlapped by the

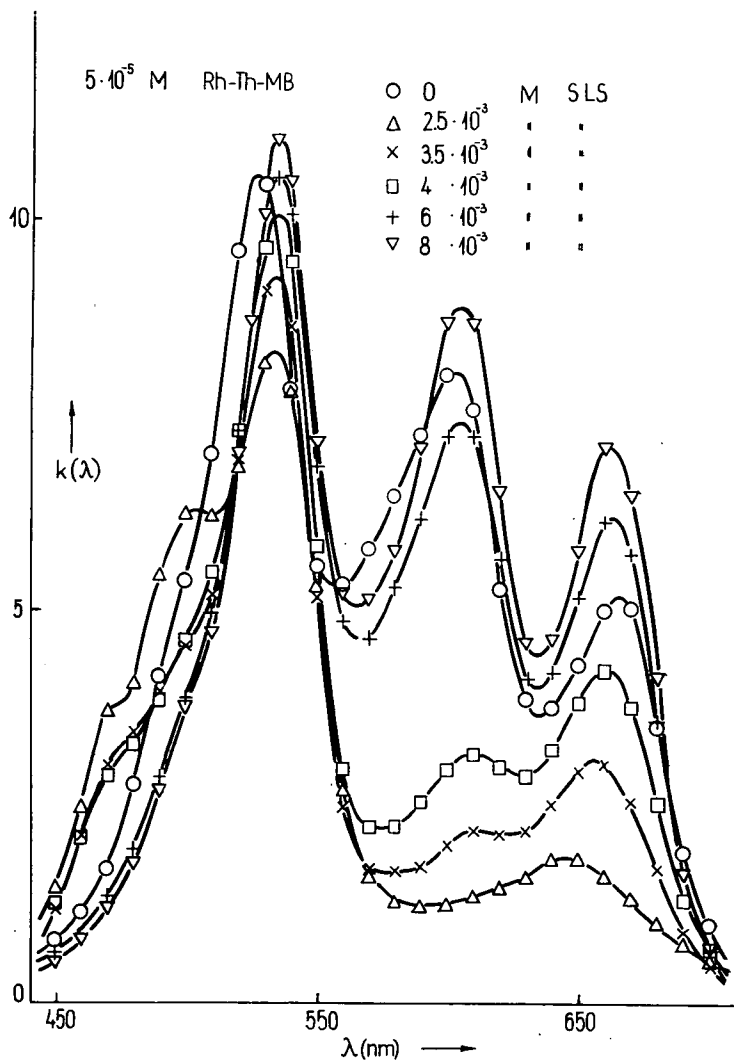


Fig. 2

$\delta$ -band (640 nm) of Th. This conception is supported by the fact that in mixed solutions at low detergent concentrations (below the c.m.c.) the maximum of the  $\alpha$ -band of MB is higher than that of Th, contrary to the respective values measured in aqueous solutions. Comparing the Figs. 1 and 2, it can be seen that, with increasing dye concentration, different types of associates can be formed.

Adding detergent to the solutions, the values of the  $\alpha$ -maximum of Rh6G (528—534 nm) first decrease, then gradually increase reaching the value measured

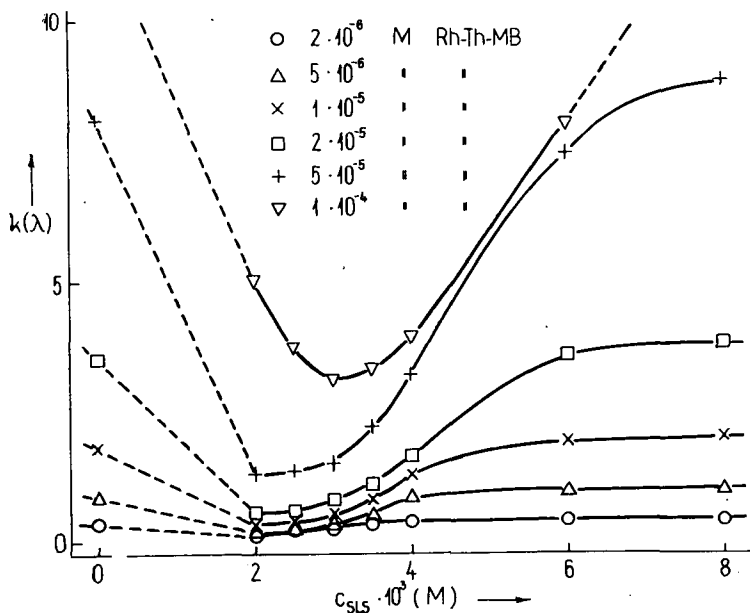


Fig. 3

in aqueous solutions. The minimum of the absorption coefficients is at the same SLS concentration ( $2 \cdot 10^{-3}$  M) for each dye concentration.

Figs. 3 and 4 show the change in the maximum of the  $\alpha$ -band (600—605 nm) and  $\gamma$ -band (465 nm) of Th, respectively, as a function of SLS concentration at different dye concentrations. It can be seen that, adding some detergent to the system, the absorption coefficients of the  $\alpha$ -band maxima of Th decrease; further increase in the SLS concentration raises the values of the maximum over those measured in aqueous solutions.

With increasing dye concentration, the increase in  $k(\lambda)$  values begins at higher and higher concentrations. This means that at a given SLS concentration, with increasing dye concentration, more and more dye-aggregates or dye-detergent complexes are formed. This statement is supported by the changes in the  $\gamma$ -band maxima of Th observed at different concentrations of dyes and detergent. The appearance of the  $\gamma$ -band of Th is attributed to the water-insoluble dye-detergent salts developed

in the system at low detergent concentrations. These salts become water-soluble at higher detergent concentrations, therefore the values of the maxima of this band decrease with increasing detergent concentration.

Comparing the minima of the curves of Fig. 3 and the maxima of the curves of Fig. 4, it can be seen that the increase in intensity of the  $\gamma$ -band takes place at

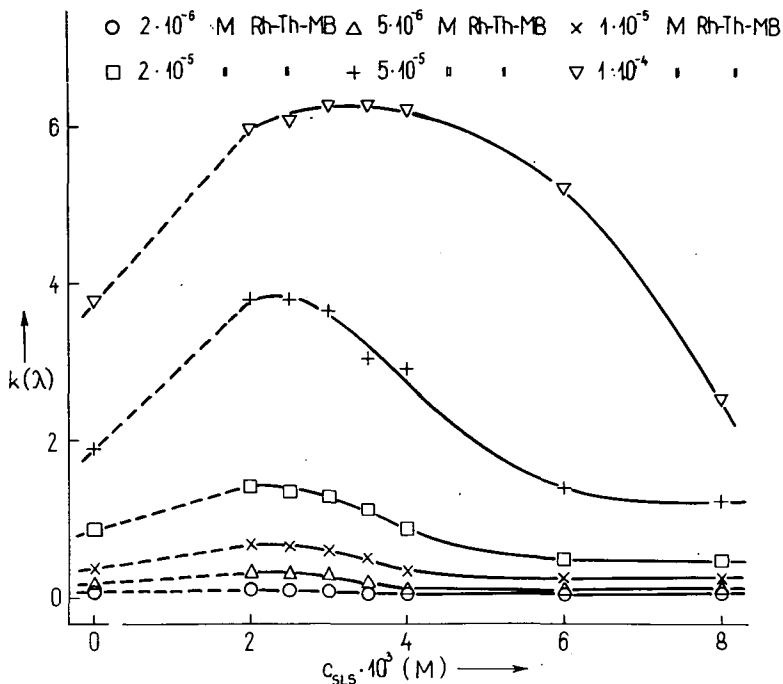


Fig. 4

the expense of the intensity of the  $\alpha$ -band, which proves that the Th monomers form complexes with detergent molecules.

Similar changes were found by investigating the changes in  $\alpha$ -band maxima (665 nm) of MB and the 500 nm maxima of MB—SLS complexes as a function of detergent concentration at different dye concentrations. The results of these experiments are presented in Figs. 5 and 6. It can be seen that at a given dye concentration the intensity of the maxima at 500 nm is the highest at the same detergent concentration where the  $\alpha$ -band intensities of MB are the lowest. Therefore, it can be stated that at high dye concentrations, MB forms dye-detergent complexes which dissolve with further increasing detergent concentration, and the intensity of the  $\alpha$ -band of MB increases again. At  $6 \cdot 10^{-3}$  and  $8 \cdot 10^{-3}$  M SLS concentrations the intensity of the  $\alpha$ -band characteristic for MB monomers exceeds the value measured in aqueous solutions. This can be explained by the circumstance that in aqueous

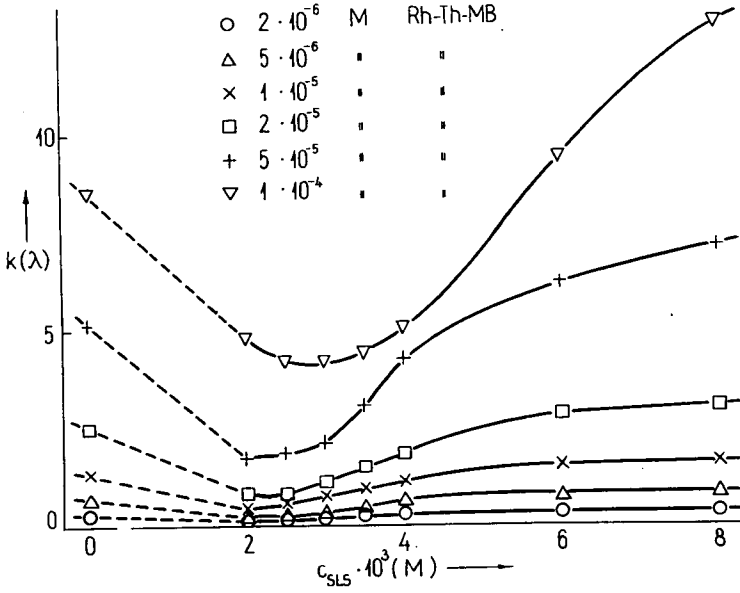


Fig. 5

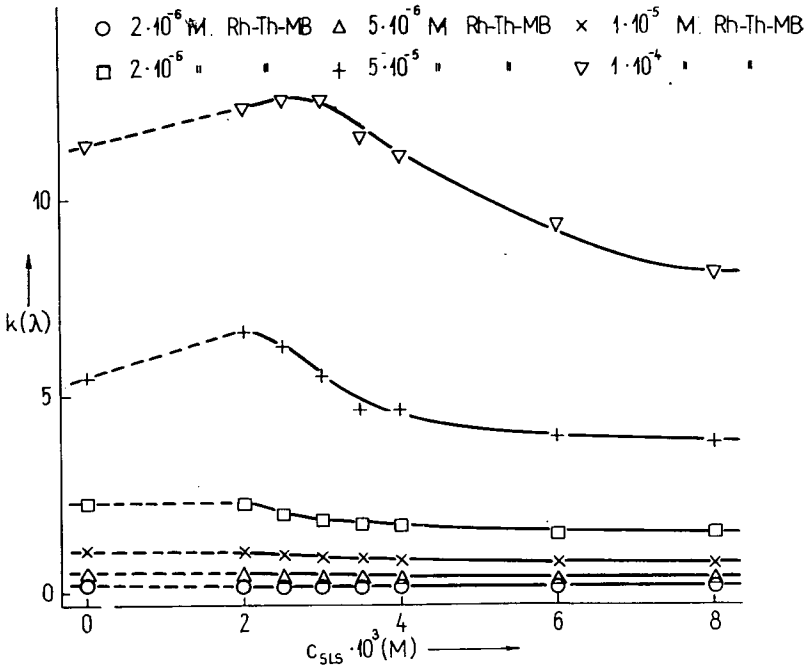


Fig. 6

solutions over  $10^{-5}$  M dye concentration, non-absorbing dye aggregates are present, which become soluble at higher detergent concentrations.

The presence or absence of the  $\beta$ -band maximum of Th (565 nm), characteristic for thionin dimers, could not be determined in mixed solutions because of the significant overlap of the absorption spectra of Rh6G and Th.

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### МИГРАЦИЯ ЭНЕРГИИ ВОЗБУЖДЕНИЯ ЭЛЕКТРОНОВ В СИСТЕМАХ ПРАВИЛЬНОЙ СТРУКТУРЫ

#### I. Абсорбционные свойства

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Водный раствор детергента (натрий-лаурилсульфат), содержащий три люминесцирующего красителя с эквимольной концентрацией, использовался в качестве *in vitro* модельной системы фотосинтеза. Эксперименты проводились с целью изучения изменений абсорбционных свойств красителей при изменении концентрации красителей и детергента. Найдено, что при повышении концентрации красителя образовались разные комплексы красителей и красителя с детергентом, которые при повышении концентрации детергента растворялись. Растворение повышает эффективность миграции энергии в таких смешанных растворах, о чём свидетельствуют флуоресцентные свойства исследованных систем.