

THE INFLUENCE OF ENERGY MIGRATION IN MICELLAR DYE SOLUTIONS ON THE PERFORMANCE OF DYE LASERS*

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Results of investigations of luminescence and laser properties of Rhodamine 6G in water solutions with Triton X-100 admixture are given. It is shown that the energy transfer between dye molecules in a micelle is a main process by which excitation energy can migrate to molecules properly oriented (for the dye laser generation). The rate of energy migration decreases whereas the yield of fluorescence increases with increasing detergent concentration each influencing the laser generation in opposite directions. A method of determining the optimal detergent concentration is given.

1. Introduction

Measurement of the degree of polarization of luminescence of dye molecules in solutions can provide information about the efficiency of processes leading to random directional distribution of emission oscillators. Knowledge of these processes is important especially for dye laser technique. The induced emission in a dye laser introduces strong directional anisotropy of emission oscillators. Processes leading to the decrease of this anisotropy, such as rotational Brownian movements, energy migration and others, when they are fast enough, may improve the efficiency of laser generation.

The aim of this paper is to present results of investigations of processes responsible for the relaxation of the directional anisotropy of dye molecules in water-detergent solutions especially under the conditions when micelles are formed. In lasing dye solutions, detergents are added to prevent dye molecules from dimerization. This makes the laser generation more efficient [1-3]. Water solutions of Rhodamine 6G with the admixture of Triton X-100 ($C_8H_{17}O(CH_2CH_2O)_{10}H$) were investigated. The anisotropy of emission¹ and the

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¹ Emission anisotropy is defined as the ratio $(I^{\parallel} - I^{\perp}) / (I^{\parallel} + 2I^{\perp})$ where I^{\parallel} and I^{\perp} are the intensities of the emitted light components whose electric vectors are, respectively, parallel and perpendicular to the electric vector of the exciting light ray.

yield of fluorescence versus dye and detergent concentrations were measured. In addition, the intensity of generation of a dye laser with such an active medium was determined. The main result of these investigations is the determination of physico-chemical conditions in which the energy migration is an efficient process leading to the depolarization of photoluminescence. Furthermore it was shown, how from investigations of fluorescence anisotropy the number of detergent molecules in one micelle may be found.

2. Experimental

Measurements of emission anisotropy were carried out using the method given in [4]. To prevent reabsorption, thin cuvettes were used. Results of measurements are illustrated in Fig 1. It can be seen, that in solutions without detergent molecules or with a concentration of detergent molecules below the critical concentration, the emission anisotropy is

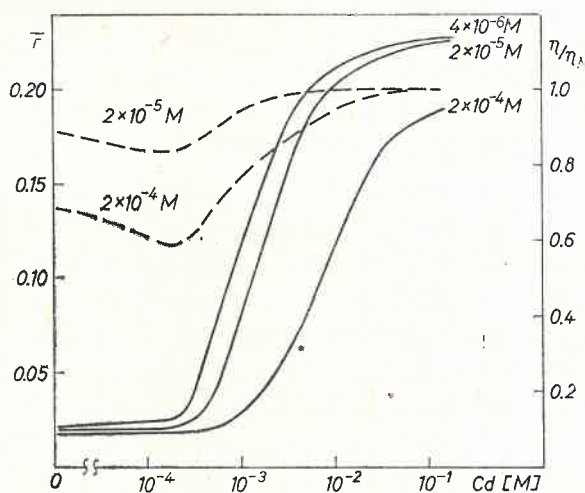


Fig. 1. Anisotropy (solid lines) and relative yield (broken line) of the fluorescence of Rh 6G solutions versus the concentration of Triton X-100, for different dye concentrations

very small. When the concentration of detergent molecules increases above the critical value², the emission anisotropy increases too, depending on the concentration of dye molecules. When the concentration of detergent molecules is fixed above its critical value (which for Triton X-100 equals 3×10^{-4} M) the fluorescence anisotropy decreases with an increase in dye molecules, which is well known as a concentrational depolarization.

Yields of fluorescence in relation to the yield of fluorescence of solutions with detergent concentration $C = 1.5 \times 10^{-1}$ M were measured. The increase in this concentration does not influence the yield of fluorescence of the solutions any more (Fig. 1). In the region of critical concentration of detergent molecules non fluorescent complexes consisting

² Critical concentration of the detergent is a concentration below which no micelles exist in solution. For a concentration higher than critical, detergent molecules form micelles.

of detergent and dye molecules are formed [5] and this is an explanation of the minimum of the yield in this region. When the investigated solutions are active media of dye lasers, the energy of the laser output could be determined. The results of such measurements with flash lamp excitation are illustrated in Fig. 2.

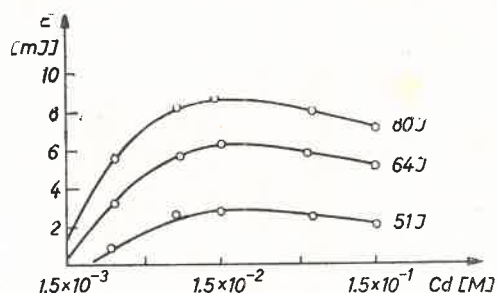


Fig. 2. Output energy of the Rh 6G dye-laser versus the concentration of Triton X-100, by different energies of pumping pulses

3. Interpretation

a. Characteristics of the solution

When the concentration of Triton X-100 in water solution exceeds its critical value, spherical micelles are formed [6, 7]. It was experimentally shown [6-8] that the Stokes diameter (extrapolated to small concentrations) of such micelles is about 96 Å, and this value is approximately constant for each micelle present in the solution. This result is consistent with the chain length of a detergent molecule which is equal to 43 Å [6]. The hydrophobic part of the detergent molecule is directed to the inside of the micelle, the polar group — (CH₂CH₂O) — which is hydrophilic is directed to the outside, to water. Rhodamine 6G molecules, which possess hydrophobic groups tend to be incorporated in micelles. There are some concentrations of detergent and dye molecules for which to a good approximation one can assume, that all dye molecules introduced to the solution are incorporated in micelles.

Micelles can be thought of as a species of high viscosity in which the rotational Brownian motions of dye molecules, are seriously quenched. Rotational Brownian motion of a micelle as a whole does not have to be taken into account in connection with depolarization of luminescence because of their rather high dimensions.

b. Emission anisotropy

The influence of rotational Brownian motions of micelles with trapped dye molecules on fluorescence anisotropy may be evaluated using the Perrin formula [9]

$$\bar{r} = \frac{\bar{r}_p}{1 + \varphi\tau} \quad \text{with} \quad \varphi = \frac{kT}{\eta v}, \quad (1)$$

where \bar{r} is the mean value of anisotropy observed under stationary conditions of excitation, \bar{r}_p — anisotropy in the case of absence of rotational depolarization, v — the volume of the micelle, η — viscosity of water and τ — fluorescence life-time. Introducing in formula (1) for v the volume of the sphere of diameter 96 Å, for the viscosity of water $\eta = 0.01 p$ and for the fluorescence mean life-time $\tau = 5.8 \times 10^{-9}$ s, we obtain $\bar{r}/\bar{r}_p = 0.95$ at room temperature. Though, the rotational Brownian motion of a micelle in water does not play any significant role.

When we assume that for concentrations of detergent well above the critical concentration, all dye molecules are trapped in micelles, then the energy transfer between dye molecules in one micelle is expected to be the main depolarizing mechanism. For a fixed concentration of detergent the increase of the concentration of dye molecules will lead to an increase in the number of dye molecule in one micelle. Because the dimensions of one micelle are rather small, the energy transfer between two molecules in one micelle is highly probable.

Among the known theories of concentrational depolarization of fluorescence of solutions [10–15] the most suitable in our case seems to be the theory developed by Jabłoński [10, 11]. If we assume, that some dye molecules in different micelles are distributed statistically and that the probability of energy transfer between all dye molecules in one micelle is the same and that there is no energy transfer between different micelles, then the conditions for using Jabłoński's theory are fulfilled. In this case, and under additional assumptions, that radiation, and radiationless transition rates, are independent of the number of dye molecules in a micelle, and that only light emitted from primarily excited molecules is polarized, the mean emission anisotropy is given by the formula [10],

$$\bar{r} = \bar{r}_0 e^{-v} \sum_{k=1}^{\infty} \frac{v^{k-1}}{(k-1)!} \left(\frac{1}{k} + \frac{k-1}{k} \frac{1}{k\Gamma\tau+1} \right), \quad (2)$$

where Γ is the probability of energy transfer between two dye molecules in one micelle, and v — average number of dye molecule in a micelle. Denoting by C_b and C_d the molar concentrations of dye molecules and detergent molecules in solution one gets

$$v = \frac{C_b}{C_d} N, \quad (3)$$

N being the number of detergent molecules in one micelle. In the particular case when $\tau^{-1} = \Gamma$, the formula (2) transforms to³

$$\bar{r} = 2\bar{r}_0 \frac{e^{-v} + v - 1}{v^2}. \quad (4)$$

Fig. 3 presents the dependence of \bar{r} versus v according to formula (4) (solid line). The extrapolation of measured values of emission anisotropy to small dye concentrations gives

³ Although the diameter of the micelle is higher than Förster's radius for dipole-dipole energy transfer between two Rhodamine 6G molecules (which is about 52 Å) still the assumption that $\tau^{-1} \approx \Gamma$ may be reasonable because the mean distance between two dye molecules incorporated in micelle is less than the diameter of a micelle.

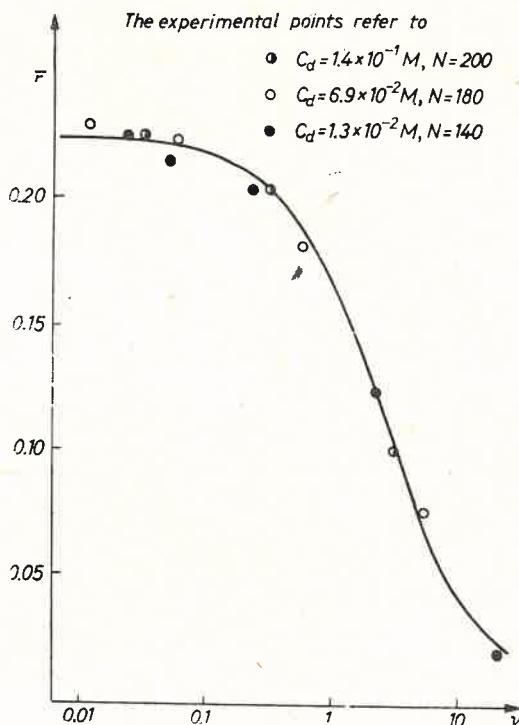


Fig. 3. The dependence of the emission anisotropy \bar{r} versus ν calculated from Eq. (4) — solid line

$\bar{r}_0 = 0.224$. Experimental points indicated in Fig. 3 are obtained for different dye and detergent concentrations. Numerical values of ν are obtained using formula (3). The number of detergent molecules N in one micelle increases slightly with an increase in the concentration of detergent molecules [16]. The value of N was determined by fitting experimental points to the theoretical curve. Obtained in such a way values of N for several detergent concentrations are given below:

$C_d[M]$	1.3×10^{-2}	6.9×10^{-2}	1.4×10^{-1}
N	140	180	200

These results are consistent with those obtained in [6-8].

It can be seen in Fig. 3 that for ν in the range $10^{-2} - 10$ experimental points fit the theoretical curve. This holds for detergent concentrations above $10^{-2} M$, when the micelles are well shaped. This result leads to an other conclusion, that the theory of concentrational depolarization developed by Jabłoński is a good tool for investigating the energy migration in micellar systems. It is to be noted, that when the concentration of the detergent molecules approaches the critical value or is lower than this value, the experimental points do not fit the theoretical curve with the assumptions used. In this case the dye molecules are in a water environment, not trapped in micelles if there are any.

Based on the results given in Fig. 3 an estimation of the rate of energy transfer between dye molecules in a micellar system can be obtained. One reads that for $\nu = 2.5$ the emission anisotropy $\bar{r} = \frac{1}{2}\bar{r}_0$ (\bar{r}_0 should be observed when no migration takes place) which means that when on the average in one micelle there are 2.5 dye molecules, half of all emitting molecules were excited via energy migration.

Experimentally obtained laser generation energy versus detergent concentration given in Fig. 2 illustrates how the energy migration matters in laser generation. Initially the generation energy increases with an increase in detergent concentration, and then with further increase in this concentration, in spite of increase in the fluorescence yield, the generation energy begins to decrease. Such behaviour seems to be a result of a compromise between the positive action of the increase in fluorescence yield and the negative effect of the lack of energy migration. In this case only part of the excited molecules possess proper directional orientation and no energy transfer from the other absorbing molecules takes place. In the case presented in Fig. 2 the optimal value of the detergent concentration is $C_d = 1.5 \times 10^{-2}$ M for dye concentration 2×10^{-4} M.

Because the emission anisotropy depends only on ν , for all equal values of $(C_d/C_b)N$ the energy migration should act similarly. As a result, when the optimal value of ν for a given dye concentration is found experimentally, one can calculate the optimal concentrations of detergent molecules for different dye concentrations.

4. Summary

Measurements of fluorescence yield, emission anisotropy and laser energy of water solutions of Rhodamine 6G with Triton X-100 admixture, were performed. The aim of these investigations was to find physico-chemical conditions under which the orientations of emission oscillators tend to uniform directional distributions. Analysis of results of these investigations leads to the conclusion that the only factor effectively acting in this direction is the energy migration between molecules present in micelles, when the concentration of detergent is high above its critical value. The quantitative description of the anisotropy of fluorescence of dye solution in such a case can be performed from the standpoint of the concentrational depolarization theory of Jabłoński with the additional assumption that luminescence centers may be identified with micelles.

Investigations of laser generation of water-detergent solutions of dye molecules indicate that there exists a distinct maximum of laser action efficiency for a given concentration of detergent admixture. This effect is the result of a competition between the increase of fluorescence yield with the increase of detergent concentration (a factor positive for laser generation), and the decrease of the "efficiency" of energy migration to dye molecules properly oriented in a given cavity. The rate of energy migration depends only on the average number of dye molecules in one micelle. It is concluded, that when the optimal concentration of detergent for a given concentration of dye in solution is found experimentally, proper concentrations of detergent for other dye concentrations can be evaluated.

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