Effect of Acceptor Concentration upon Donor Fluorescence Decay and Quantum Yield*

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The fluorescence decay times (τ/τ_0) and quantum yields (η/η_0) of rhodamine 6G (donor) in their dependence on the concentration of malachite green (acceptor) in ethanol were measured for the donor to acceptor concentration ratios γ_D/γ_A 3.48 and 0.35. At fixed γ_A, the values of τ/τ_0 and η/η_0 are markedly lower for the systems with higher γ_D/γ_A. The experimental results are compared with the theory of a multistep excitation energy transfer from donor to acceptor. Good agreement between theory and experiment was found for the critical distances $R_{OD} = 60.7$ Å and $R_{OA} = 53.8$ Å calculated from spectroscopic data. In the case of $\gamma_D/\gamma_A = 0.35$, the experimental results can also be properly described using the Förster-Galanin theory, whereas for the system with $\gamma_D/\gamma_A = 3.48$ the multistep energy transfer plays a significant role.

1. Introduction

The concentration effects in luminescent systems consisting of the donor (D) and acceptor (A) molecules, randomly distributed in space, afford valuable information on the nonradiative electronic excitation energy transfer (NEEET) from D* to A [1, 2]. In particular, this concerns the dependence of the donor photo-luminescence (PL) decay times τ on the concentration C_A of the acceptor molecules. For a proper interpretation of the experimental results, it is indispensable to know the relation between τ and C_A. If the reduced acceptor concentration exceeds considerably that of the donor, i.e., when

$$\gamma_A \gg \gamma_D\,, \tag{1}$$

and if NEEET occurs as the result of the dipole-dipole interaction, this relation is given by [3]

$$\frac{\tau_0}{\tau} = \frac{1 + \gamma_A^2 - (1.5 + \gamma_A^2)\, f(\gamma_A)}{1 - f(\gamma_A)}\,, \tag{2}$$

where

$$f(\gamma_A) = 2\,\gamma_A \exp(\gamma_A^2)\,\mathrm{erfc}(\gamma_A)\,, \quad \gamma_A = \frac{\sqrt{\pi}}{2}\,\frac{C_A}{C_{0A}}\,. \tag{3}$$

τ_0 is the PL decay time for $C_A \to 0$, C_{0A} the critical concentration and $\mathrm{erfc}(\gamma_A)$ the complementary error function. In (2) the NEEET occurring in one step only from D* to A is taken into account. However, if

$$\gamma_D \gg \gamma_A\,, \tag{4}$$

then NEEET can occur by successive single – step process in the same manner as the concentration quenching by nonluminescent dimers [1, 4]. For a multistep NEEET process, the following equation for the PL decay time has been obtained recently [5]:

$$\frac{\tau}{\tau_0} = \frac{1 + \gamma^2 - (1.5 + \gamma^2)\, f(\gamma) + \alpha_0\, \alpha\, f(\gamma)\,[f(\gamma) + \gamma^2 - 0.5] - \alpha_0\, \alpha\, \gamma^2}{[1 - f(\gamma)]\,[1 - \alpha_0\, \alpha f(\gamma)]}\,, \tag{5}$$

where

$$\gamma = \gamma_D + \gamma_A = \frac{\sqrt{\pi}}{2}\left(\frac{C_D}{C_{0D}} + \frac{C_A}{C_{0A}}\right), \quad \alpha = \frac{\gamma_D}{\gamma}\,. \tag{6}$$

α_0 is the probability that no degradation of the excitation energy occurs during the transfer between the donor molecules, and $f(\gamma)$ has the same meaning as in (2).

For $\gamma_D \ll \gamma_A$, $\alpha \to 0$ and expression (5) becomes (2), whereas for $\gamma_D \gg \gamma_A (\alpha \to 1)$ the values of τ/τ_0 calculated from (5) and (2) differ considerably.

The present paper aims at the experimental verification of expression (5) [6].

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Donor fluorescence decay times τ/τ_0 and quantum yields η/η_0 versus the acceptor concentration are given for C_D/C_A ratios equal to 5 and 0.5.

2. Experimental

Two series of alcohol solutions of rhodamine 6G (donor) and malachite green (acceptor) were prepared with values of C_D/C_A equal to 5 (system I) and 0.5 (system II). 99.8% ethyl alcohol, with 6% CH_3COOH added, was used as a solvent without further purification. Rhodamine 6G ($C_{26}H_{27}O_3N_2Cl$, m.w. = 450.98) and malachite green ($C_{25}H_{26}N_2O_4$, m.w. = 418.53) were purified by repeated crystallization from ethyl alcohol under vacuum. The mean fluorescence decay times were measured on a phase fluorometer described elsewhere [8]. For the frontal excitation we used the wavelength 510 ± 8 nm. In view of the very low absolute yield of malachite green in liquid solutions ($\eta_0 \approx 10^{-4}$) [9] one needs an 0G-5 cutoff filter ($\lambda > 548$ nm) only for the observation of the rhodamin 6G-fluorescence. The quantum yield, η/η_0, was measured in the spectral range of (560 ± 3) nm using a method proposed by Förster [10], on a device described previously [11]. Fluorescence spectra were corrected for the spectral sensitivity of photomultiplier and reabsorption according to [12].

Reabsorption and secondary fluorescence have to be taken into account.

True values for τ were calculated from the relation [13]

$$\tau = \tau'(1 - \varkappa), \qquad (7)$$

where τ' is the measured PL decay time, $\varkappa$ the ratio of the primary to the secondary fluorescence. Values of $\varkappa$ for individual concentrations were computed on an Odra 1204 digital computer, basing on the theory presented in references [14, 15]. The computations for η and τ were carried out separately due to different observation conditions. A VSU2-P spectrophotometer was used to measure the absorption spectra. All measurements were carried out at 293 K.

3. Experimental Results and Discussion

Some data concerning the absorption (ε_D) and fluorescence (f_D) spectra of rhodamine 6G (donor) and the absorption spectrum (ε_A) of malachite green (acceptor) in ethanol are given in Table 1. In the concentration range of $C_D < 10^{-2}$ M/l and $C_A < 10^{-2}$ M/l, the ε_D and ε_A spectra remained unchanged, the spectra of mixed solutions of rhodamine and malachite green were found to be additive. Thus we assume that the substances occur as monomers and do not form complexes. Considerable spectral overlaps of f_D with ε_A and f_D with ε_D (high values of overlap integrals – compare Table 1) facilitate the NEEET both from D* to A and from D* to D.

Table 2 summarizes the measured τ' values, true τ values determined from (7), as well as the values of the correction factor $\varkappa$. For both systems the changes in τ' and τ have similar character, i. e. the τ' values increase at first and then decrease with increasing C_A. The values of τ, however, remain constant over a certain range of concentrations and then rapidly drop.

Absolute PL yields $\eta(c) = \eta_0 \cdot \eta(c)/\eta_0$ of rhodamine 6G- necessary to calculate $\varkappa$, were obtained by the measurements of relative PL yield, $\eta(c)/\eta_0$

Table 1. Data characterizing the photoluminescence of ethanolic solutions of rhodamine 6G and malachite green.

n	η'	λ[nm]			ε^D_{max}	ε^A_{max}	η_0	τ
—	poise	ε_D^{max}	ε_A^{max}	f_D^{max}	$10^5 \cdot$ l/M · cm		—	[ns]
1.36	0.01	530	622	555	1.05	0.93	0.9	4.3

I_{DD}	I_{DA}	C_{OD}	C_{OA}	R_{OD}	R_{OA}	α_0	$\langle \chi^2 \rangle$	$\langle r^2 \rangle^{1/2}$ [a]
$10^{-13} \cdot$ lcm³/M		10^{-3} M/l		[Å]		—	—	[Å]
1.63	3.25	2.54	1.77	53.8	60.7	0.995	0.667	22.4

[a] mean diffusion length from Ref. [20].

Table 2. Values of the measured fluorescence decay times (τ') and those corrected for secondary effects (τ), and the values of the factor $\varkappa$ for individual acceptor concentrations.

$C_D/C_A = 5$				$C_D/C_A = 0.5$			
1 C_A [M/l]	2 τ' [ns]	3 $\varkappa$ —	4 τ [ns]	5 C_A [M/l]	6 τ' [ns]	7 $\varkappa$ —	8 τ [ns]
$2 \cdot 10^{-6}$	4.2 ± 0.1	0.026	4.10 ± 0.10	$2 \cdot 10^{-5}$	4.2 ± 0.1	0.025	4.10 ± 0.1
3.6	4.4 ± 0.2	0.043	4.20 ± 0.20	4	4.4 ± 0.1	0.045	4.20 ± 0.1
6.4	4.7 ± 0.1	0.069	4.35 ± 0.10	$1 \cdot 10^{-4}$	4.4 ± 0.1	0.079	4.05 ± 0.15
$1.1 \cdot 10^{-5}$	5.0 ± 0.1	0.114	4.45 ± 0.15	2	4.3 ± 0.1	0.098	3.90 ± 0.15
2.0	5.2 ± 0.1	0.145	4.45 ± 0.15	4	4.0 ± 0.1	0.100	3.60 ± 0.15
3.6	5.4 ± 0.1	0.198	4.35 ± 0.15	6.4	3.3 ± 0.2	0.097	3.00 ± 0.20
6.4	5.8 ± 0.1	0.236	4.45 ± 0.25	$1 \cdot 10^{-3}$	2.9 ± 0.1	0.071	2.20 ± 0.10
$1.1 \cdot 10^{-4}$	5.8 ± 0.1	0.254	4.30 ± 0.25	2	1.7 ± 0.2	0.041	1.65 ± 0.20
2	5.2 ± 0.2	0.248	3.90 ± 0.35	4	0.7 ± 0.1	0.014	0.70 ± 0.10
3.6	4.2 ± 0.1	0.192	3.40 ± 0.20				
6.4	3.2 ± 0.1	0.145	2.75 ± 0.15				
$1.1 \cdot 10^{-3}$	1.8 ± 0.2	0.086	1.65 ± 0.20				
2.0	1.0 ± 0.2	0.038	0.95 ± 0.20				

(Fig. 1), and of $\eta_{0D} = \eta_0$ measured in the absence of transfer (at infinite dilution), taken from [12]. At concentrations smaller than $6 \cdot 10^{-3}$ M/l, the PL quantum yield is constant, as shown by the figure. Therefore it can be assumed that in this concentration range, quenching of PL does not occur in the donor.

For a comparison of the experimental results with expression (5), one should determine critical concentrations C_{0D} and C_{0A} and the parameter α_0. For the latter, a value of 0.995 was used as obtained in [12] as a mean value of the quantum yield in the overlap area of the ε_D and f_D spectra of rhodamine 6G in ethanol. Critical concentrations were calculated from [16]

$$C_{0A} = 4.23 \cdot 10^{-10} n^2 / (\eta \langle \chi^2 \rangle I_{DA})^{1/2} \, M/l \,, \quad (8)$$

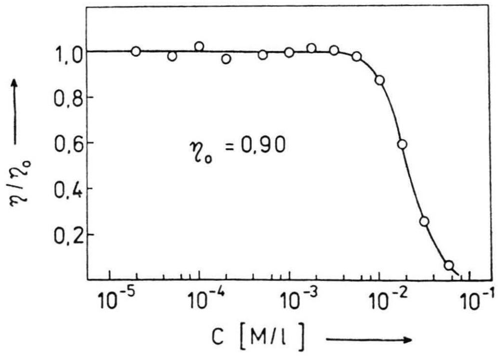

Fig. 1. Relative PL quantum yield of rhodamine 6G in ethanol vs. concentration.

where n is the refractive index of the environment and I_{DA} is the spectral overlap given by

$$I_{DA} = \int_0^\infty f_D(\tilde{\nu}) \, \varepsilon_A(\tilde{\nu}) \, d\tilde{\nu} / \tilde{\nu}^4 \,. \quad (9)$$

$f_D(\tilde{\nu})$ is the normalized donor fluorescence intensity at wavenumber $\tilde{\nu}$, and $\varepsilon_A(\tilde{\nu})$ is the acceptor molar decadic extinction coefficient at $\tilde{\nu}$. $\langle \chi^2 \rangle$ in (8) represents an orientation factor of the transition dipole moments of the interacting D* and A molecules. Calculating the critical concentrations C_{0D} and C_{0A} we assumed $\langle \chi \rangle \equiv 2/3$ in the whole concentration range. Values of C_{0D} and C_{0A}, and of the corresponding critical distances R_{0D} and R_{0A} are given in Table 1. As known [16], $\langle \chi^2 \rangle_d = 2/3$ corresponds to the case of sufficiently fast Brownian rotational motions of the molecules, i. e. when the rotation time $\tau_r \ll \tau_l$, where

$$\tau_l = [\sum_D k_{D^*D} + \sum_A k_{D^*A} + k_F + k_q]^{-1}$$

is the localization time of the excitation energy. For a statistical distribution of immobile rigid molecular dipoles, however, a value of $\langle |\chi| \rangle_s^2$ equal to 0.476 [17, 18] is valid. Since the localization time τ_l depends on the concentration of the D and A molecules, $\langle \chi \rangle^2$ should depend upon concentration also. Thus, the assumption of $\langle ^2\chi = 2/3$ and for liquid systems (when $\sim \tau_r \ll \tau_l$) is approximate only.

Let us consider the effect of this simplification upon the values of γ_D and γ_A. For any concentration $\langle \chi^2 \rangle$ can be calculated from the relation [19]

$$\langle \chi^2(\gamma) \rangle = \langle \chi^2 \rangle_{\mathrm{d}} \frac{F(\gamma)}{F(\gamma)+a} + \langle | \chi | \rangle_{\mathrm{s}}^2 \frac{a}{F(\gamma)+a}, \tag{10}$$

where $a = \tau_{\mathrm{r}}/\tau_1$, $F(\gamma)$ the same as in (2), with γ being the argument instead of γ_{A}. Function $F(\gamma)$ was obtained using an approximate formula for $\tau(\gamma)/\tau_0$ (expression (15) in [19]). If one assumes (5) to be an accurate expression for $\tau(\gamma)/\tau_0$, one obtains

$$\langle \chi^2(\gamma) \rangle = \langle \chi^2 \rangle_{\mathrm{d}} \frac{\Phi(\gamma)}{\Phi(\gamma)+a} + \langle | \chi | \rangle_{\mathrm{s}}^2 \frac{a}{\Phi(\gamma)+a}, \tag{11}$$

where

$$\Phi(\gamma) = \frac{1+\gamma^2-(1.5+\gamma^2)f(\gamma)+\alpha_0\,\alpha[f(\gamma)+\gamma^2-\tfrac{1}{2}]-\alpha_0\,\alpha f(\gamma)}{1-f(\gamma)}. \tag{12}$$

Assuming $a = 0.076$ for rhodamine 6G in ethanol ($\tau_{\mathrm{r}} = 320$ ps and $\tau_0 = 4200$ ps from Ref. [20]), we calculated $\langle \chi^2 \rangle$ as a function of γ. The results are shown in Figure 2. Solid curves were obtained from (11) for $\alpha = \gamma_{\mathrm{D}}/\gamma = 0.26$ (curve 2), and $\alpha = 0.75$ (curve 1), dottet curve – from (10). Differences in $\langle \chi^2 \rangle$ calculated from (0) and (11) are small and are completely eliminated for $\alpha \to 0$ (compare (2) and (12)). Given the values of $\langle \chi^2(\gamma) \rangle$ and assuming

$$\langle \chi^2_{\mathrm{DD}}(\gamma) \rangle \approx \langle \chi^2_{\mathrm{DA}}(\gamma) \rangle = \langle \chi^2(\gamma) \rangle,$$

one can calculate the corrected concentrations γ'_{A} (compare (6) and (8)) from

$$\gamma'_{\mathrm{A}} = \gamma_{\mathrm{A}} \langle \chi^2(\gamma) \rangle^{1/2} / (2/3)^{1/2}. \tag{13}$$

Figure 3 gives the comparison between the true decay times τ, summarized in columns 4 and 8 of Table 2, and those obtained from (5). Empty circles and triangles correspond to γ_{A} calculated for $\langle \chi^2 \rangle = 2/3$, black circles and triangles to those obtained from (13). As is seen from the figure, the differences $\gamma_{\mathrm{A}} - \gamma'_{\mathrm{A}}$ are small. Nevertheless, for the highest concentration in the case of system II, γ_{A} exceeds γ'_{A} already by about 10%. A more significant effect may be expected for higher reduced concentrations $\gamma = \gamma_{\mathrm{D}} + \gamma_{\mathrm{A}}$ and for greater α (compare Figure 2). τ_0 was set equal to 4.3 ns, the mean value over several τ in the range of the lowest concentrations. It is very close to a value of 4.2 ns obtained recently by Porter and Tredwell [20].

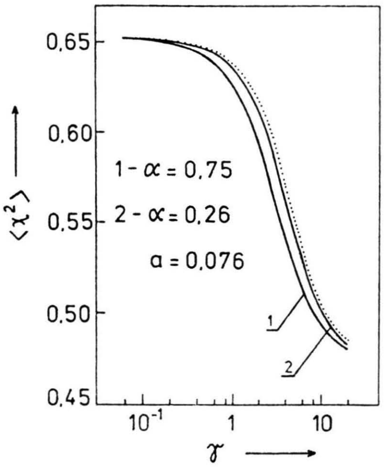

Fig. 2. Orientation factor $\langle \chi^2 \rangle$ versus reduced concentration γ. Solid lines were calculated from (11) and the dotted line from (10).

Theoretical curves 1 and 2 were calculated from (5) for $\gamma_{\mathrm{D}}/\gamma_{\mathrm{A}} = 3.48$ ($C_{\mathrm{D}}/C_{\mathrm{A}} = 5$) and $\gamma_{\mathrm{D}}/\gamma_{\mathrm{A}} = 0.35$ ($C_{\mathrm{D}}/C_{\mathrm{A}} = 0.5$), respectively. We note that at moderate and high γ_{A}, the PL decay times τ/τ_0 are significantly lower in system I. In addition, a good fit of the experimental results to expression (5) can be noted. We would like to emphasize this fact as all quantities needed for the comparison between experiment and theory were determined by independent measurements.

Figures 4 a and 4 b show the quantum yields η/η_0 for systems I ($C_{\mathrm{D}}/C_{\mathrm{A}} = 5$) and II ($C_{\mathrm{D}}/C_{\mathrm{A}} = 0.5$). Black circles denote experimental points, corrected for reabsorption and secondary fluorescence, curve 1 points computed from the relation [21]

$$\frac{\eta}{\eta_0} = \frac{1-f(\gamma)}{1-\alpha_0\,\alpha f(\gamma)} \tag{14}$$

with α_0, α and $f(\gamma)$ as in (5). For $\gamma_{\mathrm{D}} \ll \gamma_{\mathrm{A}}$, $\alpha \to 0$ and expression (14) becomes the well known Förster formula [10]

$$\eta/\eta_0 = 1 - f(\gamma_{\mathrm{A}}). \tag{15}$$

As is seen from the figures, the experimental points fit well the theoretical curves. In the case of system II, also equation (15) describes properly the experimental results (curve 3). With system I, however, the discrepancies are considerable. Similar results were obtained also in the case of other two-

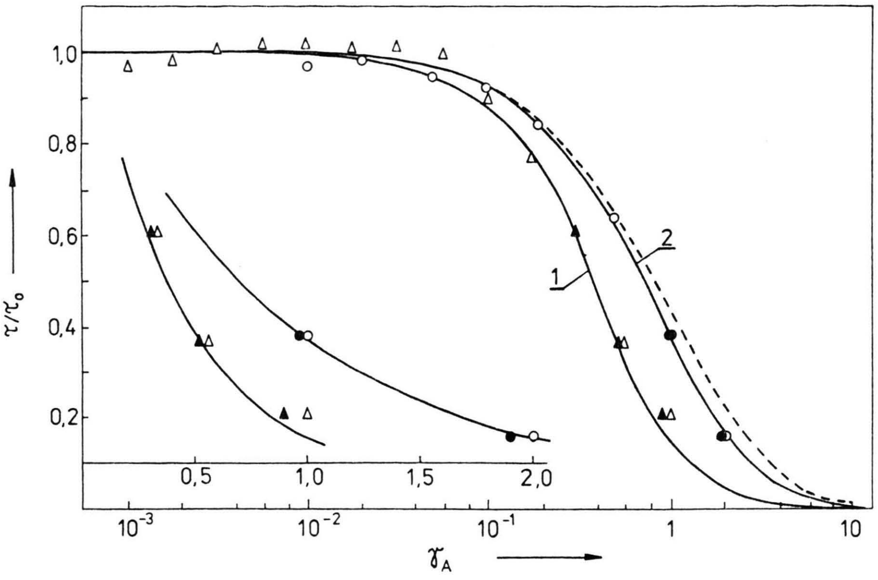

Fig. 3. Fluorescence decay time of rhodamine 6G (donor) vs. reduced concentration of malachite green (acceptor) in ethanol. △, ○ — experimental points for C_D/C_A equal to 5 and 0.5, respectively. Solid lines — calculated from (5), dashed line — from (2).

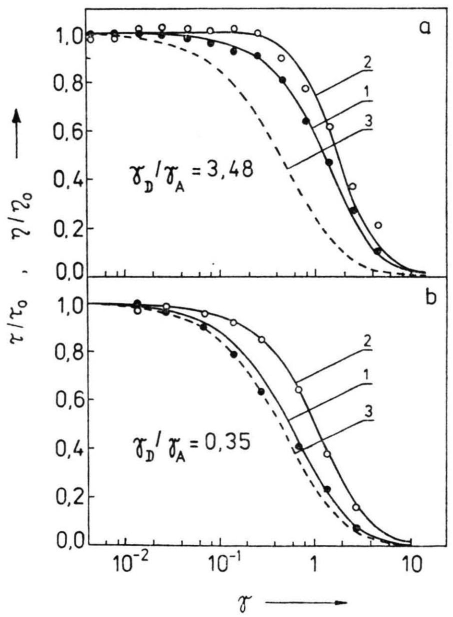

Fig. 4. Decay time τ/τ_0 and quantum yield η/η_0 of rhodamine 6G in ethanol in the presence of malachite green vs. reduced concentration γ. ○, ● — experimental points for τ/τ_0 and η/η_0. 1 and 2 theoretical curves calculated from (14) and (5), respectively, for $\alpha = 0.75$ (a) and $\alpha = 0.26$ (b), and $\alpha_0 = 0.995$. Curve 3, calculated from (15): a — system I, b — systemII.

component systems [22, 23]. For the comparison of η/η_0 and τ/τ_0 in Figs. 4 a and 4 b, we also gave the results concerning the PL decay times τ/τ_0 for these systems versus the reduced concentration $\gamma = \gamma_D + \gamma_A$. A marked deviation from proportionality between the decay time and the PL quantum yield can be noted. According to the theory, this deviation is smaller for system I having the higher γ_D/γ_A.

4. Final Comments

The PL decay times τ/τ_0 of systems with different γ_D/γ_A show that the energy transfer from the donor to the acceptor molecules is more efficient in systems with higher γ_D/γ_A. The same conclusion may be reached from the quantum yields η/η_0.

The experimental results obtained confirm the validity of formulae (5) and (14), and the necessity for the concentration changes in the decay times and quantum yield for multistep NEEET from the donor to the acceptor molecules, to be taken into account. Due to the considerable value of the mean diffusion length (compare $\langle r^2 \rangle^{1/2}$ and R_{0D} in Table 1) one should expect lower values of τ/τ_0 and η/η_0 compared with those predicted by the theory developed for rigid solutions. However, the good agreement of the experimental results with the theory permits to believe that NEEET is not influenced significantly by the material diffusion. Also the measurements of the fluorescence decay curves for rhodamine 6G in the presence of malachite green in ethanol, carried out by Porter and Tredwell [20] have shown that the system investigated may be assigned to the Förster-type kinetic behaviour [24].

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