

# INFLUENCE OF THE TEMPERATURE ON THE LOCAL TEMPERATURE OF EXCITED MOLECULES IN DYE-DETERGENT SYSTEMS

By

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The dependence of the local temperature of excited molecules on detergent concentration (from  $2 \cdot 10^{-3}$  to  $8 \cdot 10^{-3}$  M/l) and on the experimental temperature (from 298 to 343 °K) was investigated. The observed appearance of a minimum in the local temperature near the c. m. c. is explained by the dependence of the absorption and fluorescence on the concentration of detergent. A relation between local temperature and fluorescence yield of the luminescent substances was also determined.

## Introduction

A relation between the absorption and the fluorescence spectra of luminescent solutions found by MERRIT [1] could not be experimentally verified due to early apparatus. Recently STEPANOV [2] derived an universal relation between these spectra:

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

where  $f_e(\nu)$  and  $k(\nu)$  denote the fluorescence and the absorption spectra, respectively,  $D(T)$  — a constant independent of  $\nu$ ,  $T$  — the absolute temperature,  $h$  and  $k$  — Planck's and Boltzmann's constants.

In order to establish the validity of Eq. (1) ALENTSEV [3] suggested to re-write it in the form:

$$F(\nu) \equiv \lg f_e(\nu) - \lg k(\nu) - 3 \lg \nu = -h\nu/kT + \text{const.} \quad (2)$$

$F(\nu)$  is a linear function of the frequency  $\nu$ , (or the wave number  $\bar{\nu}$ ) and from the slope of the straight  $T$  can be calculated. Usually a local temperature ( $T^*$ ) higher than the experimental temperature ( $T$ ) can be obtained from the slope. This local temperature is due to the non-dissipation of excess energy of excitation during the vibrational relaxation. This statement is verified theoretically by JABLONSKI [13] and is supported by several experimental results ([3], [5], [9] and [14]).

The validity of the relation was investigated by several authors [4]—[6] and it was established for gases, solutions and solid luminescent systems. For chlorophylls the problem was first studied by KRAVTSOV [7]. Systematical investigations on the influence of solvents on the local temperature were carried out by SINGHAL and HEVESI [8]. In [9] the applicability of the relation to solutions of different chloro-

phyll derivatives; pheophytin-a and chlorin-e<sub>6</sub> was studied. RABINOWITCH *et al.* [10] and DAS *et al.* [11] applied the Stepanov's relation and its modified form given by KETSKEMÉTY *et al.* [12] to suspensions of photosynthetic algae.

In this paper the applicability of Stepanov's relation to dye-detergent solutions is studied and the dependence of the local temperature on the detergent concentration modifying the structure of the system and on the ambient temperature is investigated.

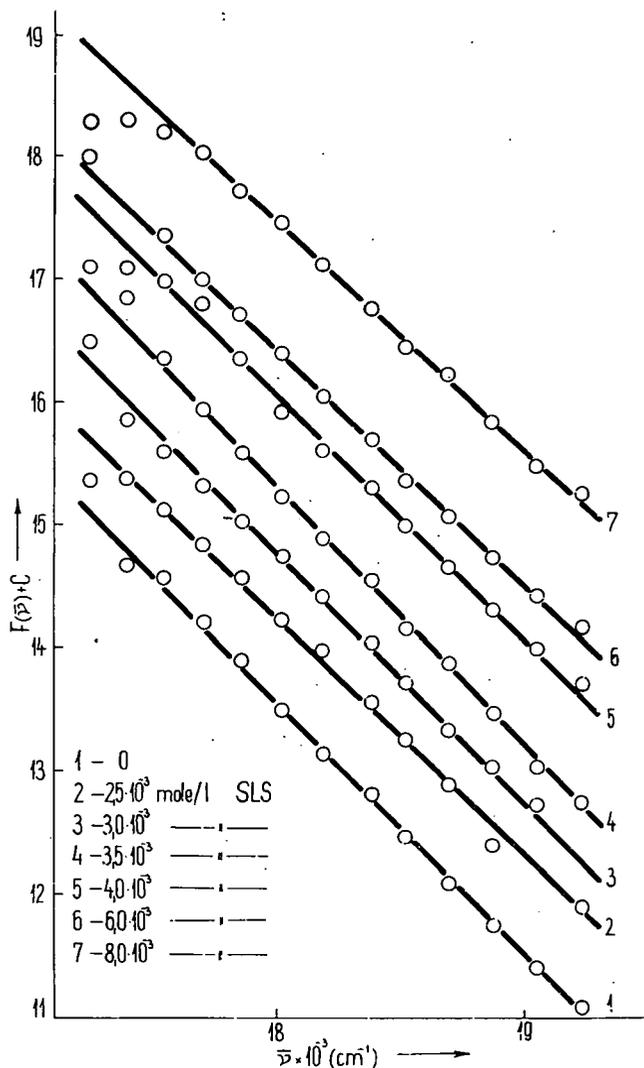


Fig. 1. The Stepanov's straight lines for aqueous solutions of  $5 \times 10^{-6}$  M Rhod 6G at different concentrations of SLS.

*Results and Discussion*

The substances studied, also the experimental methods, the composition of the systems were discussed earlier in [15–18]. In this paper only those data are given which were not discussed in the earlier papers.

In Fig. 1 the straights from Eq. (2) for aqueous solutions of  $5 \times 10^{-6}$  M/l rhodamine 6G (Rhod. 6G) with different concentrations of sodium lauryl-sulphate (SLS) are shown. The linearity of the function  $F(\nu)$  from Eq. (2) is well fulfilled in a wide range of the spectra. A similar picture was found for all the other dye-detergent systems unambiguously proving that Stepanov's relation is valid for dye-detergent systems, too. The deviation from the linearity at lower frequencies are explained in [12].

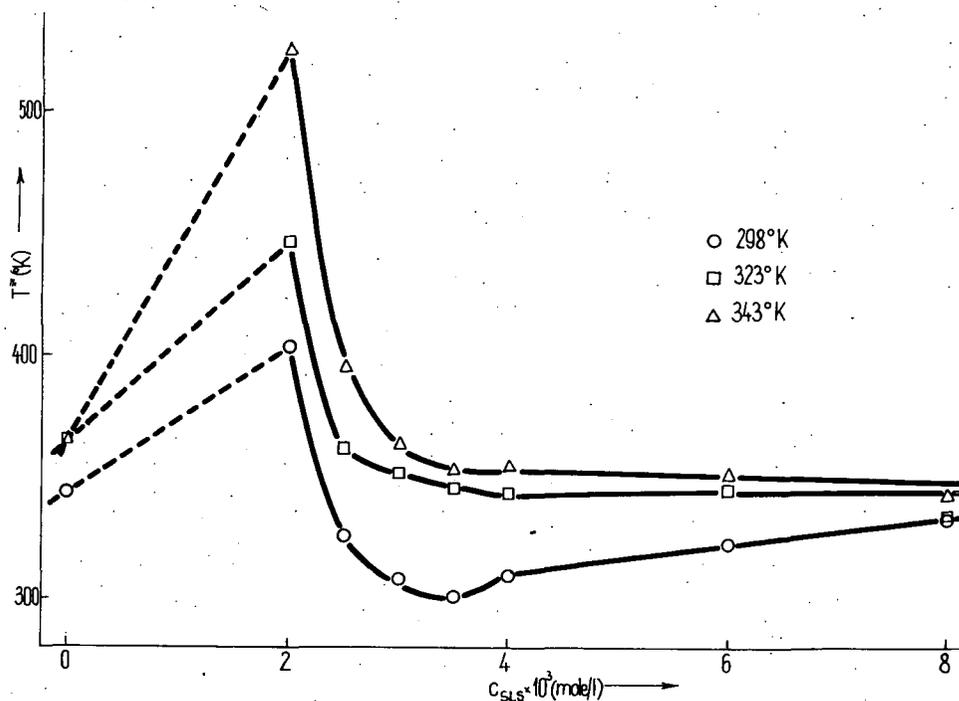


Fig. 2. The local temperatures,  $T^*$  in Rhod 6G solutions as a function of the detergent concentration and the temperature

The local temperatures  $T^*$  in solutions of Rhod 6G as a function of the concentration of detergent and the temperature are given in Fig. 2.  $T^*$  shows a maximum at  $2 \times 10^{-3}$  M/l detergent content and a minimum near the critical micelle concentration (c. m. c.), while it is constant or slightly increasing at higher detergent concentrations. Figure shows that  $T^*$  depends also on the experimental temperature. The local temperatures for  $2 \times 10^{-3}$  M/l detergent concentration are essentially higher than the experimental temperature. This can be explained by consulting

Table I, where the maximum absorption coefficients,  $k(\lambda)_{\max}$ , from [18] and the relative fluorescence intensities,  $I_{\text{rel}}$ , from [17], as well as the calculated values of local temperatures,  $T^*$ , are tabulated for different detergent concentrations and experimental temperatures. While  $k(\lambda)_{\max}$  of detergent solutions shows a decrease of 16% compared to that of the pure aqueous solution at 298°K and 343°K,  $I_{\text{rel}}$  is as low as 4% and 7%, respectively. This formally explains the high values of  $T^*$ . In addition,  $I_{\text{rel}}$  practically does not change at concentrations above the c. m. c., which explains the constancy of  $T^*$  in this concentration range.

Table I

The maximum absorption coefficients,  $k(\lambda)_{\max}$ , relative fluorescence intensities,  $I_{\text{rel}}$ , and the local temperatures,  $T^*$ , of Rhod 6G with  $5 \cdot 10^{-6}$  M concentration at different temperatures and different detergent concentrations

$C_{\text{SLS}} \cdot 10^3$ (M/l)	298°K			323°K			343°K		
	$k(\lambda)_{\max}$	$I_{\text{rel}}$ (%)	$T^*$ (°K)	$k(\lambda)_{\max}$	$I_{\text{rel}}$ (%)	$T^*$ (°K)	$k(\lambda)_{\max}$	$I_{\text{rel}}$ (%)	$T^*$ (°K)
0	0.89	100	343.5	0.84	100	365.5	0.79	100	365.5
2.0	0.75	4.08	403.3	0.80	11.1	446.5	0.67	7.19	525.3
2.5	0.79	15.6	325.6	0.79	21.9	361.4	0.76	17.9	395.6
3.0	0.84	33.3	307.9	0.81	40.0	351.2	0.75	25.7	363.4
3.5	0.88	86.7	300.6	0.85	54.5	345.4	0.79	48.7	353.2
4.0	0.92	91.9	309.5	0.84	70.9	343.5	0.78	55.8	355.2
6.0	0.94	90.4	322.3	0.88	77.5	345.4	0.83	72.0	351.2
8.0	0.94	80.5	332.5	0.89	79.7	334.3	0.83	80.5	343.5

In Fig. 3 the dependence of  $k(\lambda)_{\max}$ ,  $I_{\text{rel}}$  and  $T^*$  is shown for thionin (Th) solutions of  $5 \times 10^{-6}$  M/l on the concentration of detergent at experimental temperatures of 298°K, 323°K and 343°K. The change of  $T^*$ , at least up to the c. m. c., is similar as that for Rhod 6G, though the absolute values are somewhat less. The

Table II

The maximum absorption coefficients,  $k(\lambda)_{\max}$ , relative fluorescence intensities,  $I_{\text{rel}}$ , and the local temperatures,  $T^*$ , of Th with  $5 \cdot 10^{-6}$  M concentration at different temperatures and different detergent concentrations

$C_{\text{SLS}} \cdot 10^3$ (M/l)	298°K			323°K			343°K		
	$k(\lambda)_{\max}$	$I_{\text{rel}}$ (%)	$T^*$ (°K)	$k(\lambda)_{\max}$	$I_{\text{rel}}$ (%)	$T^*$ (°K)	$k(\lambda)_{\max}$	$I_{\text{rel}}$ (%)	$T^*$ (°K)
0	0.22	100	345.4	0.23	100	351.2	0.24	100	374.3
2.0	0.09	7.0	378.9	0.17	13.2	397.0	0.21	33.5	416.8
2.5	0.19	13.5	359.3	0.22	17.8	378.9	0.23	38.6	393.2
3.0	0.25	23.1	355.2	0.24	31.1	374.3	0.24	39.1	378.9
3.5	0.27	39.0	344.5	0.25	45.9	365.6	0.25	51.3	374.3
4.0	0.28	99.4	357.3	0.26	81.9	365.6	0.25	64.0	378.9
6.0	0.29	159.6	367.7	0.27	141.6	378.9	0.25	129.0	395.2
8.0	0.28	177.8	374.3	0.27	152.3	388.3	0.25	141.0	395.7

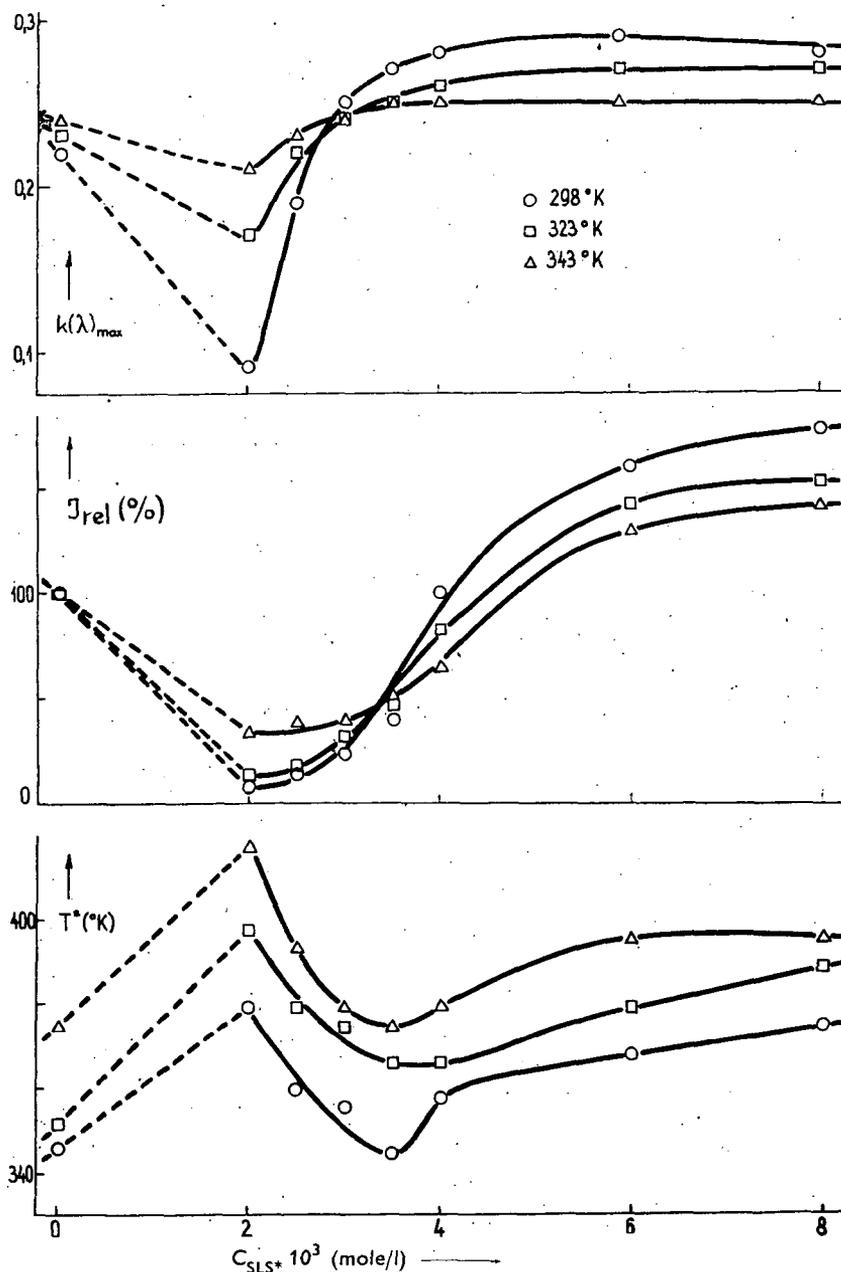


Fig. 3. The values of  $k(\lambda)_{max}$ ,  $J_{rel}$  and  $T^*$  of Th solutions with  $5 \times 10^{-6}$  M concentration at different temperatures and at different detergent concentrations.

numerical values of the quantities mentioned above, taken from [17, 18], are listed in Table II. While for  $2 \times 10^{-3}$  M/l detergent solution, at  $T = 298$  °K, the value of  $k(\lambda)_{\max}$  is about 40% of that in pure aqueous Th solutions,  $I_{\text{rel}}$  is only 7%. Consequently, the excess of the exciting energy results in a relative high local temperature,  $T^* = 378.9$  °K, exceeding the experimental temperature by 81 degrees. In the same system at 323 and 343 °K the value of  $k(\lambda)_{\max}$  is lowered by about 10% compared to  $k(\lambda)_{\max}$  of the pure aqueous solution, while the values of  $I_{\text{rel}}$  for these are only 13% and 33%, respectively. This again should result in higher local temperatures. In fact, the values of  $T^*$  are higher by 74 degrees than the experimental temperatures.

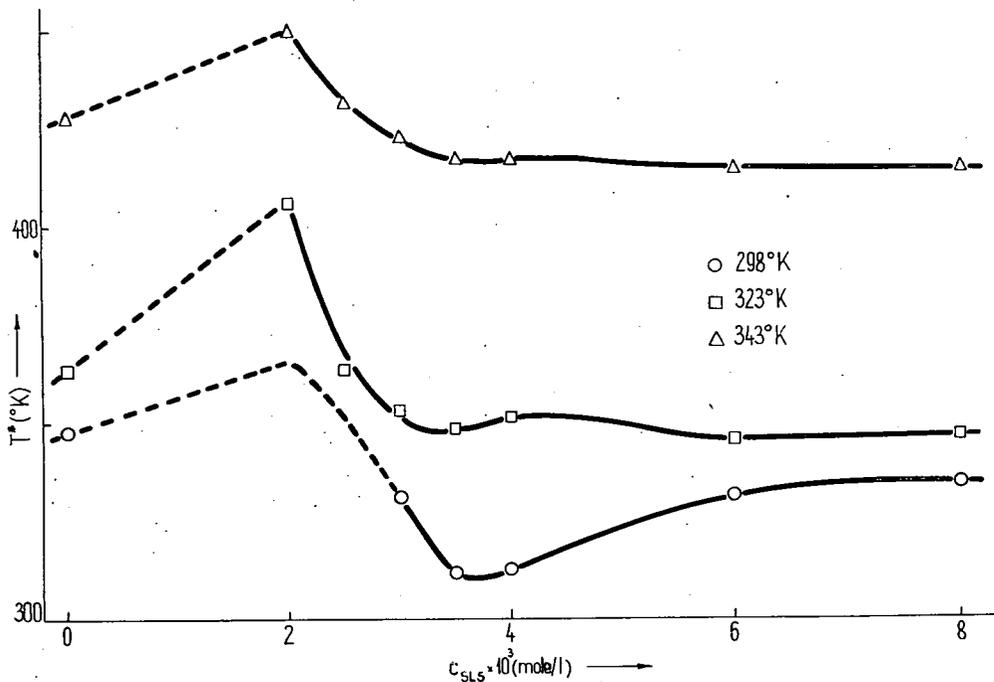


Fig. 4. The local temperatures,  $T^*$  in MB solutions versus detergent concentration at different temperatures

Fig. 4 shows the values of  $T^*$  versus detergent concentration for methylene blue (MB) solutions of  $5 \times 10^{-6}$  M/l at three experimental temperatures. It is to be mentioned that the fluorescence yield of MB solutions at 298°K is very low and the fluorescence is practically totally quenched at low detergent concentrations ([16], [19]), therefore experimental results for calculation of  $T^*$  at this temperature and concentrations were not available. As it can be seen from Fig. 4 the dependence of  $T^*$  on the concentration of detergent is not so expressed as in the case of the other dyes investigated. This can be understood by considering the absorption of the system showing similar changes. In Table III  $k(\lambda)_{\max}$  and  $I_{\text{rel}}$  are taken from [16] and the calculated values of  $T^*$  are given. While for  $2 \times 10^{-3}$  M/l detergent solution at

Table III

The maximum absorption coefficients,  $k(\lambda)_{\max}$ , relative fluorescence intensities,  $I_{\text{rel}}$ , and the local temperatures,  $T^*$ , of MB with  $5 \cdot 10^{-6} M$  concentration at different temperatures and different detergent concentrations

$C_{\text{SLS}} \cdot 10^3$ (M/l)	298 °K			323 °K			343 °K		
	$k(\lambda)_{\max}$	$I_{\text{rel}}$ (%)	$T^*$ (°K)	$k(\lambda)_{\max}$	$I_{\text{rel}}$ (%)	$T^*$ (°K)	$k(\lambda)_{\max}$	$I_{\text{rel}}$ (%)	$T^*$ (°K)
0	0.76	100	347.3	0.75	100	363.5	0.74	100	428.2
2.0	0.48	7.1	—	0.63	36.1	406.0	0.68	27.3	449.8
2.5	0.56	29.3	—	0.72	56.0	363.3	0.70	49.5	431.1
3.0	0.73	80.6	330.7	0.77	94.2	353.2	0.76	73.2	422.4
3.5	0.86	167.7	311.8	0.83	149.3	348.3	0.79	115.6	416.8
4.0	0.94	257.6	312.6	0.87	192.8	351.1	0.83	157.0	416.8
6.0	0.95	348.6	330.8	0.92	271.2	345.4	0.89	281.3	414.0
8.0	0.96	371.4	334.3	0.94	277.6	346.4	0.92	331.0	414.0

343 °K the value of  $k(\lambda)_{\max}$  is 92% of that of pure aqueous solution the value of  $I_{\text{rel}}$  is only 27%. This accounts for the high local temperature exceeding the experimental temperature by 107 degrees.

The appearance of minimum of  $T^*$  at detergent concentration near to the c. m. c. can be explained by the appearance of an optimum of the ratio of the emitted and the absorbed energies at this detergent concentration. Thus, only a small amount of the exciting energy remains in the system, consequently, the local temperature is low. At detergent concentrations above the c. m. c. the increase in  $I_{\text{rel}}$  is slightly greater than that in  $k(\lambda)_{\max}$ , therefore the local temperature is fairly constant, or shows a slow increase.

According to earlier publications [20—22] the decrease of fluorescence yield results in an increase in the local temperature. Similar results were found earlier for dye-detergent systems, too [9]. The differences between the local and the experimental temperatures,  $\Delta T (\equiv T^* - T)$ , for Rhod 6G, Th and MB solutions are given in Table IV. for different detergent concentrations at 343 °K. It can be seen that  $\Delta T$  is the lowest for Rhod 6G and the highest for MB. This is in correlation with the fluorescence yield being 1; 0,3 and 0,15 for aqueous solutions of Rhod 6G, Th and MB, respectively [17, 19]. These values differ somewhat for higher temperatures but the difference can be neglected. The changes in the fluorescence yield due to changes in detergent concentration were nearly identical for the three dyes considered, thus the connection between the local temperature and the fluorescence yield is about the same for higher temperatures, as illustrated by the data of Table IV.

Table IV

The differences between the local and the experimental temperatures,  $\Delta T (\equiv T^* - T)$ , for Rhod 6G, Th and MB solutions at different detergent concentrations and at  $T = 343$  °K.

$C_{\text{SLS}} \cdot 10^3$ (M/l)	$\Delta T$ (°K)		
	Rhod 6G	Th	MB
0	22,5	31.3	85.2
2.0	182.3	73.8	106.8
2.5	52.6	50.2	88.1
3.0	20.4	35.9	79.4
3.5	10.2	31.3	73.8
4.0	12.2	35.9	73.8
6.0	8.2	52.2	71.0
8.0	0.05	52.7	71.0

The results presented prove that the Stepanov-relation is fulfilled for dye-detergent solutions; the local temperature  $T^*$  is higher than the experimental temperature for all systems examined. The dependence of  $T^*$  on the concentration of detergent and on the experimental temperature is in close correlation with the changes in absorption and fluorescence. A similar close connection between the fluorescence yield and the local temperature of the excited molecules exists in detergent solutions, too.

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#### ВЛИЯНИЕ ТЕМПЕРАТУРЫ НА ЭФФЕКТИВНУЮ ТЕМПЕРАТУРУ ВОЗБУЖДЕННЫХ МОЛЕКУЛ КРАСИТЕЛЕЙ В РАСТВОРАХ ДЕТЕРГЕНТА

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В настоящей работе исследовалось влияние температуры и концентрации детергента на эффективную температуру возбужденных флуоресцирующих молекул. Установили, что эффективная температура во всех исследованных случаях имеет минимальное значение при критической концентрации мицеллообразования детергента. Это явление хорошо объясняется абсорбционными и люминесцентными свойствами краситель-детергент систем. Удалось установить связь между эффективной температурой возбужденных молекул и выходом люминесценции красителей.