

ON THE INFLUENCE OF SELF-QUENCHING ON CONCENTRATION DEPOLARIZATION OF FLUORESCENCE

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The range of applicability of the method of determining the effect of self-quenching on photoluminescence anisotropy proposed by Eriksen (*Phys. Norveg.*, 2, 203 (1967)) is discussed. It is shown that it may be used only in the case of luminescing systems for which concentration quenching is small.

1. Introduction

The problem of providing a theoretical description of concentration depolarization of photoluminescence (CDP) of isotropic solutions has been dealt with in a number of papers. Eriksen and Ore [1, 2] and Knox [3] have recently reviewed the existing CDP theories and discussed in detail the various simplifying assumptions accepted in them; they also proposed new improved versions of the theories. But in all of these theories concentration quenching is either entirely disregarded or taken into account in an approximate fashion¹ [5-9].

Lately, several more theoretical papers have appeared [10-13], in which attempts are made to take account of the influence of concentration quenching on the observed emission anisotropy. Despite the doubtless progress achieved in these papers, the CDP theory requires yet further improvement because of the necessity of getting a more complete description of both the self-quenching effect² and remigration of energy to D_0 molecules which are the initial absorbers of the exciting light.

Since solving this problem without introducing essential simplifying assumptions into the theory does not appear to be possible, it is worthwhile to turn our attention to an approach proposed not long ago by Eriksen [14]. Namely, he gave a method which allows the effect of self-quenching on fluorescence polarization to be estimated. In sub-

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¹ A detailed discussion on the CDP theory relating to concentration quenching of photoluminescence can be found in Ref. [4].

² This concerns above all the acceptance of definite mechanisms of external quenching in the CDP theory.

stance, it consists in calculating the corrected value of polarization p' which corresponds to the case when there is no self-quenching in the solution. If p and η denote the degree of polarization and quantum yield of the photoluminescence at a given concentration C , and η_0 the quantum yield at $C \rightarrow 0$, then according to Eriksen

$$p' = \frac{3p\eta/\eta_0}{3 - [1 - \eta/\eta_0] \cdot p} \quad (1)$$

If use is made of emission anisotropy r [15] instead of the degree of polarization p , then relation (1) can be rewritten in the simpler form

$$\frac{r'}{r_0} = \frac{r}{r_0} \cdot \frac{\eta}{\eta_0}, \quad (2)$$

where r' and r correspond to p' and p , whereas r_0 corresponds to the fundamental degree of polarization p_0 . r'/r_0 and r/r_0 denote the relative emission anisotropies without and with self-quenching taken into account, respectively. Relation (2) describes Eriksen's method very simply. Namely, in order to obtain the relative value r'/r_0 of emission anisotropy without any self-quenching effects, it suffices to multiply the values of r/r_0 and η/η_0 together; these values have to be obtained from direct measurements at the same value of c . If Eriksen's method is correct, then the values of r'/r_0 found on the basis of relation (2) may be compared with the CDP theory in its simplest form, *i.e.* when the self-quenching effect is disregarded. On the other hand, if in relation (2) we put in the place of r'/r_0 and η/η_0 the proper theoretical expressions describing the concentration-dependence of r'/r_0 and η/η_0 , the expression for r/r_0 obtained thus should describe the concentration-induced changes in emission anisotropy with self-quenching accounted for. The expression for r/r_0 obtained in this way (*cf.* Eq. (9)) will be further regarded as one corresponding to Eriksen's method, in contradistinction to the expression for r/r_0 following from the general CDP theory (*cf.* Eq. (3)).

When deriving relation (1) it was assumed that the intensity of the fluorescence emitted by D_0 molecules is unperturbed by any possible quenching in the sense that in any event "excitations" actually quenched do not become emitted in the form of light by D_0 molecules when there is no self-quenching in the solution. As this assumption does not seem to be fully justified, we shall analyze the range of applicability of the method in this paper. We shall also compare the expression for r/r_0 obtained within the framework of Eriksen's method with that obtained in the new CDP theory, *i.e.* the expressions (9) and (3).

2. The effect of self-quenching on emission anisotropy

We have recently presented a CDP theory which takes account of concentration quenching and remigration of excitation energy. Within the framework of this theory we obtained the following expression for emission anisotropy [16]:

$$\frac{r}{r_0} = (1 - \alpha_0 \alpha f) \left[1 + \frac{1}{2} \cdot \frac{(\alpha_0 \alpha f)^2}{1 - \frac{3}{4}(\alpha_0 \alpha f)^2} \right] \quad (3)$$

where

$$\alpha = \frac{\gamma_D}{\gamma_D + \gamma_{D_{11}}} \quad (4)$$

$$f = f(\gamma) = \sqrt{\pi} \gamma \exp(\gamma^2) \left[1 - \frac{2}{\sqrt{\pi}} \int_0^\gamma \exp(-t^2) dt \right] \quad (5)$$

and

$$\gamma = \gamma_D + \gamma_{D_{11}} = \frac{\sqrt{\pi} \eta_0}{2} \left[\frac{C'}{C'_0} + \frac{C''}{C''_0} \right]. \quad (6)$$

α_0 is a constant independent of concentration, C' , C'' and C'_0 , C''_0 are the concentrations of D monomers and D_{11} dimers and their critical concentrations, respectively, and η_0 is the photoluminescence quantum yield when $C'' \rightarrow 0$.

At the same time, the quantum yield of photoluminescence as a function of solution concentration was given as [10]

$$\frac{\eta}{\eta_0} = \frac{1-f}{1-\alpha_0 \alpha f} \quad (7)$$

where α and f have the same meaning as before.

When deriving expressions (3) and (7) it was assumed that the non-luminescing dimers in the solution are responsible for concentration quenching.

The studies described in Refs [11, 17, 18] show that expressions (3) and (7) give good account of the experimental data concerning the photoluminescence of glycerolic-aqueous solutions of rhodamine 6G.

We may therefore describe the concentration-dependence of r/r_0 (with account taken of self-quenching) on the one hand by means of relation (3), and on the other by means of expression (2), providing the expressions for r'/r_0 and η/η_0 are known in the latter case.

If in Eq. (3) we put $\alpha \cdot \alpha_0 = 1$, *i.e.* we assume that $\alpha_0 = 1$ and $\gamma_{D_{11}} = 0$ (compare Eq. (4)), then for r'/r_0 we get

$$\frac{r'}{r_0} = \frac{r'}{r_0}(\gamma_D) = [1-f(\gamma_D)] \left\{ 1 + \frac{1}{2} \frac{[f(\gamma_D)]^2}{1-\frac{3}{4}[f(\gamma_D)]^2} \right\}. \quad (8)$$

The acceptance of $\gamma_{D_{11}} = 0$ means disregarding the occurrence of dimers in the solution ($C'' = 0$, *cf.* Eq. (6)), whereas $\alpha_0 = 1$ means neglect of the quenching of excitation at its radiationless transfer between monomers. Expression (8), hence, describes the concentration-dependence of emission anisotropy r'/r_0 with neglect of quenching.

Considering expressions (8) and (7), together with $\gamma_D = \alpha \cdot \gamma$ (on the basis of (4) and (6)), in relation (2) yields³

$$\frac{r}{r_0} = \frac{r'}{r_0} (\gamma_D) \frac{\eta_0}{\eta} (\gamma) = [1 - f(\alpha\gamma)] \left\{ 1 + \frac{1}{2} \frac{[f(\alpha\gamma)]^2}{1 - \frac{3}{4}[f(\alpha\gamma)]^2} \right\} \frac{1 - \alpha f(\gamma)}{1 - f(\gamma)}. \quad (9)$$

Figure 1 shows expressions (3) and (9) for several values of dimerization constant⁴ K_γ and $\alpha_0 = 1$. Only in the case of extremely weak self-quenching, $K_\gamma = 0.001$, do expressions (3) and (9) give in practice the same values of r/r_0 in the entire range of concentrations (curves a_1 and b_1) which are close to values of r'/r_0 corresponding to the case when quench-

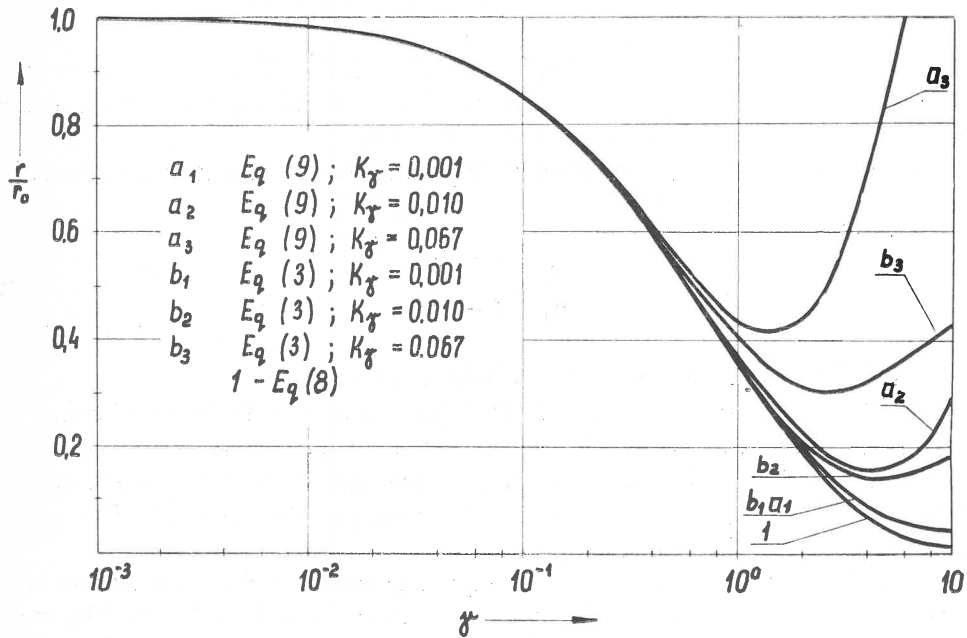


Fig. 1. Concentration-dependence of anisotropy emission of photoluminescence for various values of dimerization constant K_γ

³ In the case of luminescing systems having a small dimerization constant K_γ (compare footnote 4), the replacement of the argument $\alpha\gamma$ by γ in r'/r_0 bears no practical effect on the value of r'/r_0 . For example, for $K_\gamma = 0.01$ the maximum difference in the value of r'/r_0 calculated with $\alpha\gamma = (-1 + \sqrt{1 + 4K_\gamma\gamma})/2K_\gamma$ and γ does not exceed 0.008 in the range $0 \leq \gamma \leq 10$. But for $K_\gamma = 0.067$ this maximum difference in r'/r_0 reaches a value of 0.05 for $\gamma \in \langle 0, 10 \rangle$.

⁴ The dimensionless constant K_γ is associated with the equilibrium constant in the process of dimer formation, $K = C''/C'^2$, through the relation

$$K_\gamma = \gamma_{D_{11}}/\gamma_D^2 = 2KC_0^2D/\sqrt{\pi\eta_0} \cdot C_{0D_{11}}.$$

ing is totally disregarded (curve 1). At higher values of K_2 the runs of r/r_0 given by expressions (3) and (9) differ considerably, especially at high concentrations and large values of K_2 . But it is seen that the curves a_2 and a_3 corresponding to Eriksen's method provide r/r_0 values which are distinctly higher than for the curves b_2 and b_3 .

3. Comparison with experimental data and discussion

Eriksen compared his proposed method of calculating "corrected" p' values with some experimental results of Feofilov and Sveshnikov [19] and Szalay *et al.* [9]. For r'/r_0 appearing in relation (2) he used expressions obtained from the Förster-Ore theory [20, 21] and the Jabłoński theory [22, 23], whereas for η/η_0 he adopted the proper experi-

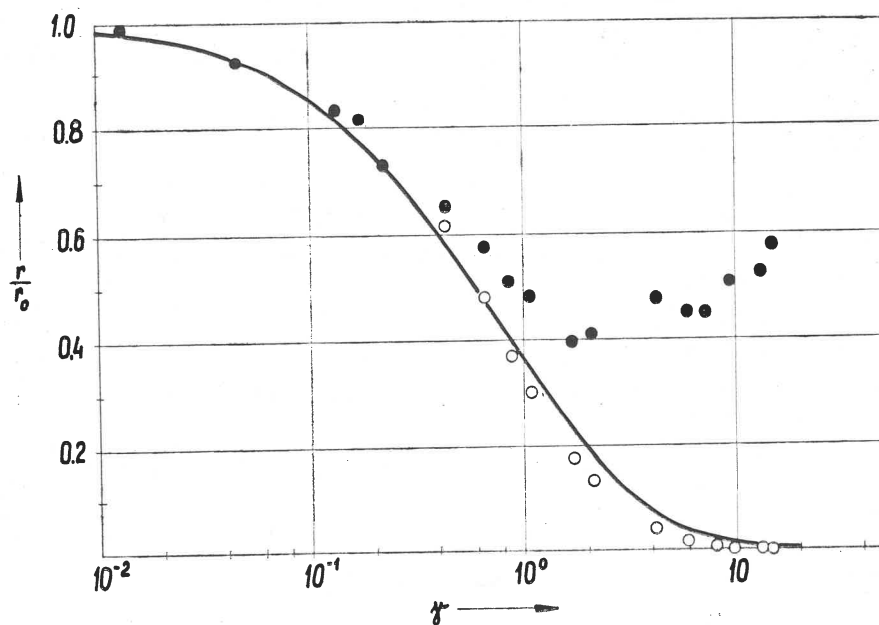


Fig. 2. Emission anisotropy of photoluminescence of rhodamine 6G in glycerolic-aqueous solution as a function of γ . ● — experimental values of r/r_0 , ○ — experimental values of r'/r_0 "corrected" on the basis of Eq. (2) and experimental values of η/η_0 adopted from Ref. [18], — — — theoretical curve of Eq. (8). γ -values were computed from Eq. (6) for $\eta_0 = 0.6$ (cf. [16,17])

mental values. The agreement of the theory in mention and experimental data was found to be good, except for the case of tryptaflavine in glycerol [14].

It should be stressed that the found adequacy of this method in the case of glycerolic solutions of Na-fluorescein, rhodamine B and yellowish eosine concerned luminescent solutions of very low self-quenching in the range of concentrations involved in the emission anisotropy measurements. This statement is supported in all of the examined cases by

the large drops in r/r_0 at the highest concentrations, which generally do not exceed 10^{-2} M (except for the data of Szalay [9]). The smallest r/r_0 values (of the order of 0.1) found in these cases show that in the examined systems the dimerization constant probably did not exceed the value $K_\gamma = 0.01$ (cf. the curves in Fig. 1). The r/r_0 curves corresponding to expressions (3) and (9) then differ only slightly (curves a_1 and b_1 or a_2 and b_2), especially when the range of concentrations is not very large (to the values $\gamma = 10$ of Fig. 1 correspond concentrations of $C \cong 10 C_0$ which considerably exceed the maximum values $C = 10^{-2}$ M at which the r/r_0 values were measured).

Figure 2 gives a comparison of the experimental results concerning concentration depolarization of the photoluminescence of rhodamine 6G in glycerolic-aqueous solution adopted from Ref. [17]. The strong concentration quenching in this system leads to a repolarization of fluorescence in the region of high concentrations. This quenching is conditioned in this case by the radiationless transfer of excitation energy from D monomers to non-luminescing $D_{||}$ dimers, the occurrence of which in the examined solutions has already been established [18]. It was also shown that the experimental r/r_0 values can be described well by expression (3) [11, 16].

The values of r'/r_0 corrected by Eriksen's method and the theoretical curve given by expression (8) are also presented in Fig. 2. It is seen here that the corrected r'/r_0 values are systematically underrated relative to the theoretical curve for $\gamma > 1$. For the highest concentrations the agreement between the corrected r'/r_0 values and the theoretical curve appears to be better. This is only apparent, however, because the r/r_0 values in this range of concentrations are very small.

The same results are presented in Fig. 3 in a bilogarithmic scale. We see that the deviation of the corrected experimental points from the theoretical curve systematically increases when γ increases. For systems having a bigger equilibrium constant K_γ , these differences would be even greater still.

What is the cause of this large difference in r/r_0 values predicted by Eriksen's method in terms of Eq. (9) and our CDP theory in the form of expression (3), especially in the range of high concentrations C and for large values of equilibrium constant K_γ ? We think that the reason why this difference occurs should be sought in the improper assumption of Eriksen that the possible quenching does not hamper the fluorescence emitted by a D_0 molecule. He argues that 1° remigration of excitation energy to D_0 molecules requires this energy to remain in the immediate neighbourhood of the D_0 molecule, and 2° in the high-concentration range at which self-quenching is observed the excitation energy may depart from the D_0 molecule considerably due to numerous intermolecular jumps, thereby rendering remigration of this energy back to D_0 molecules rather improbable. These arguments are clearly qualitative and rather unconvincing. As far as concerns argument 1°, it is primarily justified in the range of low concentrations, as then the mean intermolecular distances are large and energy migration is feasible only between the D_0 molecule and its nearest neighbour. In the high concentration region, on the other hand, there exists in truth a large possibility that multi-step excitation transfer may take place, but also the chance that the energy may return to D_0 is considerable. This point of view is confirmed by investigations on the concentration-dependence of emission anisotropy involving

excitation remigration accounted for in various degrees in the CDP theory (cf. Fig. 4 of Ref. [16]⁵).

We have demonstrated here that the CDP theory in the form of expression (3) in general predicts a different shape of the dependence of r/r_0 on concentration than does the expression (9). It is shown in the discussion that the method of calculating corrected values of p' may be used only in the case of luminescing systems in which concentration quenching is very small (small value of K_q and not too high C).

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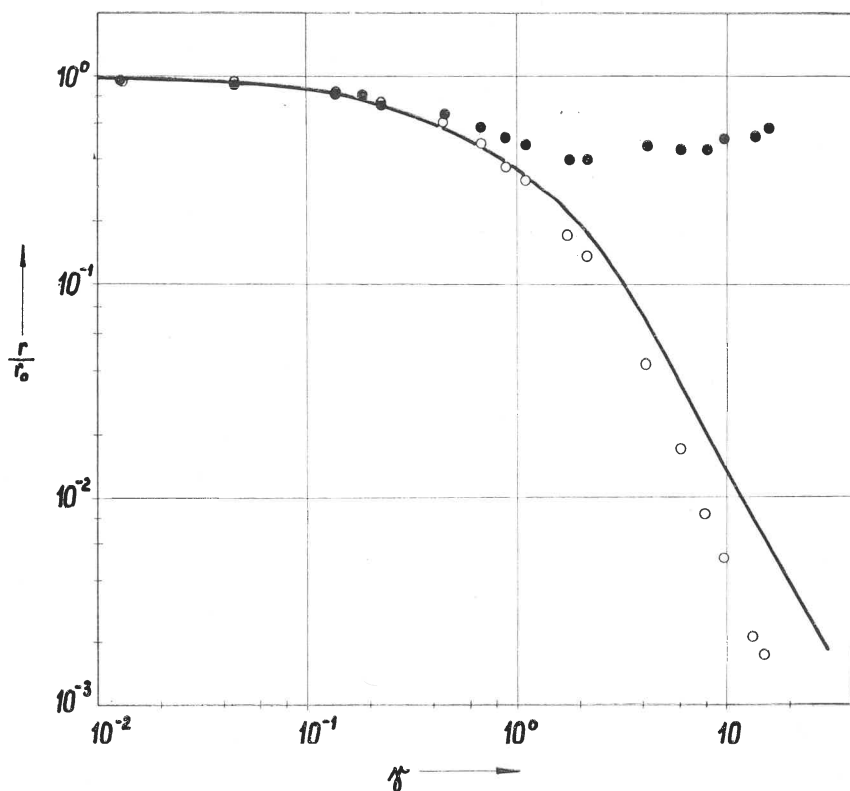


Fig. 3. The same results as in Fig. 2 in bilogarithmic scale

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