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CONCENTRATIONAL QUENCHING OF ANTI-STOKES FLUORESCENCE IN THE SOLUTIONS OF RHODAMIN 6G*, **

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An investigation of photoluminescence concentrational quenching and the association of rhodamin 6G in glycerin-water solutions for the anti-Stokes (aS) and Stokes (S) excitation has been carried out at several temperatures. It has been found that the differences between the values of the relative quantum yields, which appear to be quite noticeable for aS- and S-excitation at 285 K (at high concentrations), decrease remarkably at higher temperatures. A discussion of the obtained results is presented.

1. *Introduction*

Recently, we have found, for rhodamin solutions, that the observed changes in relative quantum yield of photoluminescence (PL) at high concentrations are smaller for anti-Stokes excitation (aS) than in the case of excitation in the Stokes region (S) [1, 2]. This effect has been explained by a drop in the absolute PL yield in the aS-region.

In this investigation we present the experimental results concerning the concentrational changes in the relative PL quantum yield of rhodamin 6G in glycerin-water solutions (R 6G–GW), obtained at different temperatures for excitation in the S- and aS-regions.

2. *Experimental*

Glycerin-water solutions of rhodamin 6G ($C_{26}H_{27}O_3Na_2Cl$, MW. 450.98) in the concentration range from 4×10^{-6} M/1 to 2.5×10^{-2} M/1 have been investigated. Rhodamin 6G made by BDH was purified by manifold crystallisation from ethyl alcohol and evaporation in vacuum and the analytically pure glycerin produced by Polish "Strem" was used without any additional purification.

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The absorption spectra $\varepsilon(\lambda)$ were measured on the VSU2-P spectrophotometer under conditions described previously [2, 3]. The values of the dimerization constant K as well as the absorption spectra of dimers $\varepsilon''(\lambda)$ and monomers $\varepsilon'(\lambda)$ were found from Förster and Levshin's method [4, 5]. The procedure for finding K, $\varepsilon''(\lambda)$ and $\varepsilon'(\lambda)$ by the least squares method has been described in Ref. [3].

Measurements of the fluorescence spectra $F(\lambda)$ and relative PL quantum yield η/η_0 were carried out for frontal excitation of the samples. The applied methods and devices were the same as in Ref. [2]. Similarly as in [2], the results of η/η_0 measurements were corrected for secondary fluorescence, emission anisotropy and inactive absorption. The emission anisotropy r/r_0 was measured by the compensation photoelectric method on the device described in [6] and the influence of the secondary fluorescence on r/r_0 was taken into account as in [7]. The investigations of concentrational changes of the absorption spectra as well as the quantum yield and emission anisotropy were carried out for several different temperatures in the range from 283 K to 353 K.

3. *Results and discussion*

The relative PL quantum yield of the R 6G–GW system was measured at Stokes excitation ($\lambda_S = 530$ nm) and anti-Stokes excitation ($\lambda_{aS} = 580$ nm). With regard to the fact that in the aS-region the coefficient of dimer absorption ε'' can remarkably surpass the coefficient of monomer absorption ε' (comp. Fig. 3 and 4), particular attention was paid to the precise finding of pure spectra $\varepsilon''(\lambda)$ and $\varepsilon'(\lambda)$. These spectra were found on the grounds of measurements of the concentrational changes in the absorption spectra of the investigated system, carried out at several temperatures in the range 283 K — 323 K. In Fig. 1 the electronic absorption spectra of R 6G–GW measured at temperatures 283 K

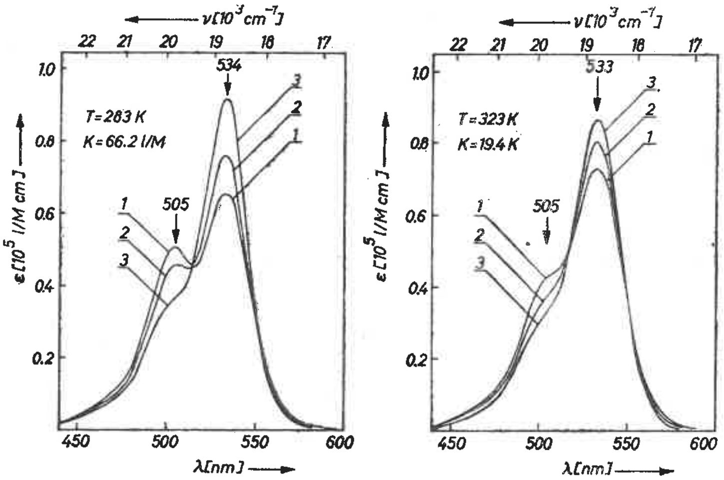

Fig. 1. The absorption spectra of glycerin-water solutions of rhodamin 6G for different dye concentrations and two temperatures, concentrations in M/l; *1* — 2.5×10^{-2}, *2* — 10^{-2}, *3* — 1.58×10^{-3}

and 323 K are presented. The typical regularity characteristic for a monomer-dimer system can be seen. It is manifested by the presence of isosbestic points and the decrease of the short-wave maximum at $\lambda = 505$ nm and the increase of the long-wave maximum at $\lambda = 535$ nm with the decreasing concentration and the rising temperature of the solution. A similar regularity in the range of high concentrations was found for intermediate temperatures which is illustrated by plots of the short- and long-wave (ε_{505} and ε_{535}) maxima versus concentration, shown in Fig. 2. The concentrational changes of the absorption spectra in the temperature range 283 K — 323 K were so large that it allowed the precise finding of the pure spectra of the monomer and the dimer. In Fig. 3 the obtained results are presented for several temperatures. As it is seen, the absorption spectrum of monomers ε' depends on the temperature T at which with increasing T ε' decreases for $\nu > \nu_{0-0}$ and ε' increases for $\nu < \nu_{0-0}$, similarly as for the solutions of rhodamin B [8].

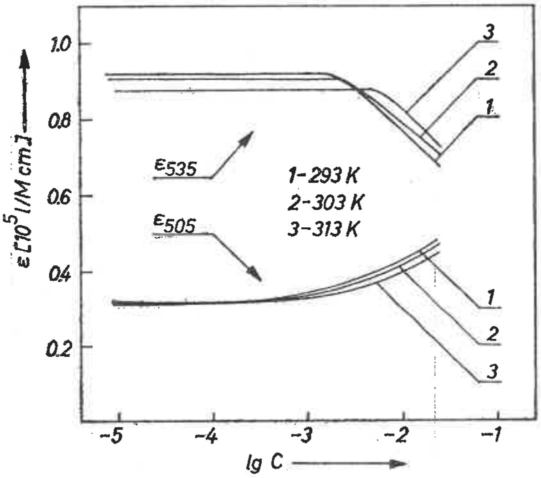

Fig. 2. Peak values (505 nm) and (535 nm) of the absorption band of the R 6G–GW solutions versus the dye concentration for different temperatures

The absorption spectrum of dimers ε'' is also dependent on temperature. This circumstance was taken into account in the calculation of the inactive absorption by dimers at different temperatures. The calculations were carried out on the basis of the relation:

$$\frac{\eta}{\eta_0} = \left(\frac{\eta}{\eta_0}\right)' \left[1 + \frac{1-x}{2x}\left(\frac{\varepsilon''}{\varepsilon'}\right)_{\lambda_{ex}}\right], \tag{1}$$

where $(\eta/\eta_0)'$ is relative PL quantum yield not corrected for inactive absorption, x — part of the total molecule number of rhodamin 6G in the form of monomers. Because at aS-excitation the correction factor in brackets strongly depends on the ratio $(\varepsilon''/\varepsilon')_{\lambda_{ex}}$, the long-wave tail of the absorption spectrum was measured in properly thick layers of the solution, in order to obtain a greater accuracy. Fig. 4 shows the obtained results for two different temperatures. Apart from the absorption spectra $\varepsilon(\lambda)$ corresponding to different solution concentrations (thin lines) the figure also shows the spectra $\varepsilon''(\lambda)$ and $\varepsilon'(\lambda)$ (solid

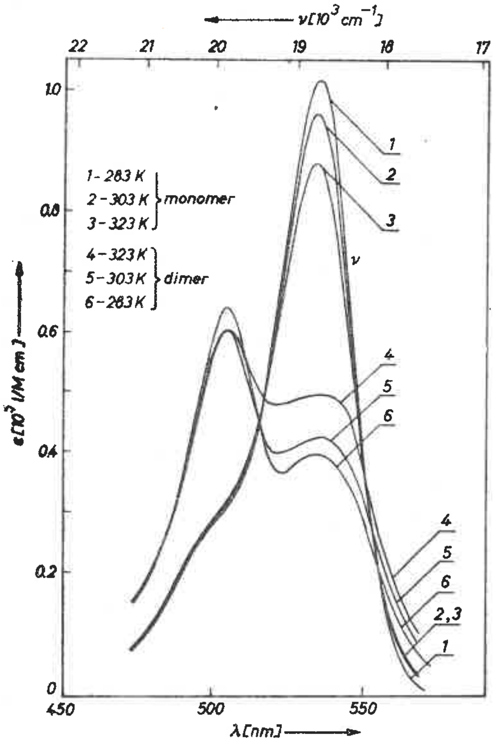

Fig. 3. Pure dimer and monomer absorption spectra of rhodamin 6G for several temperatures: $\nu_{0-0} = 18320\ \mathrm{cm}^{-1}$

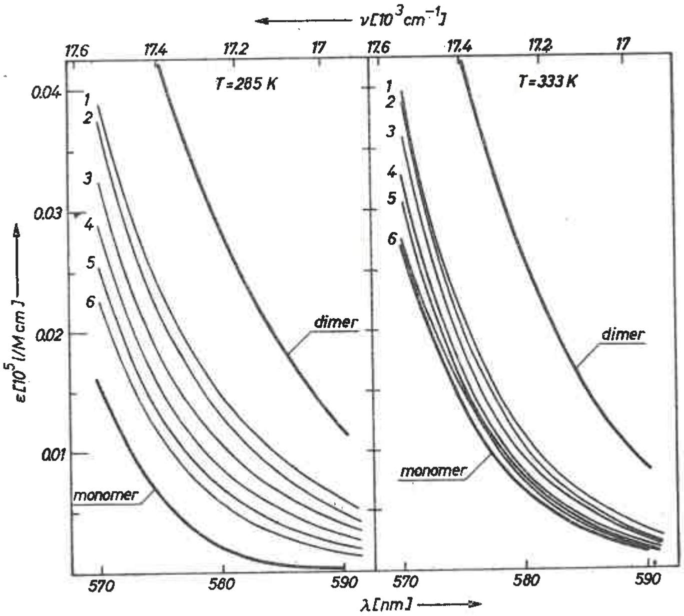

Fig. 4. The long-wave tail of the absorption spectrum of rhodamin 6G for different concentrations in M/l; *1* — 1.58×10^{-2}, *2* — 10^{-2}, *3* — 6.3×10^{-3}, *4* — 4×10^{-3}, *5* — 2.5×10^{-3}, *6* — 1.58×10^{-3}

lines). It can be seen that the increase in temperature causes a pronounced decrease in the ratio $\varepsilon''/\varepsilon'$. The concentrational changes in the absorption spectra at temperatures higher than 323 K turned out to be too small for a more precise calculation of the spectra ε'' and ε' as well as of the dimerization constant K. On account of this, the values of the constant K for higher temperatures were found from the relation:

$$K = A \exp(Q/RT), \tag{2}$$

where Q is the binding energy of the dimer, R — the gas constant. Such a procedure was justified because the values of K found at lower temperatures fitted the straight line very well in the coordinate system ($\ln K$, $1/T$). The quantity Q was found from the slope of the straight line to be 5.4 Kcal/M. It is nearly twice as small as the value of Q found for rhodamin 6G in water [3, 9]. Values of K as well as of $\varepsilon''/\varepsilon'$ for each particular temperature are listed in Table I.

TABLE I

Data characterizing rhodamin 6G in glycerin-water solutions

Solvent	T [K]	Viscosity [P]	K [l/M]	ν_S [cm^{-1}]	ν_{aS} [cm^{-1}]	$\left(\frac{\varepsilon''}{\varepsilon'}\right)_{\nu_S}$	$\left(\frac{\varepsilon''}{\varepsilon'}\right)_{\nu_{aS}}$
Glycerin +15.8% water +0.14% 10 n HCl	283	2.50	66.2	18868	17241	0.822	29.8
	293	1.05	45.4			0.824	20.2
	323	0.22	19.4			1.139	9.7
	333	0.15	15.4			1.220	8.0

Fig. 5 shows the concentrational changes of the PL quantum yield of the R 6G–GW system at S- and aS-excitation, obtained for several temperatures. The values of η/η_0 were obtained after all the corrections mentioned in Chapter 2 were performed. The inactive absorption was calculated on the basis of (1), after taking into account the values of $\varepsilon''/\varepsilon'$ and $K = (1-x)/2x^2C$ from Table I for each particular temperature. From the figure it is seen that the differences in the values of η/η_0, which are quite pronounced (at high concentrations) for the S- and aS-excitations at 285 K, remarkably decrease with increasing temperature and thus with the decreasing value of the dimerization constant.

In order to explain the regularities in the courses of η/η_0 presented in Fig. 5, we assume that the smaller value of the rate constant for the non-radiative excitation energy transfer at aS-excitation in comparison with S-excitation (Weber's red edge effect) takes place only in the first step i. e. in the process

$$D_0^* + D_1 \xrightarrow{k_{D_0D_1}} D_0 + D_1^*, \tag{3}$$

where D_0 is the molecule primarily excited by light absorption and D_1 is the active molecule from its nearest neighbourhood. So we accept that

$$k^{aS}_{D_0D_1} < k^{S}_{D_0D_1}. \tag{4}$$

The process of non-radiative electronic excitation energy transfer from monomer to dimer is a multi-step process, particularly in weakly dimerizing systems [10, 11]. In such systems molecule D_1 is usually a monomer molecule. The results presented in Fig. 5 shows that the difference in the η/η_0 courses at S- and aS-excitation is then very slight. It can be explained as follows: if the energy transfer according to scheme (3) has already taken place then the further course of the excitation energy transport from molecule D_1^* to the dimer is independent of the fact whether the molecule D_0 has been excited in the aS-region or by the frequency $\nu_S \approx \nu_{0-0}$. However, at the aS-excitation energy transfer to molecule D_1, which is a monomer, is less probable than for the S-excitation according to assumption (3) as well as by the familiar experimental fact that the PL concentrational depolarization weakens at the aS-excitation [12–15].

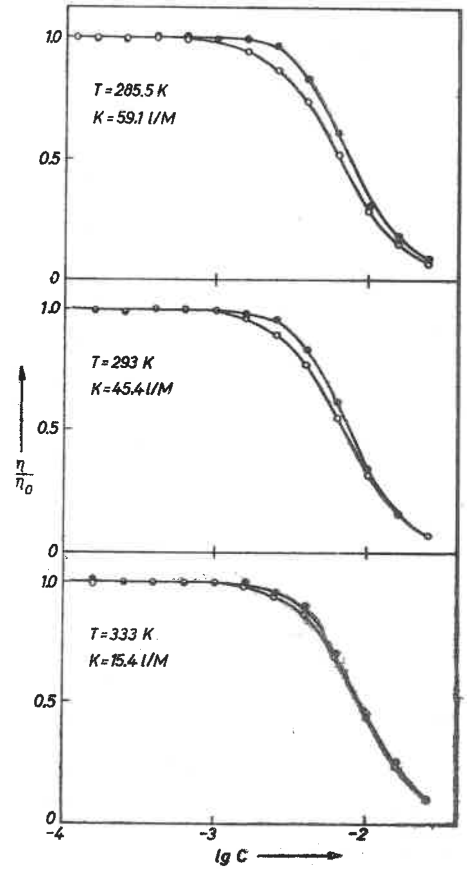

Fig. 5. Concentrational changes in the PL relative quantum yield of the R 6G–GW system at different temperatures: ○, ● — experimental points at Stokes- and anti-Stokes excitation, respectively

For the system investigated here this situation is illustrated in Fig. 6 in which the emission anisotropy[1] r/r_0 versus the concentration of rhodamin 6G in the solution is presented. As can be seen for high concentrations the differences between r/r_0 at S- and aS-excitation are pronounced. The noticeable reduction in the drop of r/r_0 at the aS-excitation indicates a greater participation of the fluorescence of molecules D_0 in the observed luminescence. It is well known that mainly D_0 molecules contribute to the degree of polarization of the observed luminescence [17–19].

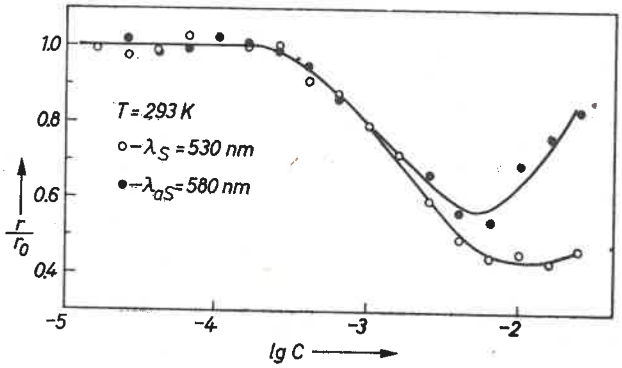

Fig. 6. PL emission anisotropy of the R 6G–GW system versus dye concentration: ○, ● — experimental points at S- and aS-excitation, respectively

From what has been said above it can be concluded that a certain difference in the courses of η/η_0 at the S- and aS-excitations should be observed even for systems of very small dimerization constants.

The pronounced effect at the aS-excitation in the case of concentrational depolarization and relatively small effect in the case of fluorescence quenching results from the fact that polarization quenching already occured after the first act of transfer, and fluorescence quenching — after reaching the non-luminescent dimers by the excitation energy. An effect equal in strength to concentrational depolarization could occur in the case of PL concentrational quenching if the nearest neighbours of molecules D_0 were dimers.

For these reasons the great differences in the courses of η/η_0 at S- and aS-excitation should be expected for strongly dimerizing systems. To a certain degree this is indicated by the results from Fig. 5 for the lowest temperature and also by the results of PL concentrational quenching measurements of rhodamin B in water at aS-excitation [1].

On the basis of that we think that inequality (4) is satisfied also in the case when the nearest nieghbours of D_0 molecules are dimers $(D_1 \equiv D_{\|})$.

It is apparently worthwhile to carry out further investigations of PL concentrational quenching for aS-excitation in strongly dimerizing systems and for greater differences in frequencies $\nu_{0-0} - \nu_{ex}$ than in the present work.

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[1] According to Jabłoński [16] the emission anisotropy r is related to the degree of polarization P as follows from $r = 2P/(3-P)$.

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