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THE INFLUENCE OF ASSOCIATION OF RHODAMINE 6G MOLECULES IN SOLUTIONS ON THE CONCENTRATION DEPENDENCE OF THE FLUORESCENCE DECAY TIME*

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Measurements of the photoluminescence (PL) decay time (τ) and the quantum yield (η/η_0) for rhodamine 6G in water (system I), glycerin-water solutions (system II) and pure glycerin (system III) were done at room temperature over a wide range of concentrations. The influence of reabsorption and the secondary fluorescence on the values of τ and η/η_0 measured were especially taken into account. The dimerization constants and critical concentrations for non-radiative electronic excitation energy transfer (NEEET) were determined for each system. It was shown that τ is approximately constant over a wide range of concentrations, but decreases in the region where the fluorescence concentration quenching occurs. It follows from our measurements that the concentration-dependent courses of τ/τ_0 and η/η_0 were practically identical for system III. For the remaining systems they differed more from each other when the dimerization constant characterizing the system under consideration was higher. The results from these experiments were compared to the theory of the concentration dependence of τ/τ_0 and considering the multistep process of NEEET from monomers to dimers. A good agreement with the theory was found for all systems investigated. A discussion of the results is given.

1. *Introduction*

It is known that rhodamine 6G has a strong tendency to associate in water and in some other solvents as well [1–5]. The concentration quenching of photoluminescence (PLCQ) and the concentration depolarization (PL CD) were investigated [1, 5–9]. However, there are relatively few works concerning the concentration-dependent changes of fluorescence decay time for such solutions [10, 11] despite the fact that solutions of rhodamine 6G are widely used as active media of dye lasers. This paper presents results of measure-

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ments of PL decay times for rhodamine 6G in water, glycerin-water and glycerin solutions which were done for a wide range of dye concentrations. Special attention was given to the influence of secondary effects, that is, the reabsorption and secondary fluorescence on the values of τ measured. A comparison of the corrected values of τ with known theoretical formulae concerning these phenomena is given.

2. *Experimental part*

A. Materials

Rhodamine 6G (British Drug Houses LTD) was purified by repeated cristallization from ethyl alcohol and evaporation in a vacuum. Waterless glycerin (Fluka AG) was used without additional purification and the water was distilled three times using a quartz apparatus. Table I summarizes some of the data concerning rhodamine 6G in the solvents investigated.

B. Measurements of photoluminescence decay time

Measurements of mean PL decay time were done using a phase fluorometer built by one of us (J. T. [12]). The design of the fluorometer is similar to that of Bauer et al. [13, 14] with some modifications. For measurements of τ a light modulator made of fused quartz and controlled by a piezoelectric transducer was used. The frequency of the control signal was 5124.5 kHz.

The fluorescence was excited with a wavelength $\lambda = 530$ nm. A 50 W incandescent lamp (TGL 11659) was the light source. The wavelength was selected with monochromator (SPM-2 type). The fluorescence was observed in the region where $\lambda > 548$ nm. A cut-off filter OG-5 was used for this.

The excitation and measurements were carried out on the same side of the sample with the exciting beam directed at an angle of 60° to the direction of observation which was normal to the sample surface.

The influence of reabsorption and secondary fluorescence on the decay time of radiation was undertaken according to Budó and Szalay [15] based on the formula:

$$\tau = \tau'(1-\kappa), \tag{1}$$

where τ is the true PL decay time and τ' is the measured time, κ denotes the secondary-to--primary fluorescence intensity ratio. Factor κ has been calculated from the exact theory given in Refs. [16, 17].

In order to determine κ the quantum yield as well as the absorption and fluorescence spectra should be known. The quantum yield and the fluorescence spectra were measured with an apparatus described elsewhere [18]. However, the absorption spectra were measured with a VSU2-P spectrophotometer. All the measurements were carried out at a fixed temperature of 293 K over a wide range of concentrations. For calculations of κ values an Odra 1204 digital computer was employed.

3. *Results of measurements*

Measurements of the fluorescence decay time τ, as a function of concentration were done out for rhodamine 6G in water (system I), water-glycerin mixtures (system II) and glycerin (system III). The reabsorption and secondary fluorescence were done according to (1) in order to obtain the true[1] values of τ. Factor κ depends on the concentration for fixed excitation and observation wavelengths λ and λ'. For these measurements a large part of the fluorescence band was recorded. The cut-off filter used was OG-5, $\lambda > 548$ nm for $l = 0.4$ cm thickness. Therefore, the mean value of κ resulting from the averaging over the fluorescence band and taking into account the transmissivity for filter OG-5 was employed. Values of $\eta = \eta(c)$ which were necessary for the calculation of κ [16] were determined using the values of $\eta_0 = \eta(0)$ as shown in Table II together with the results of measurements of the concentration dependence of the relative yield η/η_0 (Fig. 3).

TABLE I

Characteristic data of solutions investigated

System	Dye	Solvent	η'	T	K	Concentration range M/l
			P	K	1/M	
1	2	3	4	5	6	7
I-R6G/W	Rhodamine 6G M.W. 450.98	$H_2O+0.1\%$ 10 n HCl	0.01	293	2580	$10^{-5}-5\times10^{-3}$
II-R6G/G-W		Glycerin + 10% $H_2O+0.1\%$ 10 n HCl	1.7	293	19.5	$10^{-5}-2\times10^{-2}$
III-R6G/G		Glycerin + 0.1% 10 n HCl	11.5	293	3.7	$10^{-5}-3.2\times10^{-2}$

Fig. 1 shows the dependence of the fluorescence decay time in the systems studied on concentration. The open and black circles represent values of τ without and with a correction for secondary effects. The corrected values of τ/τ_0 are almost constant within a wide range of concentrations. For system I, the decrease of τ/τ_0 occurs at the lowest concentration (Fig. 1a). For the remaining systems such a decrease occurs at considerably higher concentrations. This drop is due to the concentration quenching of fluorescence. This is evident from measurements of the quantum yield dependence on concentration (Fig. 3).

For each system the mean value of τ for the range of the lowest concentration was taken for τ_0.

Measurements of τ_0 for samples of sufficiently small thickness[2], where secondary effects could be neglected [19], were also done. Slightly lower values of τ_0 were then ob-

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[1] For the measurements a cuvette of considerable thickness ($l = 0.05$ cm) was used.

[2] When $2.3\,\varepsilon_{\max}cl < 0.1$ where $\varepsilon_{\max}$ is the maximum value of the extinction coefficient, c is the concentration, and l is the sample thickness.

TABLE II

Values of parameters characterizing photoluminescence of rhodamine 6G solutions

System	τ_0	η_0	K_γ	$\alpha_0{}^a$	$\alpha_0{}^b$	$\alpha_0{}^c$	$I_{\lambda'}$	$I_{\lambda''}$	c_{OD}	$c_{OD''}$	R_{OD}	$R_{OD''}$	$\sqrt{\langle r^2 \rangle}{}^d$	χ^2
	ns	—	—	—	—	—	10^{-13} lcm^3/M		10^{-3} M/l		Å		Å	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
I-R6G/W	4.4	0.77	10.9	0.8	0.8	0.8	0.96	1.19	3.38	3.05	48.9	50.6	17.3	0.667
II-R6G/G-W	4.25	0.95	0.1	1.0	0.75	1.0	1.54	2.77	3.36	2.53	49.0	53.9	1.3	0.476
III-R6G/G	4.25	0.95	0.02	0.98	0.80	0.98	1.50	2.77	3.49	2.56	48.4	53.9	0.5	0.476

[a] for η/η_0 curves calculated according to (9); [b] and [c] for τ/τ_0 curves calculated according to (2) and (10), respectively; [d] values of $\sqrt{\langle r^2 \rangle}$ calculated for a temperature $T = 293$ K, effective molecule radius $\sigma = 6$ Å and values of viscosity coefficient η' as shown in column 4 of Table I.

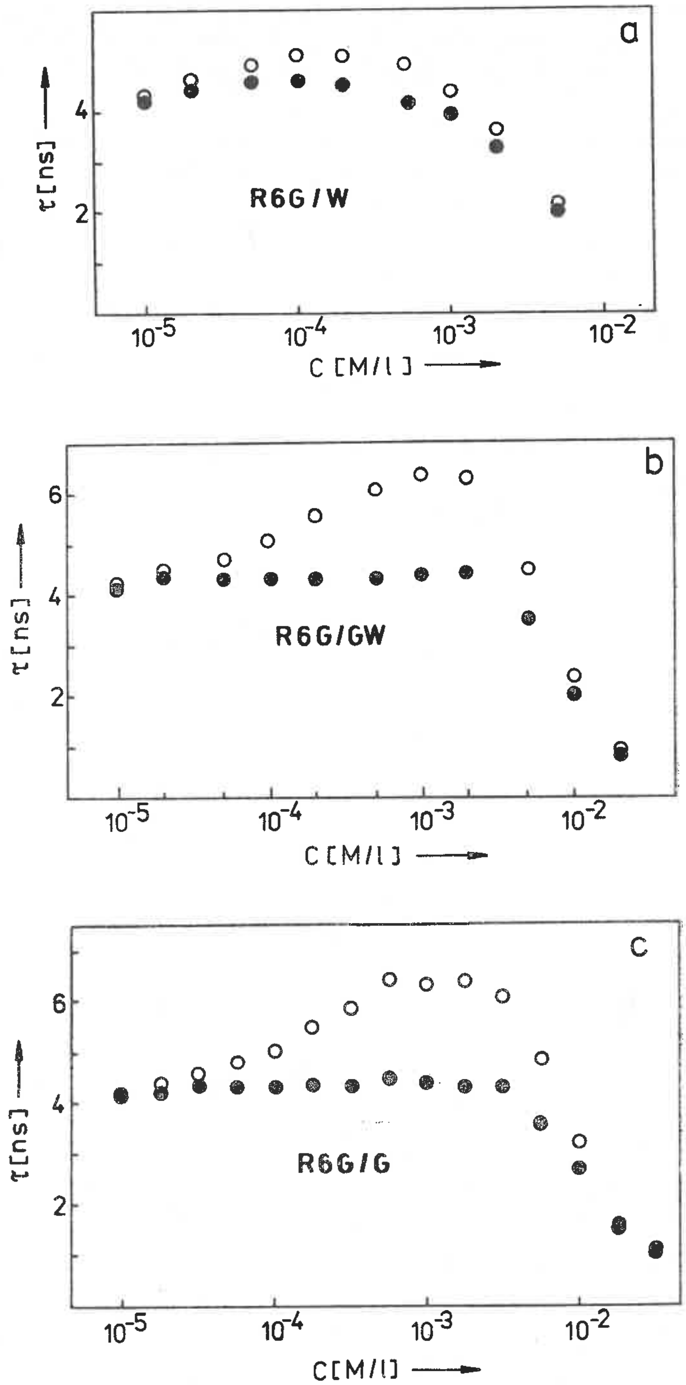


Fig. 1. Photoluminescence decay time for rhodamine 6G in (a) water, (b) glycerin-water solutions, and (c) glycerin, at room temperature; ○ — measured values τ', ● — true values τ, corrected based on (1)

tained. The difference was 0.25 ns for system I and 0.15 ns for systems II and III. The absolute quantum yield for the fluorescence of rhodamine 6G was determined relative to the absolute yield of rhodamine 6G in ethyl alcohol ($\eta_0 = 0.9$ [20]) by comparing areas under the emission spectra.

The values of τ_0 and η_0 obtained are given in Table II. The PL decay time for rhodamine 6G in water was also measured by others [11, 21–23]. A value of τ_0 equal to 4.4 ns was reported in [22] while in papers [11], [21] and [23] values 3.7 ns, 3.8 ns and 5.5 ns were given. The latter values were obtained using laser excitation while the value of $\tau_0 = 4.4$ ns was a result of fluorometric measurements.

4. *Comparison of experimental results with theoretical predictions*

Recently [24] we derived a formula for the fluorescence decay time as dependent on the reduced concentration of active molecules under an assumption that two kinds of molecules, namely donor molecules D and acceptor molecules A, are only present in the solution and that the NEEET process occurs due to dipole-dipole interaction. This formula is:

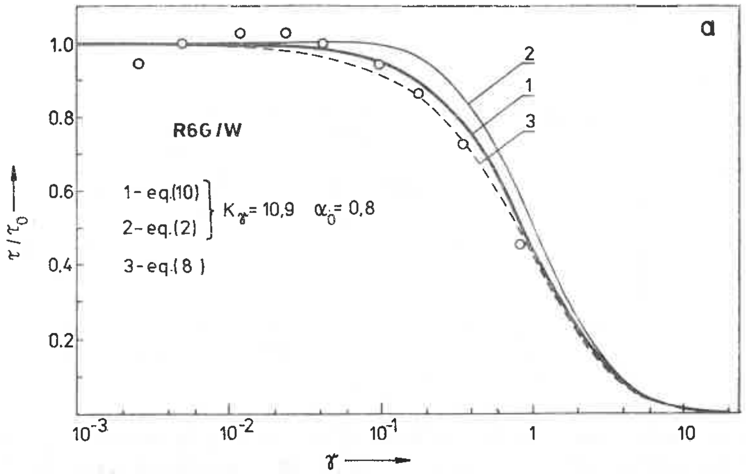
$$\frac{\tau}{\tau_0} = \frac{1+\gamma^2-(1.5+\gamma^2)f(\gamma)}{[1-f(\gamma)]\,[1-\alpha_0\alpha f(\gamma)]}, \tag{2}$$

where

$$f(\gamma) = \sqrt{\pi}\,\gamma \exp(\gamma^2)\,[1-\mathrm{erf}(\gamma)], \tag{3}$$

$$\gamma = \gamma_D+\gamma_A = \frac{\sqrt{\pi}}{2}\left(\frac{c_D}{c_{OD}}+\frac{c_A}{c_{OA}}\right), \tag{4}$$

$$\alpha = \frac{\gamma_D}{\gamma_D+\gamma_A}, \tag{5}$$



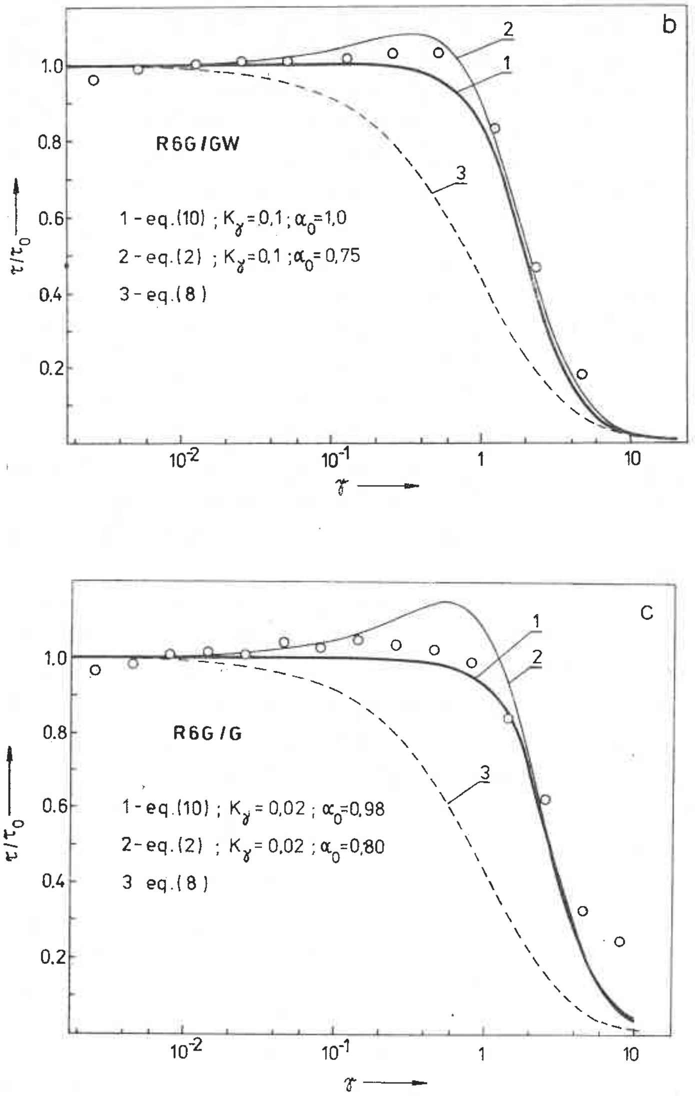


Fig. 2. Photoluminescence decay time for rhodamine 6G as dependent on the concentration in (a) water, (b) glycerin–water solutions, and (c) glycerin; ○ — experimental points, ——— — theoretical curves

C_D and C_A, and C_{OD} and C_{OA} denote the concentrations and critical concentrations of the donor and acceptor; α_0 is the probability that no degradation of the excitation energy occurs during the energy transfer between donors.

Formula (2) was derived assuming that the history of excitation energy in a molecule of any order does not affect its present behavior.

If only monomers D and dimers D″ are present in the solution, C_A, C_{OA} and γ_A in formulae (4) and (5) should be substituted with $C_{D''}$, $C_{OD''}$ and $\gamma_{D''}$. If the dimers are not luminescent then their presence in the solution leads to the concentration quenching, and thus to a drop in the yield of η and a shortening of the decay time, τ. To make a comparison of experimental results with formula (2), possibly it is necessary to determine the concentrations C_D and $C_{D''}$ previously, as well as the critical concentrations C_{OD} and $C_{OD''}$ of the monomers and dimers. The dimerization constants, K, have been determined for systems I and II from concentration-dependent changes in the absorption spectra according to [5]. For system III, where absorption spectra were practically unchanged in the entire range of concentrations, the equilibrium constant, K, and critical concentrations C_{OD} and $C_{OD''}$ were determined from concentration-dependent variations of the emission anisotropy, r/r_0 and the quantum yield, η/η_0, according to the method described in [25, 26]. The values for the parameters necessary to make comparisons of experimental results with formula (2) are given in Table II. For system I, where the viscosity was low, C_{OD} and $C_{OD''}$ were calculated assuming $\langle\chi^2\rangle = 2/3$ which corresponds to fast rotating dipoles. For systems II and III $\langle\chi^2\rangle = 0.476$ was taken. This value of $\langle\chi^2\rangle$ corresponds to motionless dipoles and its application there is justified, especially for high concentrations [27].

Experimental values of τ/τ_0 corrected for the secondary effects are shown in Fig. 2 and theoretical curve *2* calculated according to (2) for the values of dimerization constant[3] as shown in Table II.

It can be seen from Fig. 2 that the theoretical curves satisfactorily describe the dependence of τ/τ_0 on the concentration especially in the concentration range where the decrease of τ/τ_0 occurs. Mainly the PL quenching by nonluminescent dimers is responsible for this drop. For rhodamine 6G in water there is a considerable discrepancy between the experimental results and curve 2 in the concentration range described. This could be caused by an additional quenching due to the diffusion of molecules D and D'' in the time τ (condition (7) that is not satisfied sufficiently see columns 12, 13 and 14 in Table II). Diffusion was not accounted for in formula (2) since as this formula follows from a theory developed for rigid solutions[4]. For systems characterized by a higher dimerization constant K_γ, (such as system I), the drop was observed at lower concentrations than for systems where K_γ is lower (systems II and III). The theoretical curves were calculated for the parameter $\alpha_0 < 1$ (column 6, Table II). This means that beside the quenching by dimers, also monomer quenching should have been accounted for in order to obtain a good agreement between theoretical and experimental results. For the mean displacement, $\sqrt{\langle r^2\rangle}$, of active molecules in the translational Brownian movement the following inequality was satisfied for systems II and III:

$$\sqrt{\langle r^2\rangle} = \sqrt{\frac{kT\tau_0}{\pi\eta'\sigma}} \ll R_0, \tag{7}$$

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[3] The dimensionless dimerization constant, K_γ, is related to the constant $K = \frac{C_{D''}}{C_D^2}$ by

$$K_\gamma = \frac{2KC_{OD}^2}{C_{OD''}}. \tag{6}$$

[4] This is also true for formulae (8) and (10).

where R_0 is the critical distance (columns 12 and 14, Table II). Thus, the effect of material diffusion on the NEEET process can be neglected in these systems.

Theoretical studies on the influence of concentration on the decay time were done by Vavilov [28] and also by Galanin [29]. The theory developed by Vavilov had a semi--phenomenological nature and a formula for τ/τ_0 derived within its concept included several empirical constants. No such constants were used in Galanin's theory. According to him [29, 30]

$$\frac{\tau}{\tau_0} = \frac{1+\gamma_A^2-(1.5+\gamma_A^2)f(\gamma_A)}{1-f(\gamma_A)}, \tag{8}$$

where $\gamma_A = \frac{\sqrt{\pi}}{2}\frac{c_A}{c_{OA}}$, and $f(\gamma_A)$ is given by formula (3).

Formula (8) was applied in [29] among others to describe the concentration-dependent changes of τ/τ_0 for fluorescence of single-component systems, namely glycerin solutions of fluorescein, rhodamine 5G and acridine orange. In this work it was assumed that all dye molecules were monomers and nonexcited monomer molecules were regarded as acceptor molecules[5]. It follows then that $\gamma_A \approx \gamma$. Curve *3* calculated according to (8) is also plotted in Fig. 2. It is evident that the drop in the experimentally determined τ/τ_0 occured at much higher concentrations than that predicted by (8). This is especially true for weakly dimerizing systems (systems II and III). It might be expected that for strongly dimerizing ($\gamma_{D''} \gg \gamma_D$) systems formula (8) could only provide an adequate description of experimental results for τ/τ_0. This was confirmed to a certain degree by results obtained for rhodamine 6G in water (Fig. 2a) for high concentrations of $\gamma_{D''} \approx \gamma_D$. Note that formula (2) becomes formula (8) in the particular case when $\gamma_A \gg \gamma_D$.

Fig. 3 shows experimentally determined values of the fluorescence quantum yield, η/η_0, corrected for secondary effect[6], together with theoretical curves calculated according to formula [31]:

$$\frac{\eta}{\eta_0} = \frac{1-f(\gamma)}{1-\alpha_0\alpha f(\gamma)}, \tag{9}$$

where α_0, α, $f(\gamma)$ and γ are those specified for (2). The continuous curves describing η/η_0 were plotted for values of K_γ identical to those for the τ/τ_0 curves. However, values of α_0 were, as a rule, different (colmuns 5–6, Table II). The difference in α_0 for η/η_0 as described by (9) and τ/τ_0 described by (2) is not justified from the physical grounds. The values of α_0 should be identical in both cases. A better agreement with experimental results for τ/τ_0 can be obtained when the following formula is used:

$$\frac{\tau}{\tau_0} = \frac{1+\gamma^2-(1.5+\gamma^2)f(\gamma)+\alpha_0\alpha f(\gamma)\,[f(\gamma)+\gamma^2-0.5]-\alpha_0\alpha\gamma^2}{[1-f(\gamma)]\,[1-\alpha_0\alpha f(\gamma)]}. \tag{10}$$

This formula was derived recently [32] based on kinetic equations (8) given in [31].

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[5] D, A and γ in the present work correspond to M_1, M_2, and q, respectively, in Galanin's paper [29].

[6] True values of η/η_0 were calculated using the same values of κ as in calculations of true decay times τ/τ_0.

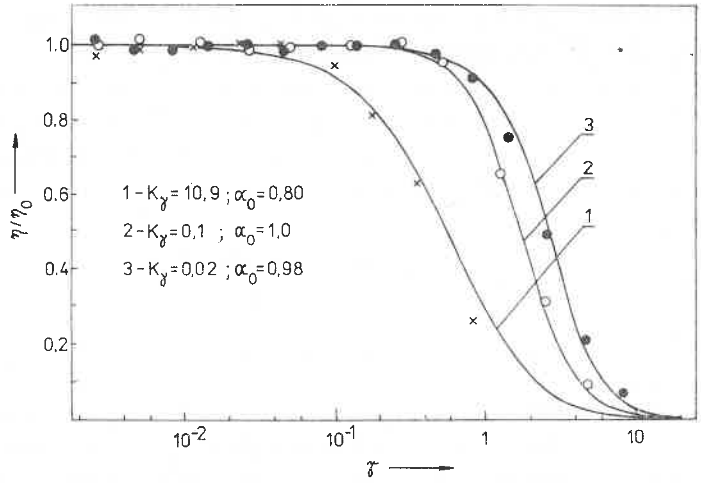

Fig. 3. Quantum photoluminescence yield of rhodamine 6G showing its dependence on the reduced concentration γ. ×, ○, ● — experimental points for system I, II and III, respectively; ——— — theoretical curves calculated according to (9).

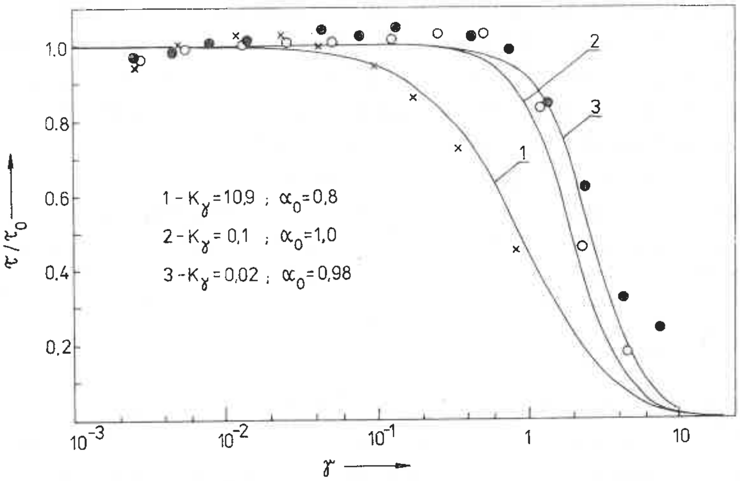

Fig. 4. PL decay time for rhodamine 6G in systems as in Fig. 3. ×, ○, ● — experimental points, ——— — theoretical curves according to (10)

Fig. 4 shows the experimental results for τ/τ_0 together with theoretical curves calculated according to (10) for the same values of K_γ and α_0 as those employed for the calculation of the quantum yield curves. A good agreement of formula (10) with experimental results within the whole range of concentrations is evident. Curves calculated according to (10) are also shown in Fig. 2 (curves *1*) in order to make comparisons of formula (10) with formulae (2) and (8). Unlike curves *2*, calculated according to (2), curves *1* do not show any maxima, and for high concentrations they fit the experimental results as well as curves *2*. In the absence of the fluorescence quenching in a solution $\alpha = \alpha_0 = 1$ formula (10) leads to $\tau/\tau_0 = 1$, while for extremaly intensive quenching by dimers ($\gamma_{D''} \gg \gamma_D$, $\alpha \to 0$) it takes the form of (8) as obtained by Galanin.

It is noteworthy that formula (10) and formula (9) for the quantum yield of photoluminescence were derived without any deviations from rigorous mathematics.

5. *Concluding remarks*

Measurements of concentration-dependent changes of fluorescence decay times, τ/τ_0, were done for rhodamine 6G in solutions exhibiting different tendencies towards dimerization. It was observed that fluorescence decay times corrected for secondary effects remain constant within a wide range of concentrations and decrease rapidly at some concentration. The higher the dimerization constant characterizing the system, the lower is that concentration. For the drop to occur the concentration quenching by nonluminescent dimers appears to be largely responsible. This is evident from the form of the concentration-dependent changes in the quantum yield η/η_0, for which there is a close correlation with analogous curve of τ/τ_0, Figs 3–4. It appears that the relation, $\tau/\tau_0 = \eta/\eta_0$, is best satisfied for rhodamine 6G in glycerin. That is, for a system characterized by a low dimerization constant, K. For system I (rhodamine 6G in water) deviations from proportionality between τ/τ_0 and η/η_0 are the greatest. The observed behavior of τ/τ_0 and η/η_0 for photoluminescence in solutions showing different tendencies towards dimerization can be described correctly by expressions (10) and (9). These relations were obtained assuming a multistep non-radiative energy transfer from excited monomers to nonluminescent dimers. Also formula (2) provides a correct description of concentration resolved of τ/τ_0. However, this is assuming an increased contribution of monomer quenching in the solution.

REFERENCES

[1] V. L. Levshin, J. G. Baranova, *Opt. Spektrosk.* **6**, 55 (1959).
[2] H. L. Arvan, N. J. Zaitseva, *Opt. Spektrosk.* **10**, 272 (1961).
[3] L. V. Levshin, *Izv. Akad. Nauk. SSSR Ser. Fiz.* **29**, 1245 (1965).
[4] J. E. Selvyn, J. I. Steinfeld, *J. Phys. Chem.* **76**, 762 (1972).
[5] C. Bojarski, G. Obermueller, *Acta Phys. Pol.* **A50**, 389 (1976).
[6] J. G. Baranova, V. L. Levshin, *Opt. Spektrosk.* **10**, 362 (1961).
[7] V. L. Levshin, *Izv. Akad. Nauk. SSSR Ser. Fiz.* **27**, 540 (1963).
[8] C. Bojarski, J. Kuśba, G. Obermueller, *Z. Naturforsch.* **26a**, 255 (1971).
[9] L. V. Levshin, J. Yu. Biechli, T. D. Slavnova, V. I. Jushakov, *Opt. Spektrosk.* **36**, 503 (1974).
[10] K. A. Selanger, J. Falnes, T. Sikkeland, *J. Phys. Chem.* **81**, 1960 (1977).
[11] J. Knof, F. J. Theiss, J. Weber, *Z. Naturforsch.* **33a**, 98 (1978).
[12] J. Tyrzyk, *Z. Nauk. Politechn. Gdańsk.* **242**, 111 (1975) (in Polish).
[13] R. K. Bauer, M. Rozwadowski, *Bull. Acad. Pol. Sci., Ser. Sci. Math. Astron. Phys.* **7**, 365 (1959).
[14] R. K. Bauer, K. J. Rudik, *Acta Phys. Pol.* **35**, 259 (1969).
[15] A. Budó, L. Szalay, *Z. Naturforsch.* **18a**, 90 (1963).
[16] A. Budó, I. Ketskeméty, *Acta Phys. Hung.* **7**, 207 (1957); **14**, 167 (1962).
[17] I. Ketskeméty, J. Kuśba, *Acta Phys. Chem. Szeged* **23**, 375 (1977).
[18] C. Bojarski, G. Obermueller, J. Kuśba, *Z. Nauk. Politechn. Gdańsk.* **181**, 3 (1971) (in Polish).
[19] I. Ketskeméty, J. Dombi, R. Horvai, J. Hevesi, L. Kozma, *Acta Phys. Chem. Szeged* **7**, 17 (1961).

[20] I. Ketskeméty, J. Kuśba, *Acta Phys. Chem. Szeged* **20**, 239 (1974).
[21] R. R. Alfano, S. L. Shapiro, W. Yu, *Opt. Commun.* **7**, 191 (1973).
[22] I. Ketskeméty, L. Gati, A. Györi, L. Kozma, *Acta Phys. Hung.* **43**, 109 (1977).
[23] M. E. Mack, *J. Appl. Phys.* **39**, 2483 (1968).
[24] C. Bojarski, E. Grabowska, *Acta Phys. Hung.* **46**, 113 (1979).
[25] C. Bojarski, *J. Lumin.* **5**, 371 (1972).
[26] J. Dudkiewicz, *Acta Phys. Pol.* **A49**, 239 (1976).
[27] C. Bojarski, J. Dudkiewicz, *Chem. Phys. Lett.* **67**, 450 (1979).
[28] S. I. Vavilov, *Zh. Eksp. Teor. Fiz.* **13**, 13 (1943).
[29] M. D. Galanin, *Trudy Fiz. Inst. Akad. Nauk SSSR* **12**, 3 (1960).
[30] V. M. Agranovitsh, M. D. Galanin, *Transfer of Electronic Excitation Energy in Condensed Media*, Moskva 1978 (in Russian).
[31] C. Bojarski, J. Domsta, *Acta Phys. Hung.* **30**, 145 (1971).
[32] R. Twardowski, C. Bojarski, *Z. Naturforsch.* (in press).