

THE INFLUENCE OF VISCOSITY ON OPTICAL PROPERTIES OF DYE-DETERGENT SYSTEMS

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The influence of glycerol on absorption and luminescence properties of dye-detergent systems containing $5 \cdot 10^{-6}$ mole/l thionine (Th) has been studied. With increasing glycerol percentage the critical micelle concentration (c. m. c.) of these systems results to be shifted towards higher detergent concentrations. The solubilizing effect of the detergent is decreased but not fully hindered by glycerol. In solutions of the same detergent concentration the increase in luminescence intensity with increasing glycerol percentage is stronger than that of the absorption coefficient of the Th monomers. The ordered structure of water-detergent systems is found also in aqueous glycerol-detergent solutions. Accordingly, these systems can also be used as a model in studying physical processes of photosynthesis.

Introduction

For studying physical processes of photosynthesis, suitable aqueous detergent solutions (e.g. of sodium laurylsulphate, SLS) containing organic dyestuff were used as models [1]. In these systems, above the critical micelle concentration (c.m.c.), the cationic dyestuffs rhodamine 6G (Rh 6G), thionine (Th) and methylene blue (MB), bound to SLS micelles [2], played the role of the photosynthesizing pigments [3—5].

Earlier investigations showed, that in these systems of ordered structure, similarly as in the photosynthesizing units of plants, monomer, dimer and polymer associations (aggregates) of the dyestuffs are present and bonding (adsorption) to the detergent molecules occurs [6, 7]. It has been shown, furthermore, that the local concentration of the dyestuffs in the micelles is higher, than that in the solution, i.e. the distribution of the dyestuffs in aqueous SLS solutions is not homogeneous [7]. Inductive resonance energy transfer, as accepted for energy migration between photosynthesizing pigments, is characteristic also in the case of the organic dyestuffs mentioned above [8—9]. The migration of the absorbed light energy occurs in the direction (Rh 6G → Th → MB), similarly as in the direction of P-700 between the photosynthesizing pigments [3, 5].

Investigations on the polarization of luminescence of chlorophyll showed that *in vivo* the molecule does not change its place during the life-time of the excited state, i.e. it is bound rather firmly. On the other hand, the low degree of polarization shows that the location of the molecules *in vivo* is not ordered. In the case of liquids

of low viscosity the dyestuff molecules may change their location more freely. By increasing the viscosity of the solvent it is possible to stabilize the position of the molecules in a certain degree [10].

To support this conception experimentally, we tried to influence the ordered structure of an aqueous detergent—glycerol system by changing the glycerol concentration (expressed in volume %). We studied the effect exerted on the micelle formation by the glycerol as a "foreign" solvent, and further the effect of increased concentrations of glycerol and detergent on the light absorption and emission of Th.

Materials and methods

The Th concentration was $5 \cdot 10^{-6}$ mole/l, according to [11]. The detergent (SLS) concentrations varied from $2 \cdot 10^{-3}$ mole/l to $1 \cdot 10^{-2}$ mole/l [3]. The concentrations of glycerol were 0, 15, 30, 45 and 60 volume percents. Each of the five series studied consisted of solutions of nine different SLS concentrations. Measurements were made at constant temperature (25 ± 1 °C). Changes in transport properties (viscosity, conductivity) were used to determine the c.m.c. Viscosity was determined using a Höppler viscosimeter Type U-10. The solutions were prepared, conductivity, absorption and emission spectra were measured as described in [4—6].

Experimental results and discussion

As well known, the viscosity η and conductivity τ is significantly changed by increasing the glycerol concentration. At the same SLS concentration the viscosity η increases rapidly as a function of the glycerol—water ratio [12], while the conductivity shows a less quick decrease. Therefore it is to be expected that the c.m.c. values determined from measurements of η and τ [13], respectively, will show differences. These are found in fact in the data of Table I, which gives the values of c.m.c. determined with both methods. It can be seen, however, that — irrespective of the method — the c.m.c. of the systems is shifted towards higher detergent concentrations with increasing glycerol concentration.

The increase in glycerol concentration and the consecutive increase in c.m.c. exert a significant effect on the light absorption of dyestuff—detergent systems. Fig. 1 shows the absorption spectra of Th solutions containing 30% glycerol and four different concentrations of detergent. As shown in the figure, four maxima are

Table I

	$C_{(\text{glycerol})}$ (%)				
	0	15	30	45	60
	c.m.c. (SLS) 10^3 mole/l				
c.m.c. determined on the base of conductivity	3.3	4.0	4.5	5.7	7.0
c.m.c. determined on the base of viscosity	3.0	3.5	4.5	6.0	7.0

found in the spectra below the c.m.c. ($4.5 \cdot 10^{-3}$ mole/l SLS), while above the c.m.c. only two bands can be seen. Our results are in accordance with [3, 12]. The maxima at 600 nm and 565 nm can be attributed to monomer and dimer forms of the dye (bands $k_{\alpha}(\lambda)$ and $k_{\beta}(\lambda)$, respectively). The maximum observed at 460 nm may be due to Th-SLS complex salts (band $k_{\gamma}(\lambda)$) and the maximum at 640 nm to the light absorption of higher Th aggregates (band $k_{\delta}(\lambda)$).

The values of these maxima for each of the five glycerol concentrations are plotted vs. detergent concentration in Figs. 2 and 3. These figures show that the values of $k_{\alpha}(\lambda)_{max}$ and $k_{\beta}(\lambda)_{max}$ are significantly lower, while $k_{\gamma}(\lambda)_{max}$ is significantly higher

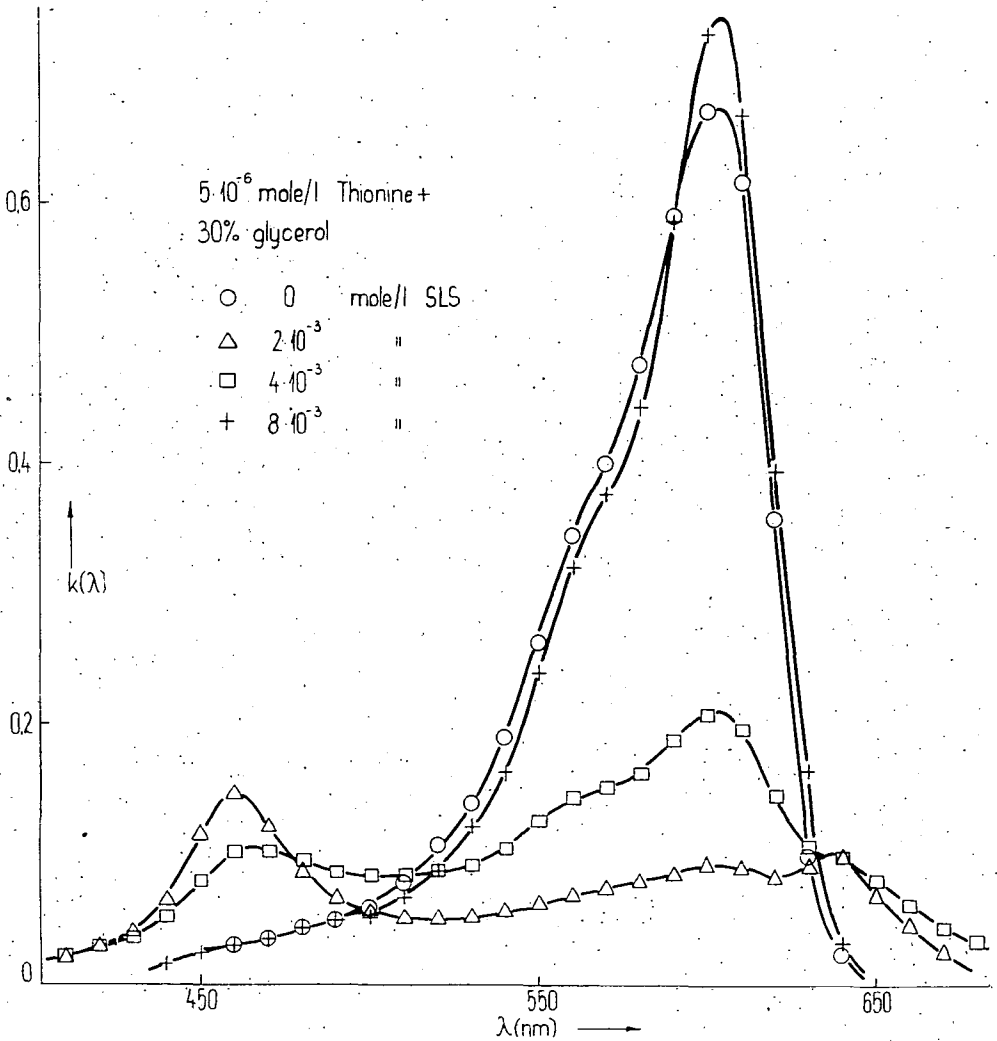


Fig. 1

Table II

glycerol %	0		15		30		45		60	
	$k_g(\lambda)_{\max}$ %	$f_d(\lambda)_{\max}$ %	$k_g(\lambda)_{\max}$ %	$f_d(\lambda)_{\max}$ %	$k_g(\lambda)_{\max}$ %	$f_d(\lambda)_{\max}$ %	$k_g(\lambda)_{\max}$ %	$f_d(\lambda)_{\max}$ %	$k_g(\lambda)_{\max}$ %	$f_d(\lambda)_{\max}$ %
SLS 10^3 mole/l										
0	100	100	100	100	100	100	100	100	100	100
2	15.3	10.1	14.1	7.1	13.4	8.3	16.2	8.8	19.4	17.8
3	35.6	29.2	25.8	13.4	19.4	10.8	18.4	12.6	21.0	19.7
4	102.0	62.8	85.0	61.3	31.2	15.9	23.1	21.0	26.0	23.7
4.5	—	—	107.0	120.0	87.0	74.0	—	—	—	—
5	114.0	128.5	111.0	126.5	107.5	105.0	31.5	24.3	28.7	28.1
6	117.0	136.0	113.0	137.0	110.0	124.0	73.0	76.0	39.4	34.3
7	—	—	—	—	—	—	114.0	135.0	52.2	46.5
8	117.5	139.0	114.0	139.0	111.0	124.5	116.5	140.0	69.5	70.0

for $2 \cdot 10^{-3}$ mole/l SLS concentration than those for pure aqueous solutions. With increasing detergent concentration the values of $k_{\alpha}(\lambda)_{\max}$ become "saturated", the values of $k_{\beta}(\lambda)_{\max}$ show maxima, while those of $k_{\gamma}(\lambda)_{\max}$ decrease to reach a constant value. The changes in the values of $k_{\delta}(\lambda)_{\max}$, not shown in our figures, are of similar character as those of $k_{\gamma}(\lambda)_{\max}$.

The changes observed at the same glycerol concentration may be explained by the solubilizing effect of SLS [14]. Namely, the detergent dissolves, though in a less extent, the Th aggregates and Th-SLS complexes existing at low SLS concentration even below the c.m.c. Intensive solubilization occurs only with the formation of micelles, as shown by the steep increase in the $k_{\alpha}(\lambda)_{\max}$ and $k_{\beta}(\lambda)_{\max}$ curves and the maximum of the $k_{\gamma}(\lambda)_{\max}$ curves. At SLS concentrations much higher than the c.m.c., first the dissolution of the dyestuff-detergent complexes comes to an end, than the decrease in the number of dimers and the resulting increase in that of monomer Th molecules ceases.

In the systems investigated, only the Th monomers show luminescence; therefore it is easier to survey the changes in the emission spectra by means of the values of $f_q(\lambda)_{\max}$, than by those of the absorption spectra. In Fig. 4 $f_q(\lambda)_{\max}$ is plotted for five series of solutions with different glycerol concentrations. As can be seen, the shape of the curves is similar to that of the $k_{\alpha}(\lambda)_{\max}$ curves, with the difference that the changes in $f_q(\lambda)_{\max}$, compared with pure aqueous solutions (without

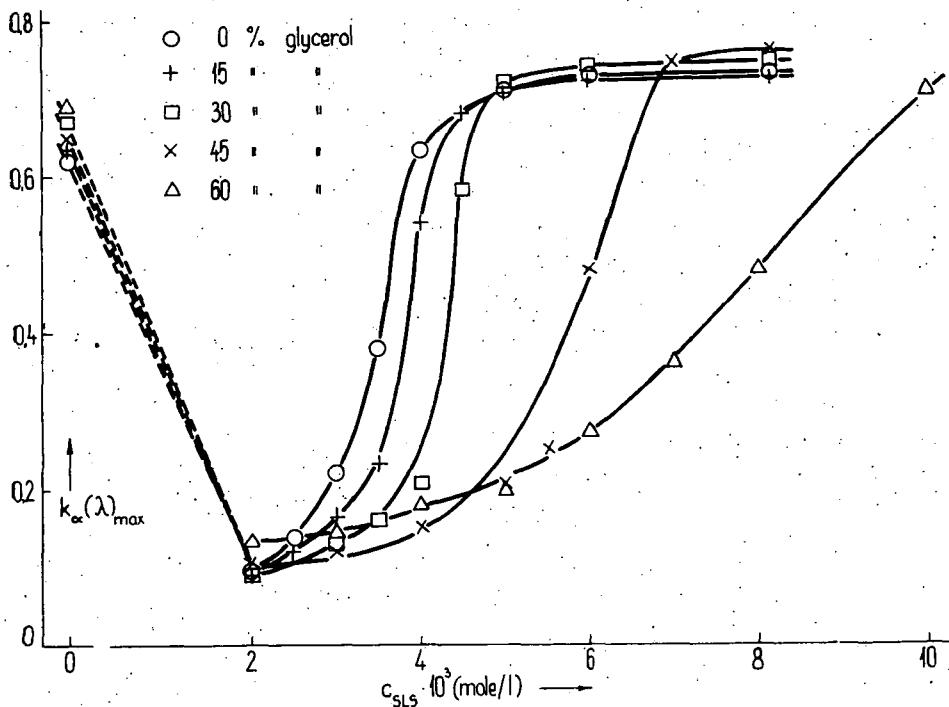


Fig. 2

glycerol), are more expressed for each glycerol concentration than in the case of $k_{\alpha}(\lambda)_{\max}$.

The changes in intensity of emission become more conspicuous from the data of Table II, in which the changes in intensity of aqueous detergent solutions are compared with $k_{\alpha}(\lambda)_{\max}$ and $f_{\alpha}(\lambda)_{\max}$ values of solutions containing no detergent. It can be seen from the table that below c.m.c. significant decreases, above c.m.c. increases in the respective values were found. Higher glycerol concentrations act against the above increase of intensity.

Fig. 2 shows that the $k_{\alpha}(\lambda)_{\max}$ values of aqueous solutions are slightly increased with increasing glycerol concentration. This increase may be explained by a decrease of the dimer forms. This is supported by the decrease in the $k_{\gamma}(\lambda)_{\max}$ values of aqueous solutions shown in Fig. 3. However, the increase in $k_{\alpha}(\lambda)_{\max}$ may also be due to

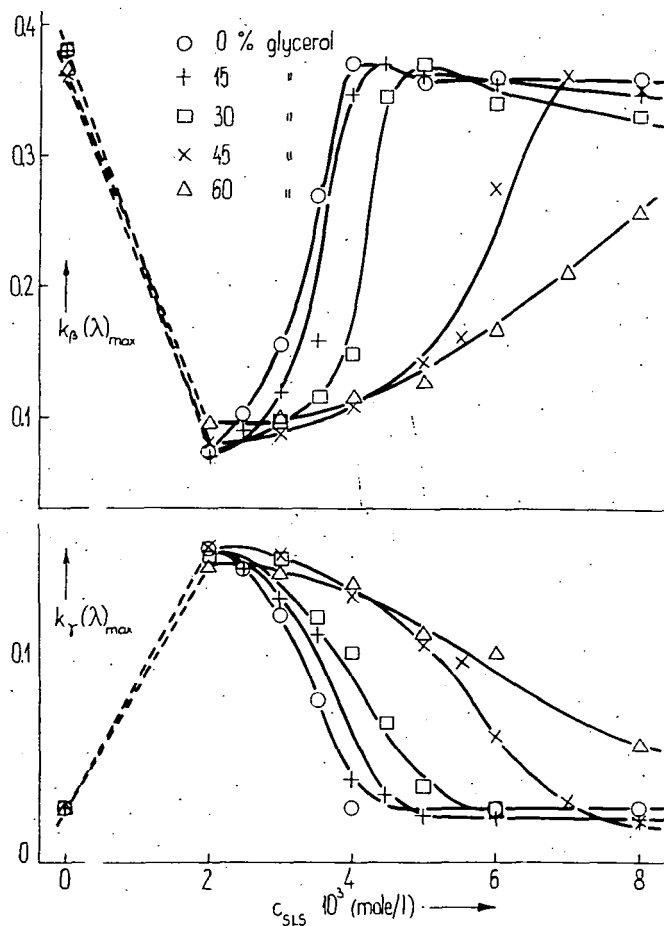


Fig. 3

dissolution caused by the glycerol of dyestuff associations of higher order, absorbing beyond the wavelength range investigated.

On the other hand, the $f_q(\lambda)_{max}$ values of aqueous solutions show greater increases owing to glycerol than the values of $k_x(\lambda)_{max}$. This may be explained as follows: with increasing glycerol concentration, the probability of extinction of excited molecules decreases, e. g. by the decreasing probability of kinetic collisions of molecules during the life-time of excitation. This may be caused by higher viscosity of the solvent, which shows an exponential increase as a function of glycerol concentration [12], while the emission increases linearly. Another explanation may be found in differences between macroscopic and microscopic viscosity [16].

Our results show that, by increasing the glycerol concentration in aqueous detergent solutions, the c.m.c. is shifted towards higher detergent concentrations. The solubilizing effect of the detergent is decreased, but not totally hindered by glycerol. This can be explained by the fact that, with increasing glycerol concentration, the dielectric constants of the solutions undergo changes (the refractive index increases, the dielectric constant decreases [15]) and hereby the conditions of micelle-formation are changed. It can be stated, furthermore, that in solvent systems consisting of mixtures of water, SLS, and glycerol micelles are also formed, though at higher detergent concentrations, thus permitting the formation of ordered lamellar structures. Therefore, these systems can also be used as models for studying photosynthesizing systems.

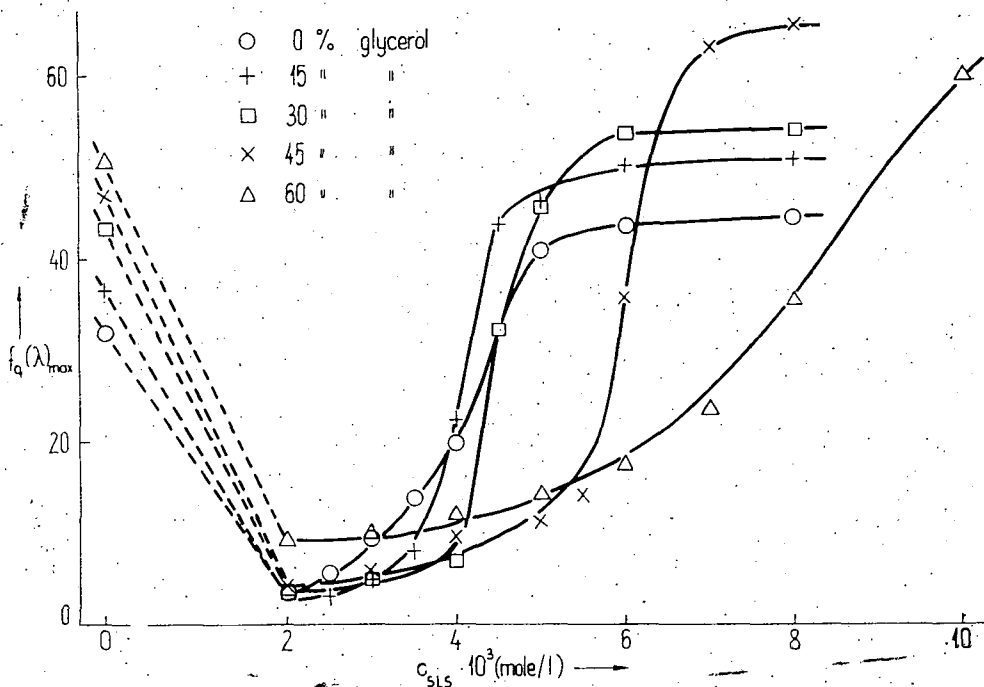


Fig. 4

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ВЛИЯНИЕ ВЯЗКОСТИ НА ОПТИЧЕСКИЕ СВОЙСТВА СИСТЕМ
КРАСИТЕЛЬ-ДЕТЕРГЕНТ

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В работе исследовалось влияние глицерина на абсорбционные и люминесцентные свойства систем краситель-детергент, содержащих $5 \cdot 10^{-6}$ моль/л тионина (Th). Критическая концентрация мицеллообразования (ККМ) с увеличением содержания глицерина смещается в сторону более высокой концентрации детергента. Солюбилизирующее действие детергента в присутствии глицерина уменьшается. В растворах, содержащих одинаковую концентрацию детергента, интенсивность люминесценции с увеличением количества глицерина сильнее возрастает, чем абсорбционный коэффициент мономерной формы тионина. В растворах вода-глицерин-детергент тоже образуется такая же упорядоченная структура как и в системах вода-детергент. Следовательно, эти системы можно использовать при исследовании физических процессов фотосинтеза в качестве модельной системы.