A STUDY OF CONCENTRATION DEPOLARIZATION AND QUENCHING OF PHOTOLUMINESCENCE IN SOLUTIONS

By C. Bojarski, A. Bujko, J. Dudkiewicz, J. Kuśba and G. Obermüller

Institute of Physics, Technical University, Gdańsk*

(Received January 10, 1973)

The concentration-dependence of emission anisotropy r/r_0 and quantum yield η/η_0 of the photoluminescence of glycerol-water solutions of rhodamine B in two systems of viscosities 7.4 P and 0.72 P is investigated. The experimental data are compared with the new theory of concentration depolarization (*J. Lumin.*, **5**, 413 (1972)) and concentration quenching of photoluminescence (*Acta Phys. Hungar.*, **30**, 145 (1972)), which takes account of excitation energy remigration and concentration quenching by non-luminescing dimers. The theory is found to agree well with the experimental data within a wide range of concentrations, and an additional mechanism of external quenching (apart from the quenching by dimers) independent of concentration is revealed. The dimerization constants, concentrations and critical distances are determined for each particular system.

1. Introduction

A theory of concentration depolarization of photoluminescence (CDP) has recently been developed [1] which takes account of both self-quenching and remigration of excitation energy. This approach includes remigration of excitation to molecules D_0, being the primary absorbers of the exciting light, from molecules D_1 and D_2, of which D_1 is the nearest neighbour of D_0 and D_2 is the nearest (or second after D_0) neighbour of D_1. As concerns self-quenching, it was assumed that it is mainly conditioned by the presence of non-luminescing $D_{||}$ dimers in the solution, although a possibility of excitation energy degradation during its transfer among monomers is also acceptable. Theoretical considerations are based on the luminescence center model known as the "most probable path model". The center is assumed to consist of a molecule D_0 and molecules D_1, D_2, ..., D_m, a molecule D_K of which is the nearest neighbour of the molecule D_{K-1} (or second-nearest after D_{K-2}). It is assumed that excitation energy may be passed on only between neighbouring molecules belonging to the center, but there may be multiple oscillations of excitation energy between the molecules D_{K-1} and D_K. All molecules belonging to a lumines-

* Address: Instytut Fizyki, Politechnika Gdańska, Majakowskiego 11/12, 80-952 Gdańsk-Wrzeszcz, Poland.

cence center are assumed to be monomers. Quenching by dimers is taken into account, however, because it is assumed possible that radiationless energy transfers may occur between any of the molecules $D_0, D_1, \ldots, D_m$ and any molecule $D_{||}$ in the solution. Basing, among other things, on these assumptions, leads to the following expressions for emission anisotropy [1]:

$$\frac{r}{r_0} = (1-\varphi)\left\{1+\frac{\varphi^2}{4}\left[\frac{\overline{Q}}{1-\overline{Q}(2-\overline{Q})\varphi^2}+\frac{1-\overline{Q}}{1-(1-\overline{Q}^2)\varphi^2}+\frac{1}{1-(1-\overline{Q}+\overline{Q}^2)\varphi^2}\right]\right\} \tag{1}$$

where

$$\varphi = \alpha_0 \alpha f \tag{2}$$

$$\alpha = \frac{\gamma_D}{\gamma_D+\gamma_{D||}} \tag{3}$$

$$f = \sqrt{\pi}\,\gamma \exp(\gamma^2)\left[1-\frac{2}{\sqrt{\pi}}\int_0^{\gamma} e^{-t^2}dt\right] \tag{4}$$

$$\gamma = \gamma_D+\gamma_{D||} = \frac{\sqrt{\mathfrak{N}\eta_0}}{2}\left(\frac{C'}{C_0'}+\frac{C''}{C_0''}\right) \tag{5}$$

α_0 denotes the probability of the non-occurrence of excitation energy quenching during its transfer between monomers, η_0 is the absolute yield of the photoluminescence of the solution when the concentration C tends to zero, C' and C'' are the concentrations of monomers and dimers, and C_0' and C_0'' are the critical concentrations for the transfer of excitation energy to monomers D and dimers $D_{||}$.

Besides

$$\overline{Q} = \frac{16}{27}\cdot\frac{\overline{P(\frac{27}{16}x)}}{\overline{P(x)}}, \qquad x = \frac{C'}{C_0'} \tag{6}$$

where

$$\overline{P}(x) = x\left[\mathrm{Ci}\,(x)\sin x-\mathrm{Si}\,(x)\cos x+\frac{\pi}{2}\cos x\right]. \tag{7}$$

The function $\overline{Q}$ was introduced by Eriksen and Ore [2]. It defines the probability of the molecule D_{K-1} being the nearest neighbour of D_K when the molecule D_K is the nearest neighbour of D_{K-1}, assuming there is a statistical distribution of molecules D in the olution. Ci and Si denote the functions of integral cosine and sine, respectively[1].

By adopting the same assumptions as above regarding the self-quenching mechanisms, n expression was obtained for the quantum yield of fluorescence as a function of concentration [7],

$$\frac{\eta}{\eta_0} = \frac{1-f(\gamma)}{1-\alpha_0\alpha f(\gamma)} \tag{8}$$

[1] The function $\overline{P(x)}$ has been given by Dexter [3] and Ore [4,5]. A similar expression was also obtained y Förster 6].

where $f(\gamma)$, α_0, α and γ have the same meaning as before. It must be emphasized that in deriving formula (8) account was taken of a possible radiationless transfer of energy from an excited monomer to an unexcited dimer through many steps, *viz.*,

$$D^*+D+\ldots+D+D_{||} \xrightarrow{k_{DD}} D+D^*+\ldots+D+D_{||} \xrightarrow{k_{DD}} \ldots \xrightarrow{k_{DD}}$$

$$D+D+\ldots+D^*+D_{||} \xrightarrow{k_{DD_{||}}} D+D+\ldots+D+D^*_{||}. \tag{9}$$

Here, k_{DD} and $k_{DD_{||}}$ are the rates of radiationless transfer of excitation energy to a monomer and to a dimer, respectively. According to Förster [8], in the case of dipole-dipole interaction between molecules D^* and D or D^* and $D_{||}$ this rate is

$$k_{DD} = k_F \left(\frac{R'_0}{R}\right)^6 \tag{10}$$

where $k_F = 1/\tau_0$ is the photoluminescence emission rate, τ_0 being the mean lifetime of the molecule D^* in the excited state when $C'' = 0$, R is the distance between the molecules D^* and D, and R'_0 is the so-called critical distance.

2. *Experimental*

To check the theory of concentration depolarization of photoluminescence (CDP) and concentration quenching of photoluminescence (CQP) given in the form of formulae (1) and (8), two series of glycerol-water solutions of rhodamine B were prepared. At 288 K the viscosity of the first series was 7.4 poise (system I), whereas that of the other was 0.725 poise (system II). The rhodamine B ($C_{28}H_{31}Cl\,N_2O_3$, mol. wt 479.03), manufactured by GMBH & Co. (Schuchardt), was additionally purified, precipitating the inorganic constituents three times by dissolving the dye in ethyl alcohol and then evaporating the solution in vacuum. The analytically pure glycerine of domestic manufacture ("Strem") was used without additional purification. In order to prevent alterations in the dissociation of the solution when more diluted, 0.1% (by volume) of 10 n HCl was added[2].

The absorption spectra were measured with a VSU 2-P spectrophotometer. The thicknesses of the layers of solution were such that extinction at the absorption maximum did not exceed unity. In the case of solutions of concentrations $C > 5 \times 10^{-3}$ M use was made of special miniature trays enabling the absorption to be measured in layers 10 to 2 μm thick. The fluorescence spectra were measured at frontal excitation of the sample with the apparatus described elsewhere [10].

The fluorescence was excited by the light of a filament lamp passed through an IF 525 nm interference filter. The fluorescence spectra were corrected for the spectral sensitivity of the photomultiplier and for reabsorption according to a known technique [11, 12].

[2] In principle, the electrolyte did not have to be added, for as follows from the papers by Levshin *et al.* [9] the absorption spectrum of rhodamine B in aqueous solutions is independent of the *pH* index.

The quantum yield of photoluminescence was measured in the spectral range (585 ± 5) nm on the same set-up used in the fluorescence spectrum measurements. The basis for these measurements was the method described in Refs [13, 14], and they were corrected for the share of secondary fluorescence in the observed luminous emission [15] and for the anisotropy of the spatial distribution of this emission, conditioned by the state of polarization of the fluorescent emission [16].

Emission anisotropy was measured by the compensation photoelectric method developed by Tumerman [17] and Wille [18] with the apparatus described in Ref. [19]. The luminescence was excited by the light of a DRSz-250 high-pressure mercury lamp through an Mon 546 nm filter. On the observation side an OG–3 cutoff filter ($\lambda > 570$ nm) was employed. The experimental values of emission anisotropy were corrected for secondary fluorescence by the method given in Ref. [19].

3. Comparison of experimental data with theory

Measurements of emission anisotropy r/r_0 and quantum yield η/η_0 of photoluminescence were carried out within a broad range of concentrations, from 1.6×10^{-5} M to 4×10^{-2} M in the case of system I and from 4×10^{-5} M to 2.5×10^{-2} M in the case of system II. The values of r/r_0 and η/η_0 have been corrected for secondary fluorescence and other effects distorting the results according to the methods mentioned in Sec. 2.

Table I presents the corrected r/r_0 and η/η_0 values together with the experimental error margins. In the case of emission anisotropy these errors are the sum of the standard error stemming from fluctuations of the measured values of the angular settings of the Arago compensator and the error of the determination of the fundamental anisotropy[3] r_0. In the case of quantum yield, on the other hand, they are the sum of the standard error of photoluminescence intensity fluctuations and the error of determining η_0.

A comparison of the experimental values of r/r_0 and η/η_0 with the theoretical expressions (1) and (8), which are functions of the same argument γ, requires knowledge of the critical concentrations C_0' and C_0'', absolute yield η_0, and the concentrations C' and C'' for the various gross concentrations C of active molecules in the solution (*cf.* Eq. (5)). In addition, it is necessary to know the value of the parameter α.

If the absorption spectra of a given system demonstrate a sufficiently strong dependence on concentration, then C_0'', C' and C'' can be determined experimentally. Thus, the dimerization constant K (and thereby C' and C'') and the absorption spectrum of dimers $\varepsilon''(\nu)$ as well can be determined from the family of absorption curves corresponding to various concentrations C by the method devised by Förster [20] and Levshin [21], whereas the critical concentrations from the relation [8]

$$C_0 = 4.23 \cdot 10^{-10} \cdot \frac{n^2 \cdot \bar{\nu}^2}{(\eta_0 \overline{\kappa^2} \cdot \overline{\varepsilon(\nu)})^{\frac{1}{4}}} \tag{11}$$

[3] The values of r_0 corresponding to the fundamental degrees of polarization P_0 (determined as the average values corresponding to the lowest concentrations) are given in Table II.

TABLE I

Concentrational changes of emission anisotropy and quantum yield of photoluminescence of glycerol--water solutions of rhodamine B

	Rhodamine B					
	System I — 7.4 P			System II — 0.72 P		
No	C	r/r_0	η/η_0	C	r/r_0	η/η_0
	M/l			M/l		
1	1.6×10^{-5}	1.000 ± 0.005	—	4.0×10^{-5}	0.982 ± 0.009	—
2	2.5×10^{-5}	0.984 ± 0.007	—	8.0×10^{-5}	0.952 ± 0.025	1.009 ± 0.012
3	4.0×10^{-5}	0.923 ± 0.005	—	1.0×10^{-4}	0.945 ± 0.015	—
4	5.0×10^{-5}	0.918 ± 0.005	—	1.2×10^{-4}	0.961 ± 0.015	0.989 ± 0.010
5	6.4×10^{-5}	0.930 ± 0.005	—	1.6×10^{-4}	0.926 ± 0.012	0.980 ± 0.010
6	8.0×10^{-5}	0.919 ± 0.006	—	2.0×10^{-4}	0.886 ± 0.013	0.976 ± 0.015
7	1.0×10^{-4}	0.919 ± 0.006	1.000 ± 0.004	2.5×10^{-4}	0.859 ± 0.019	1.008 ± 0.024
8	1.3×10^{-4}	0.910 ± 0.006	—	3.2×10^{-4}	0.854 ± 0.019	0.994 ± 0.012
9	1.6×10^{-4}	0.908 ± 0.006	—	4.0×10^{-4}	0.830 ± 0.013	0.993 ± 0.008
10	2.0×10^{-4}	0.895 ± 0.005	—	5.0×10^{-4}	—	$1.005\pm$
11	2.5×10^{-4}	0.874 ± 0.005	—	6.0×10^{-4}	0.800 ± 0.020	0.995 ± 0.009
12	3.0×10^{-4}	0.838 ± 0.005	—	8.0×10^{-4}	0.740 ± 0.012	0.993 ± 0.011
13	4.0×10^{-4}	0.828 ± 0.005	1.004 ± 0.011	1.0×10^{-3}	0.700 ± 0.010	0.968 ± 0.022
14	5.0×10^{-4}	0.796 ± 0.005	—	1.3×10^{-3}	0.630 ± 0.008	0.952 ± 0.025
15	6.4×10^{-4}	0.770 ± 0.005	—	1.6×10^{-3}	0.584 ± 0.010	0.943 ± 0.033
16	8.0×10^{-4}	0.729 ± 0.006	—	2.0×10^{-3}	0.537 ± 0.007	0.900 ± 0.018
17	1.0×10^{-3}	0.672 ± 0.004	0.993 ± 0.012	2.5×10^{-3}	0.472 ± 0.007	0.832 ± 0.017
18	1.3×10^{-3}	0.605 ± 0.002	—	3.0×10^{-3}	0.453 ± 0.007	0.784 ± 0.027
19	1.6×10^{-3}	0.562 ± 0.004	—	4.0×10^{-3}	0.386 ± 0.006	0.695 ± 0.025
20	2.0×10^{-3}	0.506 ± 0.004	0.967 ± 0.005	5.0×10^{-3}	0.339 ± 0.005	0.609 ± 0.011
21	2.5×10^{-3}	0.459 ± 0.002	—	6.4×10^{-3}	0.307 ± 0.005	0.501 ± 0.009
22	3.0×10^{-3}	0.400 ± 0.003	—	8.0×10^{-3}	0.281 ± 0.004	0.385 ± 0.009
23	4.0×10^{-3}	0.307 ± 0.003	0.936 ± 0.014	1.0×10^{-2}	0.264 ± 0.004	0.300 ± 0.033
24	5.0×10^{-3}	0.263 ± 0.001	0.864 ± 0.008	1.3×10^{-2}	0.251 ± 0.005	0.187 ± 0.005
25	6.4×10^{-3}	0.192 ± 0.002	0.798 ± 0.004	1.6×10^{-2}	0.228 ± 0.005	0.128 ± 0.004
26	8.0×10^{-3}	0.168 ± 0.001	0.696 ± 0.004	2.0×10^{-2}	0.228 ± 0.005	0.092 ± 0.006
27	1.0×10^{-2}	0.158 ± 0.002	0.618 ± 0.004	2.5×10^{-2}	0.218 ± 0.005	0.052 ± 0.002
28	1.3×10^{-2}	0.110 ± 0.002	0.484 ± 0.008			
29	1.6×10^{-2}	0.094 ± 0.002	0.402 ± 0.003			
30	2.0×10^{-2}	0.081 ± 0.002	0.308 ± 0.003			
31	2.5×10^{-2}	0.060 ± 0.001	0.233 ± 0.003			
32	3.0×10^{-2}	0.056 ± 0.001	0.167 ± 0.002			
33	4.0×10^{-2}	$0.063\pm0\,001$	$0.112\pm0\,001$			

Here, n is the refractive index of the medium, $\bar{\nu}$ the mean value of the wave number, and $\overline{\varepsilon(\nu)}$ the mean value of the molar decimal coefficient of extinction in the region where the spectra $\varepsilon(\nu)$ and $F(\nu)$ overlap, $F(\nu)$ being the spectral distribution of fluorescence expressed in terms of numbers of quanta (normalized to unity, *i.e.* $\int_0^\infty F(\nu)d\nu = 1$). The quantity $\overline{\kappa^2}$

is a constant, the value of which depends on the mutual orientation of the oscillators bound with the interacting molecules. It equals 2/3 in the case of fast rotational Brownian motion of both molecules (p. 85 in Ref. [6]) and 0.476 in the case of random, though fixed, orientations of the oscillators [22]. In Eq. (11) C_0 is expressed in M/l, ν in cm^{-1}, and $\overline{\varepsilon(\nu)}$ in l/M·cm.

In the case of the systems investigated here, the aforementioned method of Förster and Levshin for determining C_0'' could not be used because of the very weak dependence of the absorption spectra on concentration. But determination of the critical concentrations C_0' did not present any difficulty.

Figure 1 gives the absorption spectrum of monomers ε', the fluorescence spectrum F and the product $\varepsilon' \cdot F$ for glycerol-water solutions of rhodamine B. Using these results, $\overline{\varepsilon'}$ was determined and then C_0' by accepting $\overline{\kappa^2} = 2/3$ in Eq. (11). In order to be able to com-

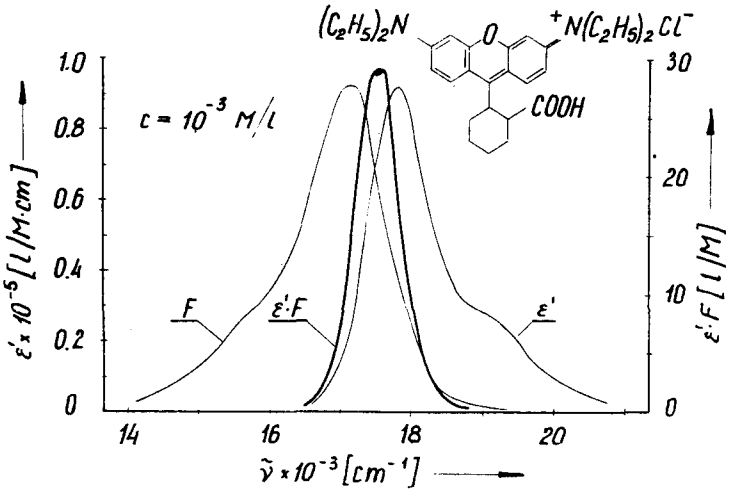

Fig. 1. Absorption spectrum of monomers ε', quantum fluorescence spectrum F in arbitrary units, and the product $\varepsilon' \cdot F$ for a glocerol-water solution of rhodamine B ($\eta_{288K} = 7.4$ P)

pare the experimental data given in Table I with the theory it is necessary to know the values of the argument γ corresponding to the various concentrations C. Approximate values of γ may be found by assuming that $C'' \ll C'$ in the whole range of concentrations. Such an assumption is justified[4] because in glycerol-water solutions association is much weaker than in aqueous solutions. With it, relation (5) yields

$$\gamma \cong (\pi\eta_0)^{\frac{1}{2}} \cdot C/2C_0' . \tag{12}$$

Since $C_0 \sim \eta_0^{-\frac{1}{2}}$ (*cf.* Eq. (11)),

$$\gamma = 1.71 \cdot 10^9 \frac{(\overline{\varepsilon'(\nu)})^{\frac{1}{2}}}{n^2 \cdot \bar{\nu}^2} \cdot \eta_0 \cdot C. \tag{13}$$

The value of η_0 was determined from Eq. (13) by fitting the experimental points pertaining to emission anisotropy in the range of low and moderate concentrations to the trace of

[4] On the example of glycerol-water solutions of rhodamine 6 G and Na-fluorescein we found the dimerization constant to be strongly dependent on the water content in the solution.

TABLE II

Data characteristic of rhodamine B solution for comparing experimental results with theory

Number of system	Name of object	η	C_0'	C_0''	R_0'	R_0''	n	ε'	$\bar{\varepsilon}''$	$\varkappa$	ν'	K_γ	K	η_0	P_0	r_0
		P	10^{-3} M/l		Å		—	10^5 l/M · cm		—	cm^{-1}	—	l/M	—	%	—
I	Rhodamine B	7.4	2.59	2.03	53.5	58.0	1.47	0.244	0.399	1.278	17520	0.001	0.23	0.71	46.6	0.368
II		0.72	2.56	1.99	53.9	58.6	1.40			1.286	17640	0.002	0.41	0.75	43.5	0.339

the theoretical r/r_0 *vs* γ curve. Thus values of η_0 equal to 0.71 and 0.75 were obtained for the systems I and II, respectively; they agree well with the value of 0.71 quoted by Demas and Crosby [23].

Values of γ calculated from relation (13) are given in Table III. These calculations were carried out with the use of values of $\overline{\varepsilon'(\nu)}$, η_0, n and $\bar{\nu}$ characterizing each particular system presented in Table II. Now, having the experimental values of r/r_0, η/η_0 and γ,

TABLE III

Values of parameters γ and γ' calculated from relations (13) and (5), respectively, and dimer concentrations C related to concentrations of glycerol-water solutions of rhodamine B

No	System I			System II			
	C	γ	C''	C	γ	γ'	C''
	M/l	—	M/l	M/l	—	—	M/l
1	1.6×10^{-5}	4.61×10^{-3}	5.8×10^{-11}	4.0×10^{-5}	1.32×10^{-2}	1.32×10^{-2}	6.6×10^{-10}
2	2.5×10^{-5}	7.20×10^{-3}	1.4×10^{-10}	8.0×10^{-5}	2.64×10^{-2}	2.64×10^{-2}	2.6×10^{-9}
3	4.0×10^{-5}	1.15×10^{-2}	3.6×10^{-10}	1.0×10^{-4}	3.30×10^{-2}	3.30×10^{-2}	4.2×10^{-9}
4	5.0×10^{-5}	1.44×10^{-2}	5.6×10^{-10}	1.2×10^{-4}	3.96×10^{-2}	3.96×10^{-2}	5.5×10^{-9}
5	6.4×10^{-5}	1.84×10^{-2}	9.2×10^{-10}	1.6×10^{-4}	5.28×10^{-2}	5.28×10^{-2}	1.1×10^{-8}
6	8.0×10^{-5}	2.30×10^{-2}	1.4×10^{-9}	2.0×10^{-4}	6.60×10^{-2}	6.60×10^{-2}	1.7×10^{-8}
7	1.0×10^{-4}	2.88×10^{-2}	2.3×10^{-9}	2.5×10^{-4}	8.18×10^{-2}	8.18×10^{-2}	2.6×10^{-8}
8	1.3×10^{-4}	3.74×10^{-2}	3.8×10^{-9}	3.2×10^{-4}	1.06×10^{-1}	1.06×10^{-1}	4.2×10^{-8}
9	1.6×10^{-4}	4.61×10^{-2}	5.8×10^{-9}	4.0×10^{-4}	1.32×10^{-1}	1.32×10^{-1}	6.5×10^{-8}
10	2.0×10^{-4}	5.76×10^{-2}	9.0×10^{-9}	5.0×10^{-4}	1.65×10^{-1}	1.65×10^{-1}	1.0×10^{-7}
11	2.5×10^{-4}	7.20×10^{-2}	1.4×10^{-8}	6.0×10^{-4}	1.98×10^{-1}	1.98×10^{-1}	1.5×10^{-7}
12	3.0×10^{-4}	8.64×10^{-2}	2.0×10^{-8}	8.0×10^{-4}	2.64×10^{-1}	2.64×10^{-1}	2.6×10^{-7}
13	4.0×10^{-4}	1.15×10^{-1}	3.6×10^{-8}	1.0×10^{-3}	3.30×10^{-1}	3.30×10^{-1}	4.1×10^{-7}
14	5.0×10^{-4}	1.44×10^{-1}	5.6×10^{-8}	1.3×10^{-3}	4.29×10^{-1}	4.29×10^{-1}	6.7×10^{-7}
15	6.4×10^{-4}	1.84×10^{-1}	9.2×10^{-8}	1.6×10^{-3}	5.28×10^{-1}	5.28×10^{-1}	1.1×10^{-6}
16	8.0×10^{-4}	2.30×10^{-1}	1.4×10^{-7}	2.0×10^{-3}	6.60×10^{-1}	6.60×10^{-1}	1.7×10^{-6}
17	1.0×10^{-3}	2.88×10^{-1}	2.3×10^{-7}	2.5×10^{-3}	8.25×10^{-1}	8.25×10^{-1}	2.6×10^{-6}
18	1.3×10^{-3}	3.74×10^{-1}	3.8×10^{-7}	3.0×10^{-3}	9.90×10^{-1}	$9.90\times10^{-}$	3.7×10^{-6}
19	1.6×10^{-3}	4.61×10^{-1}	5.8×10^{-7}	4.0×10^{-3}	1.32	1.32	6.0×10^{-6}
20	2.0×10^{-3}	5.76×10^{-1}	9.0×10^{-7}	5.0×10^{-3}	1.65	1.65	7.7×10^{-6}
21	2.5×10^{-3}	7.20×10^{-1}	1.4×10^{-6}	6.4×10^{-3}	2.11	2.11	1.7×10^{-5}
22	3.0×10^{-3}	8.64×10^{-1}	1.9×10^{-6}	8.0×10^{-3}	2.64	2.63	2.6×10^{-5}
23	4.0×10^{-3}	1.15	3.6×10^{-6}	1.0×10^{-2}	3.30	3.29	4.1×10^{-5}
24	5.0×10^{-3}	1.44	5.6×10^{-6}	1.3×10^{-2}	4.29	4.27	6.8×10^{-5}
25	6.4×10^{-3}	1.84	9.2×10^{-6}	1.6×10^{-2}	5.28	5.26	1.0×10^{-4}
26	8.0×10^{-3}	2.30	1.4×10^{-5}	2.0×10^{-2}	6.60	6.56	1.6×10^{-4}
27	1.0×10^{-2}	2.88	2.3×10^{-5}	2.5×10^{-2}	8.25	8.18	2.5×10^{-4}
28	1.3×10^{-2}	3.74	3.8×10^{-5}				
29	1.6×10^{-2}	4.61	5.7×10^{-5}				
30	2.0×10^{-2}	5.76	8.5×10^{-5}				
31	2.5×10^{-2}	7.20	1.5×10^{-4}				
32	3.0×10^{-2}	8.64	2.0×10^{-4}				
33	4.0×10^{-2}	11.50	3.5×10^{-4}				

the task is to "choose" appropriate theoretical curves defined by Eqs (1) and (8). Let us note that the functions r/r_0 and η/η_0 defined by these expressions are related to γ also through the quantity α, which is defined by Eq. (3). Assuming that in the solution there are solely monomers and dimers and the mass action law holds, the dependence of α on γ is uniquely defined, *viz.*,

$$\alpha = \frac{(1+4\gamma K_\gamma)^{\frac{1}{2}}-1}{2\gamma K_\gamma} \tag{14}$$

where K_γ is a dimensionless dimerization constant related to the constant

$$K = C''/C'^2 \tag{15}$$

by

$$K_\gamma = \gamma_{D_{||}}/\gamma_D^2 = \frac{2KC_0'^2}{(\pi\eta_0)^{\frac{1}{2}} \cdot C_0''}. \tag{16}$$

Presented in Fig. 2 are the concentration dependences of r/r_0 and η/η_0 for two different values of K_γ and α_0. The bold continuous lines concern emission anisotropy (*1a*, *2a*) and quantum yield (*1b*, *2b*) for $\alpha_0 = 1$, and the thin continuous lines correspond to $\alpha_0 = 0.9$.

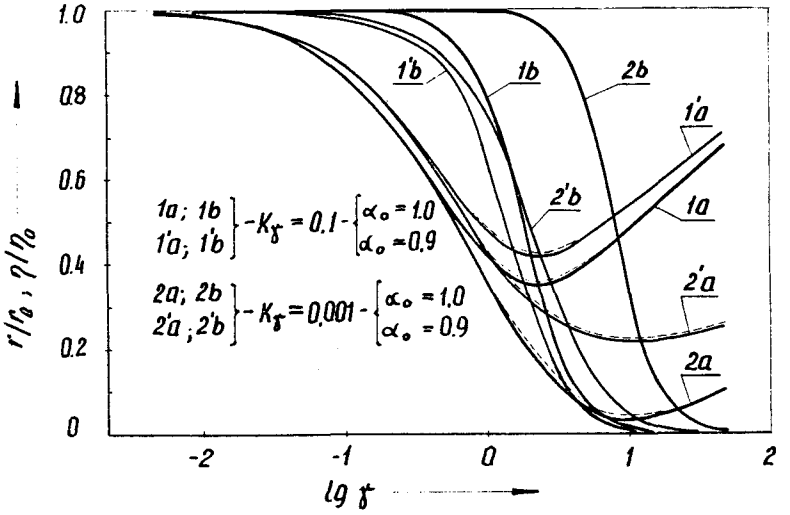

Fig. 2. Theoretical curves of emission anisotropy r/r_0 and quantum yield η/η_0 determined by formulae (1) and (8) for various values of K_γ and α_0

The new CDP theory also predicts a repolarization effect which occurs at lower concentrations (smaller γ) the bigger is the value of K_γ. This effect coincides closely with the strong drop in quantum yield which for larger K_γ occurs at smaller γ (*cf.* curves *1b* and *2b*). The dotted line in the figure depicts the r/r_0 traces corresponding to the expression [1]

$$\frac{r}{r_0} = (1-\varphi)\left[1+\frac{1}{2}\cdot\frac{\varphi^2}{1-\frac{3}{4}\varphi^2}\right] \tag{17}$$

which is obtained from Eq. (1) by formally[5] putting $\overline{Q} = 1/2$. φ has the same meaning as in Eq. (1). It is seen that Eq. (17) is a very good approximation of Eq. (1) in the entire range of concentrations and different values of K_γ. For the examined systems I and II the equilibrium constant K_γ and the parameter α_0 were found by selecting from the family

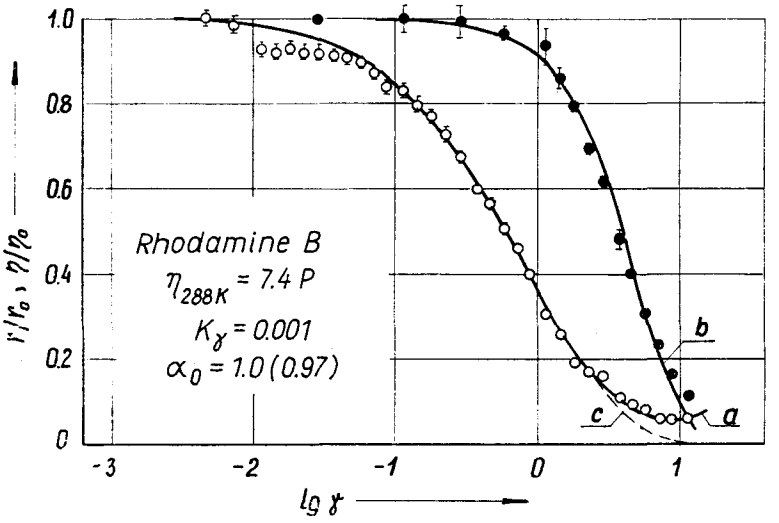

Fig. 3. Concentration-dependence of emission anisotropy r/r_0 and quantum yield η/η_0 of the photoluminescence of glycerol-water solutions of rhodamine B; *a* and *b* — theoretical curves (Eqs (1) and (8)), *c* — theoretical curve (1) with $K_\gamma = 0$ and $\alpha_0 = 1$, ○, ● — experimental values of r/r_0 and η/η_0, I — experimental errors

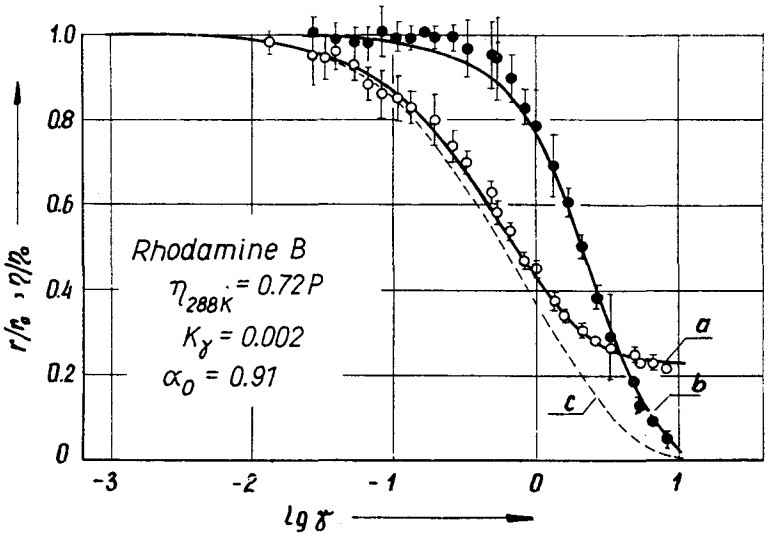

Fig. 4. The same dependences as in Fig. 3 for system II

of theoretical curves corresponding to different K_γ and α_0 those curves which fit the appropriate experimental results best. It must be emphasized that the choice of K_γ and α_0 is not arbitrary, which may be seen from the graphs presented here (*cf.* curves *2a* and *2b*, *2'a* and *2'b*, *etc.*). Hence, experimental data may be fitted to theoretical curves simultaneously only for a definite K_γ and α_0 pair. Knowledge of K_γ, α_0 and the values of the argument γ

[5] It is known that $0.6 < \overline{Q} < 1$ for $x \in (0, \infty)$.

corresponding to the various concentrations C permits experimental data to be compared with theory. In Figs 3 and 4 the experimental results concerning emission anisotropy and quantum yield given in Table I are compared with the theoretical formulae (1) and (8).

The experimental results concerning both systems are in good agreement with theory within the examined ranges of concentrations. In the case of system I (*cf.* Fig. 3), in the small C range the experimental values of r/r_0 lie distinctly below the theoretical curve. A similar effect for glycerine solutions of rhodamine B had been observed by Pheofilov and Sveshnikov [24], and recently Dale and Bauer [25] got the same effect in the case of glycerol-water solutions of Na-fluorescein.

The dashed line in Figs 3 and 4 represents the theoretical r/r_0 values defined by Eq. (1) for $K = 0$ and $\alpha_0 = 1$. This curve corresponds to the case when self-quenching in the solution

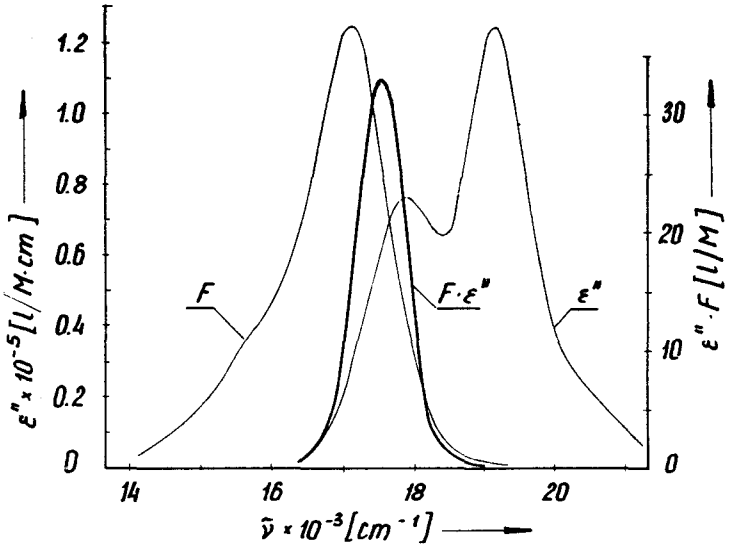

Fig. 5. Absorption spectrum of dimers ε'', quantum fluorescence spectrum F and their product $\varepsilon'' \cdot F$ for an aqueous solution of rhodamine B

is wholly negligible. Its trace is practically identical with that of theoretical curves predicted by other CDP theories which do not account for self-quenching (*cf.* Fig. 1 in Ref. [26]). It is clearly seen that in the range of large γ (large C) the experimental values of r/r_0 deviate considerably from the dashed curve; this is especially true for the system II having a larger K_γ value. The retardation of the depolarization process in the range of high C's is very closely related with concentration quenching. This shows up in the quantum yield *versus* concentration curves. And so, in the case of the system II, having a larger water content, the drop in η/η_0 begins at smaller γ than in the case of system I. There is seen a good agreement of experimental results concerning concentrational changes of quantum yield with the CQP theory for both systems, but for system I this compatibility was achieved for a value $r_0 = 0.97$, somewhat differing from unity used for describing the r/r_0 *vs* concentration relationship of this system. It must be made clear, however, that this compatibility stems from, among other things, the consideration of the multi-stage mechanism of energy transfer from an excited monomer molecule D^* to a dimer molecule $D_{||}$ according to the scheme (9) in the CQP theory.

4. Dimerization constant

We have recently proposed in [27] a method of determining the concentration C' of dimers (thereby the dimerization constant K) based on measurements of r/r_0 and η/η_0 against concentration and comparing the results with expressions (1) and (8). This method had been checked on the example of glycerol-water solutions of rhodamine 6 G, whereby it was found that the values of C'' thus obtained agreed well with those determined on the basis of spectroscopic measurements [28].

It follows from Eq. (16) that when the value of K_γ is known for a given system it is possible to find the dimerization constant K if the values of C_0', η_0 and C_0'' are established. The critical concentration C_0'' could not be determined in a manner similar to that used for finding C_0' (*i.e.* on the basis of relation (11)) because of the very weak dependence of the absorption curves on concentration in the glycerol-water solutions or, in other words, owing to the impossibility of finding the absorption spectra of dimers $\varepsilon''(\nu)$. Notwithstanding, the absorption spectra of rhodamine B in aqeuous solutions demonstrate a strong enough concentration dependence to enable the dimer spectrum $\varepsilon''(\nu)$, thereby C_0'' also, to be determined [20, 29, 30]. Figure 5 presents the absorption spectrum $\varepsilon''(\nu)$ taken from Ref. [20], the fluorescence spectrum F, and their product $F \cdot \varepsilon''$ for an aqueous solution of rhodamine B. Moreover, $\bar{\varepsilon}'$ and C_0' have also been determined. We found the ratio of mean values of absorption spectra, $\varepsilon''/\varepsilon'$, in the region where they overlap the fluorescence spectrum F to be equal to 1.634. Hence, regarding relation (11), we obtained $\kappa_W = C_0'/C_0'' \cong (\varepsilon''/\varepsilon')^{1/2} = 1.278$ with an accuracy to the factor $(\nu'/\nu'')^2$ which is nearly equal to unity. If the value of C_0' for the glycerol-water solution is known directly from the measurements and $\kappa_{GW} = C_0'/C_0''$ is assumed to have the same value for both the glycerol-water and aqueous solutions ($\kappa_{GW} = \kappa_W$), it is possible to find C_0'' for the former solution[6]. Table II gives the found values of C_0'' and C_0' and their corresponding critical distances R_0'' and R_0'. Also given are the values of dimerization constant K determined on the basis of relation (16), whereas in Table III the values of dimer concentration C'' corresponding to these constants are presented. The obtained values of K are very small as compared with the value $K = 1190$ l/M which we found for the aqueous solution of rhodamine B at 288 K. This fact explains the very weak dependence of the absorption spectra on concentration of the examined systems.

5. Final remarks

If the values of the constants C_0', C_0'', η_0 and the concentrations of monomers C' and dimers C'' are known, it is possible to determine the values of γ on the basis of relation (5).

Table III holds the γ values thus calculated for system II, having a larger value of dimerization constant. Even in the range of highest concentrations the values of γ calculated

[6] We have previously used an identical procedure for determining C_0'' for glycerol-water solutions of Na-fluorescein [31].

on the basis of the simplified relation (13) and the relation (5) differ only slightly (the maximum difference does not exceed 1 per cent). This is proof of the adequacy of the approximate relation (13) in the case of the examined systems. For systems featuring large K values, relation (13) ceases to be valid already in the range of moderate concentrations as in the case of glycerol-water solutions of rhodamine 6 G [28]. In the case of such systems, however, determining γ directly from relation (5) does not present any greater difficulties. The experimental results presented in Figs 3 and 4 are in good agreement with the new theory of concentration depolarization and quenching in a wide range of concentrations. It may therefore be supposed that the assumptions accepted in the theory regarding the mechanism of external quenching of photoluminescence are correct, especially as concerns the role of dimers as traps for excitation energy transferred to them in radiationless way from monomers in a single step or many [28, 32]. Still unexplained is the problem of excitation energy quenching when it is transferred between monomers. In the case of the systems examined here it was necessary to assume $\alpha_0 < 1$, which would be proof of an additional mechanism of photoluminescence quenching independent of concentration. To elucidate this problem further research has to be carried out.

This work was supported by the Polish Academy of Sciences within the project 3.2.08.

REFERENCES

[1] C. Bojarski, *J. Lumin.*, **5**, 413 (1972).
[2] E. L. Eriksen, A. Ore, *Phys. Norv.*, **2**, 159 (1967).
[3] D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).
[4] A. Ore, *J. Chem. Phys.*, **31**, 442 (1959).
[5] A. Ore, *J. Chem. Phys.*, **33**, 31 (1960).
[6] Th. Förster, *Fluoreszenz Organischer Verbindungen*, Göttingen 1951.
[7] C. Bojarski, J. Domsta, *Acta Phys. Hungar.*, **30**, 145 (1971).
[8] Th. Förster, *Ann. Phys.* (Germany), **2**, 55 (1948).
[9] V. L. Levshin, V. K. Gorshkov, *Opt. i Spektrosk.*, **10**, 759 (1961).
[10] C. Bojarski, G. Obermüller, J. Kuśba, *Zeszyty Naukowe Politechniki Gdańskiej*, Nr 181, 3 (1971) in Polish.
[11] A. Jabłoński, *CR Seanc. Soc. Pol. Phys.*, **7**, 1 (1926).
[12] A. Bączyński, M. Czajkowski, *Bull. Acad. Pol. Sci. Ser. Sci. Math. Astron. Phys.*, **8**, 651 (1960).
[13] Th. Förster, *Z. Naturforsch.*, **4a**, 321 (1949).
[14] J. Kuśba, *Zeszyty Naukowe Politechniki Gdańskiej*, Nr 191, 91 (1972), in Polish.
[15] J. Dombi, J. Hevesi, R. Horvai, *Acta Phys. Chem. (Szeged)*, **5**, 20 (1959).
16] J. Dudkiewicz, *Zeszyty Naukowe Politechniki Gdańskiej*, No 191, 55 (1972), in Polish.
17] L. A. Tumerman, *Dokl. Akad. Nauk SSSR*, **58**, 1945 (1947).
18] H. Wille, *Optik*, **9**, 84 (1952).
19] J. Dudkiewicz, *Zeszyty Naukowe Politechniki Gdańskiej*, **181**, 121 (1971), in Polish.
20] Th. Förster, E. König, *Z. Elektrochem.*, **61**, 344 (1957).
21] V. L. Levshin, J. G. Baranova, *Opt. i Spektrosk.*, **6**, 55 (1959).
22] M. Z. Maksimov, I. M. Rozman, *Opt. i Spektrosk.*, **12**, 606 (1962).
23] J. N. Demas, C. A. Crosby, *J. Phys. Chem.*, **75**, 991 (19571).
24] P. P. Pheofilov, B. J. Sveshnikov, *Zh. Eksp. Teor. Fiz.*, **10**, 1372 (1940).
25] E. R. Dale, R. K. Bauer, *Acta Phys. Pol.*, **A40**, 853 (1971).

[26] C. Bojarski, J. Dudkiewicz, *Acta Phys. Pol.*, **A42**, 331 (1972).
[27] C. Bojarski, *J. Lumin.*, **5**, 371 (1972).
[28] C. Bojarski, J. Kuśba, G. Obermüller, *Z. Naturforsch.*, **26a**, 255 (1971).
[29] J. E. Selwyn, J. I. Steinfeld, *J. Phys. Chem.*, **76**, 762 (1972).
[30] Jun'ichiro Muto, *Jap. J. Appl. Phys.*, **11**, 1217 (1972).
[31] C. Bojarski, J. Dudkiewicz, *Z. Naturforsch.*, **27a**, 1751 (1972).
[32] C. Bojarski, *Z. Phys. Chem.*, Frankfurt, **75**, 242 (1971).