

Energy Transfer in Dye Solutions of Micellar Structure

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A theoretical description of micellar dye solutions containing donors and acceptors is developed. It is proved experimentally that the luminescent characteristics of Water-Triton X-100 solutions of Coumarine 1 as a donor and Rhodamine 6G as an acceptor are consistent with the proposed theory. It is shown that the probability of energy transfer between dye molecules and the number of detergent molecules in a micelle may be obtained.

1. Introduction

It is well known that dye solutions change their characteristics when detergents are added. Detergent molecules above a critical concentration constitute micelles in aqueous solutions. These micelles are shaped differently depending on the kind of detergent and solvent. Spherical, ellipsoidal or lamellar micelles have been recognized [1–3]. The polar part of the detergent molecule is directed towards the water phase and the nonpolar part towards the center of the micelle building a hydrocarbon core. Some detergents, e.g. Ammonyx LO, Triton X-100, Sodium Dodecyl Sulfate and others are used as disintegrating agents in dye solutions and are widely used in laser technology to increase the efficiency of dye lasers [4–7]. This disintegration is due to the tendency of dye molecules to penetrate into detergent micelles. Physicochemical conditions can be found in which all dye molecules are embedded in micelles [8].

Under such conditions micelles can be treated as microregions where the dye concentration is higher than in the solution as a whole. In these circumstances the probability of energy transfer between dye molecules is highly increased. Micellar solutions were also used as model systems in investigations of photosynthesis [9, 10]. From the practical point of view, e.g. of laser technology, it is important to form micellar dye solutions of desired properties. For this a mathematical description of such systems is necessary.

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The aim of this paper is to give a description of micellar dye solutions containing two kinds of dye molecules, one being a donor (D) and the other an acceptor (A) of excitation energy. The micelles with incorporated dye molecules are thought as luminescent centers and Jabłoński's theory of the quenching of luminescence [11, 12] is used. It is to be noted that the luminescence centers in micellar dye solutions are real physical objects of well defined shape.

The presented theory is proved to be correct for aqueous solutions of Coumarine 1 as donor, Rhodamine 6G as acceptor and Triton X-100 as detergent at various concentrations. It is shown that the probability of donor-acceptor energy transfer, the mean distance between donor and acceptor and the number of detergent molecules in a micelle can be determined.

2. Theoretical

We consider a dye solution with detergent molecules of supercritical concentration, where the structure of the micelles is well defined. In the volume V of the solution there are \mathcal{N} micelles, N_A acceptors and N_D donors. We assume that the acceptor and donor molecules are randomly and independently distributed between micelles. On the basis of experimental data [13–15] we assume that the micelles are of a similar size. The probability that in a micelle there are n_A acceptor and n_D donor molecules is then given by

$$P(n_A, n_D) = \mathcal{N}^{-N_A} \binom{N_A}{n_A} (\mathcal{N} - 1)^{N_A - n_A} \cdot \mathcal{N}^{-N_D} \binom{N_D}{n_D} (\mathcal{N} - 1)^{N_D - n_D} \quad (1)$$

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with

$$\sum_{n_A=0}^{N_A} \sum_{n_D=0}^{N_D} P(n_A, n_D) = 1. \quad (2)$$

It is easy to show that when

$$\mathcal{N} \gg 1, \quad N_A \gg n_A, \quad N_D \gg n_D, \quad (3)$$

then (1) reduces to

$$P(n_A, n_D) \approx \exp[-(v_A + v_D)] \frac{v_A^{n_A} v_D^{n_D}}{n_A! n_D!}, \quad (4)$$

which is known as Smoluchowski's formula [16].

In this formula v_A and v_D are the mean values of the number of acceptor and donor molecules in one micelle, that is

$$v_A = N_A/\mathcal{N}, \quad v_D = N_D/\mathcal{N}. \quad (5)$$

The probability that an absorbed photon will cause the excitation of a donor or acceptor molecule in a micelle is given by

$$G_A(n_A, n_D) = \frac{E_A n_A}{E_A v_A + E_D v_D} P(n_A, n_D), \quad (6)$$

$$G_D(n_A, n_D) = \frac{E_D n_D}{E_A v_A + E_D v_D} P(n_A, n_D), \quad (7)$$

where

$$E_A = (\int I(\tilde{r}) \sigma_A(\tilde{r}) d\tilde{r}) / (\int I(\tilde{r}) d\tilde{r}), \quad (8)$$

$$E_D = (\int I(\tilde{r}) \sigma_D(\tilde{r}) d\tilde{r}) / (\int I(\tilde{r}) d\tilde{r}), \quad (9)$$

$I(\tilde{r})$ is the intensity of the excitation and $\sigma_A(\tilde{r})$ and $\sigma_D(\tilde{r})$ are the cross sections for the absorption of donor and acceptor molecules, respectively. In the case of monochromatic excitation the expressions (8) and (9) reduce to $E_A = \sigma_A$, $E_D = \sigma_D$.

The existence of two excited molecules in one micelle is excluded. That means that low intensity excitation is assumed. More, if nearly all dye molecules are incorporated in micelles and the mean distance between micelles is large enough, the energy migration outside a micelle can be neglected. Also the reabsorption process as mechanism of energy transfer between dye molecules can be neglected if thin layers are used.

In this paper we discuss the intensity of fluorescence, but not its polarization. Three possibilities have to be considered:

1. Primary excitation of a donor molecule and emission from one of the donor molecules.

2. Primary excitation of a donor molecule and emission from an acceptor molecule.
3. Primary excitation of an acceptor molecule and emission from an acceptor molecule.

Energy transfer $A \rightarrow D$ has not been considered. It is evident that energy transfers $D \rightarrow D$ and $A \rightarrow A$ do not influence the emission spectrum of the solution but are important in the discussion of the polarization of luminescence.

Let $\eta_{DD}(n_A, n_D)$, $\eta_{DA}(n_A, n_D)$ and $\eta_{AA}(n_A, n_D)$ be averaged quantum efficiencies of fluorescence as functions of the amounts of donors and acceptors in the micelles (n_A, n_D) , corresponding to the cases 1, 2 and 3, respectively. Then the following expressions for observed yields of fluorescence of donor and acceptor molecules are obtained:

$$\Phi_D = \sum_{n_A=0}^{N_A} \sum_{n_D=0}^{N_D} G_D(n_A, n_D) \eta_{DD}(n_A, n_D), \quad (10)$$

$$\Phi_A = \sum_{n_A=0}^{N_A} \sum_{n_D=0}^{N_D} [G_A(n_A, n_D) \eta_{AA}(n_A, n_D) + G_D(n_A, n_D) \eta_{DA}(n_A, n_D)]. \quad (11)$$

To take into account various configurations of molecules in isotropic dye solutions several methods were developed [12, 17–25]. The Jabłonski's method [12] can be easily adopted for micellar solutions. The starting point is a system of differential equations describing probabilities of localization of excitation in different dye molecules in a micelle:

$$\begin{aligned} \dot{P}_i^D(t) = & - \left(\gamma_D + q_D + \sum_{j=1}^{n_D} \mu_{ij} + \sum_{k=1}^{n_A} \mu'_{ik} \right) P_i^D \\ & + \sum_{j=1}^{n_D} \mu_{ji} P_j^D, \quad i = 1, 2, \dots, n_D, \end{aligned} \quad (12a)$$

$$\begin{aligned} \dot{P}_l^A(t) = & - \left(\gamma_A + q_A + \sum_{j=1}^{n_A} \mu''_{lj} \right) P_l^A \\ & + \sum_{j=1}^{n_A} \mu'_{jl} P_j^D + \sum_{j=1}^{n_A} \mu''_{jl} P_j^A, \\ & l = 1, 2, \dots, n_A, \end{aligned} \quad (12b)$$

where p_i^D , p_l^A are probabilities of localization of energy at the time t (after excitation) in a donor and acceptor molecule, respectively, where the indices i and l numerate donor and acceptor molecules in a micelle, μ_{rs} the probability of energy transfer $D_r \rightarrow D_s$, μ'_{rs} the probability of energy transfer $D_r \rightarrow A_s$, μ''_{rs} the probability of energy transfer $A_r \rightarrow A_s$, γ_A , q_A , γ_D , q_D the probabilities

of radiative and radiationless electronic transition in donors and acceptors, respectively. For a given configuration of dye molecules in a micelle the probabilities are known quantities, and the system of equations (12) can be solved.

Knowing $p_l^A(t)$ and $p_l^D(t)$, the probabilities of the emission of radiation of any donor or acceptor molecule and the probabilities of radiationless deactivation of these molecules can be calculated. For example, the probability of the emission of an acceptor molecule A_l is given by the formula

$$F_l^A = \gamma_A \int_0^\infty p_l^A(t) dt, \quad (13)$$

whereas the probability of the radiationless transition in this molecule is

$$Q_l^A = q_A \int_0^\infty p_l^A(t) dt. \quad (14)$$

To get the average probability that the emission or radiationless deactivation will occur in a given molecule one has to average over the configurations of the dye molecules.

It is easy to show that the yield η_{AA} is independent of the number of molecules A and D and of their configuration in a micelle. It has to be noted that in the case when one of the molecules A, say A_k , is primarily excited (initial conditions for this case are $p_i^D(0)=0$, $p_l^A(0)=0$ for all i and l except for $l=k$ when $p_k^A(0)=1$) all probabilities $p_i^D(t)$ remain 0. Taking this into account one can get from (12b) the equation

$$\sum_{l=1}^{n_A} \dot{P}_l^A(t) = -(\gamma_A + q_A) \sum_{l=1}^{n_A} p_l^A(t), \quad (15)$$

with the solution

$$\sum_{l=1}^{n_A} \dot{P}_l^A(t) = \exp\{-(\gamma_A + q_A)t\}. \quad (16)$$

One gets immediately

$$\begin{aligned} \eta_{AA} &= \gamma_A \int_0^\infty \sum_{l=1}^{n_A} p_l^A(t) dt \\ &= \gamma_A / (\gamma_A + q_A) = \eta_A. \end{aligned} \quad (17)$$

The obtained result that the energy transfer does not influence the yield of luminescence is correct when we assume equal probabilities γ_k and q_k for all acceptor molecules in a micelle.

To find the yields η_{DD} and η_{DA} is much more complicated. In the papers [26, 27], dealing with

the concentrational depolarisation of isotropic solutions, a procedure is shown which can lead to the evaluation of these efficiencies. In this paper η_{DD} and η_{DA} are obtained using the approximation that the probability of energy transition $D \rightarrow A$ is equal for all donor-acceptor pairs in a micelle. That means that

$$\mu'_{ik} = \mu, \quad i = 1, 2, \dots, n_A, \quad k = 1, 2, \dots, n_D. \quad (18)$$

Using (12), (18) and proper initial conditions one can get (in the way similar to that leading to (17))

$$\eta_{DD} = \frac{\gamma_D}{\gamma_D + q_D + n_A \mu} = \eta_D \frac{1}{1 + n_A \mu \tau_D}, \quad (19)$$

and

$$\eta_{DA} = n_A \tau_D \mu \frac{\eta_A}{1 + n_A \tau_D \mu} \quad (20)$$

where

$$\tau_D = \frac{1}{\gamma_D + q_D}, \quad \eta_D = \frac{\gamma_D}{\gamma_D + q_D}. \quad (21)$$

With the approximation used, η_{DD} and η_{DA} depend only on the number of acceptor molecules in micelles and on μ .

Taking into account (1), (6), (7), (10), (11), (17), (19) and (20) one gets the following formulae for observed yields of fluorescence of donors and acceptors:

$$\Phi_D = \frac{E_D v_D \eta_D}{E_A v_A + E_D v_D} S, \quad (22)$$

$$\Phi_A = \frac{E_A v_A \eta_A}{E_A v_A + E_D v_D} \left[1 + \frac{E_D v_D}{E_A v_A} (1 - S) \right], \quad (23)$$

and

$$\frac{\Phi_D}{\Phi_A} = \frac{\eta_D}{\eta_A} \left[\left(1 + \frac{E_A v_A}{E_D v_D} \right) \frac{1}{S} - 1 \right]^{-1}, \quad (24)$$

where

$$S = \mathcal{N}^{-N_A} \sum_{n=0}^{N_A} \frac{1}{1 + \alpha n} \binom{N_A}{n} (\mathcal{N} - 1)^{N_A - n}, \quad (25)$$

and

$$\alpha = \mu \tau_D. \quad (26)$$

Expression (25) depends only on the number of acceptor molecules and micelles in the volume V and parametrically on α . It is easy to show that for large N and N_A the expression (25) goes over in a good approximation to

$$S = e^{-v_A} \sum_{n=0}^{\infty} \frac{1}{1 + \alpha n} \frac{v_A^n}{n!}. \quad (27)$$

Particular cases of (25) and (27) are

$$S = 1 \quad \text{for } \alpha = 0, \quad (28)$$

$$S = \frac{\mathcal{N}}{N_A + 1} \left[1 - \left(1 - \frac{1}{\mathcal{N}} \right)^{N_A + 1} \right] \quad (29)$$

$$\approx \frac{1 - \exp(-v_A)}{v_A}, \quad \text{for } \alpha = 1,$$

$$S = \left(1 - \frac{1}{\mathcal{N}} \right)^{N_A} \approx \exp(-v_A), \quad \text{for } \alpha = \infty. \quad (30)$$

The case $\alpha = 0$ is a trivial one, no energy transfer $D \rightarrow A$ takes place. The second limiting case, $\alpha = \infty$, accounts for a situation where no donor emission is possible when in a particular micelle at least one acceptor molecule is present. In this case (22) has the form of the well known Perrin's formula [28] describing a selfquenching configuration.

Because of the finite size of the micelles, which are real physical objects in the solution, the parameter α can not be chosen arbitrarily. In this lies the main difference between micellar and homogeneous dye solution (the choice of $\alpha = 1$ in the last case defines the radius of the active sphere of the luminescence centrum [29, 30]).

3. Experimental

In our experiments Coumarine 1 was used as donor, Rhodamine 6G as acceptor and Triton X-100 as detergent. Mixed aqueous solutions of these substances are known as good active media in dye laser technology [6]. Triton X-100,



is a non-ionic detergent. Its critical concentration, above which micelles are formed, is 3×10^{-4} mol/l. In the present investigation the concentration was in the range 0.5×10^{-2} mol/l to 9×10^{-2} mol/l. The concentration of the dye molecules used was in the range 10^{-5} mol/l to 10^{-3} mol/l. Emission spectra were measured at various concentrations of the components. At the excitation wave length used (365 nm), the cross section of Coumarine 1 is much higher than that of Rhodamine 6G. The ratio of E_A/E_D (cf. (8) and (9)) is equal to 0.202. Fig. 1 illustrates the dependence of the fluorescence of the solution for different detergent concentrations. With decreasing detergent concentration the intensity of donor emission band is decreasing and

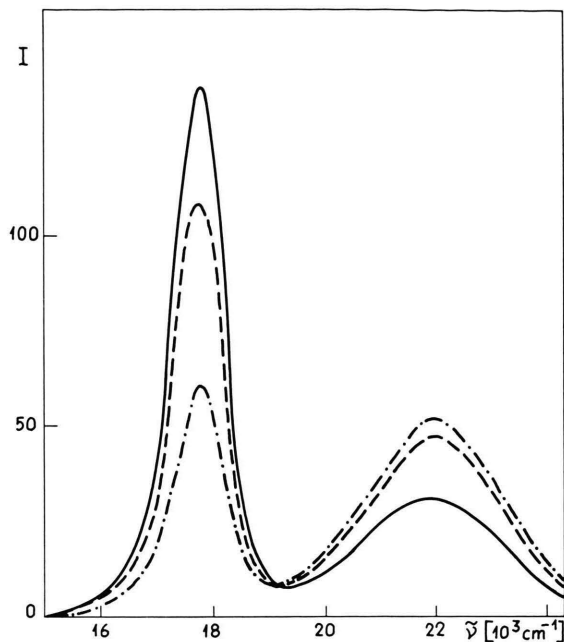


Fig. 1. Fluorescence spectra of mixed (equimolar 5×10^{-5} mol/l) solutions of Coumarine 1 (short wave band) and Rhodamine 6G (long wave band) with different concentrations of Triton X-100.

— $C_d = 0.5 \times 10^{-2}$ mol/l;
 ---- $C_d = 2.25 \times 10^{-2}$ mol/l;
 - · - · $C_d = 9 \times 10^{-2}$ mol/l.

that of the acceptor emission band is increasing. This is due to the fact that when the number of micelles is decreasing, the dye concentration in the micelles increases [8, 31, 32]. The mean number of acceptor and donor molecules in one micelle may be expressed by the molar concentrations of acceptor C_A , donor C_D and detergent C_d in solution and the number of detergent molecules (N_d) forming one micelle. One gets

$$v_A = \frac{C_A}{C_d} N_d, \quad v_D = \frac{C_D}{C_d} N_d. \quad (31)$$

Taking into account that the ratio of the intensities of the fluorescence of the donor and acceptor bands in their maximum is proportional to Φ_D/Φ_A , (24) may be given in the form

$$\frac{I_D}{I_A} = K \frac{\eta_D}{\eta_A} \left[\left(1 + \frac{E_A C_A}{E_D C_D} \right) S^{-1}(v_A, \alpha) - 1 \right]^{-1}, \quad (32)$$

where k is a constant depending on the spectral sensitivity of the experimental set up.

Assuming that the presence of donor molecules does not influence the number of detergent mole-

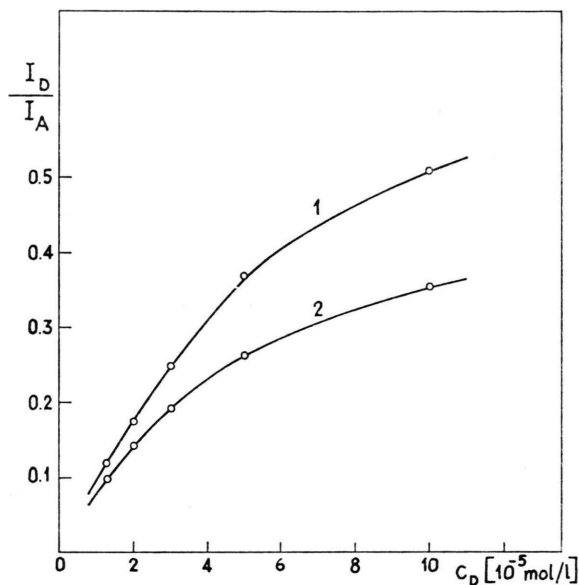


Fig. 2a.

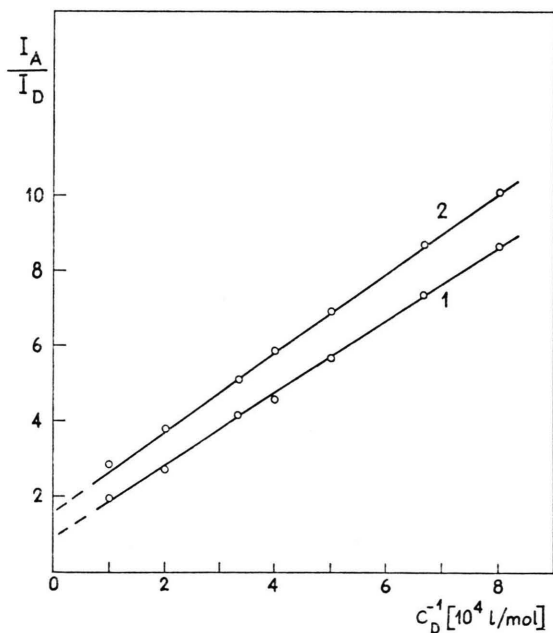


Fig. 2b.

Fig. 2. Ratio of Coumarine 1 to Rhodamine 6G fluorescence intensities versus concentration of Coumarine 1.

1: $C_d = 9 \times 10^{-2}$ mol/l,

2: $C_d = 2,25 \times 10^{-2}$ mol/l; $C_{Rh} = 10^{-4}$ mol/l;

a) I_D/I_A versus C_D , b) I_A/I_D versus C_D^{-1} .

cules in micelles, the expression S given by (27) depends only on the concentration of acceptor and detergent molecules, whereas it is independent of the number of donor molecules. In that case according to (32) a linear dependence of $(I_D/I_A)^{-1}$ versus C_D^{-1} should be observed. This is illustrated in Fig. 2b, where appropriate experimental points lie in good approximation on a straight line. The slopes and intersections with the y -axis determine S values for a given concentration of acceptor and detergent molecules in the solution. Also the quantity $k(\eta_D/\eta_A)$ may be determined.

The S values for different acceptor concentrations can also be determined by measuring I_D/I_A versus acceptor concentrations or changing simultaneously both dye concentrations (Figure 3). When changing the dye concentrations in such a way that always $C_A = C_D$, the ratio I_D/I_A depends only on S . Experimental and theoretical S values are given in Figure 4.

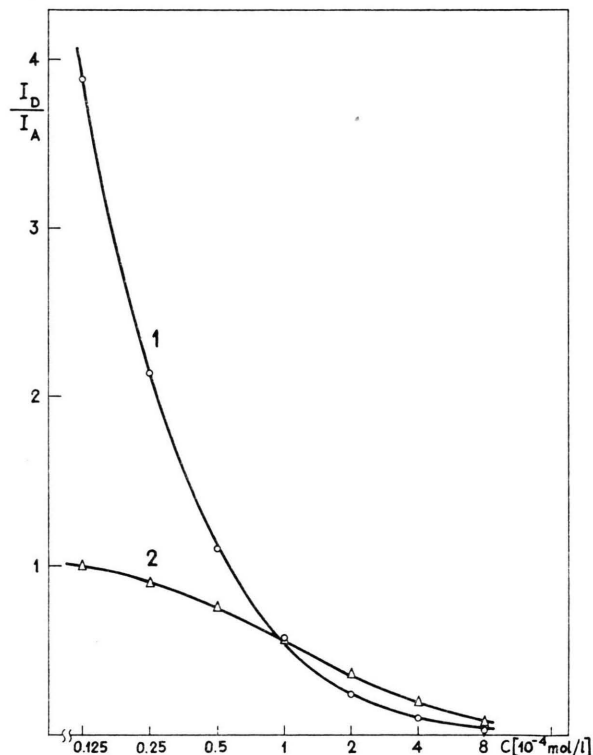


Fig. 3. Ratio of Coumarine 1 to Rhodamine 6G fluorescence intensities versus concentration of dye molecules.

$C_d = 4.5 \times 10^{-2}$ mol/l, 1: $C_{Cou} = 10^{-4}$ mol/l, C_{Rh} = varied, 2: both Coumarine and Rhodamine 6G equimolar concentrations varied.

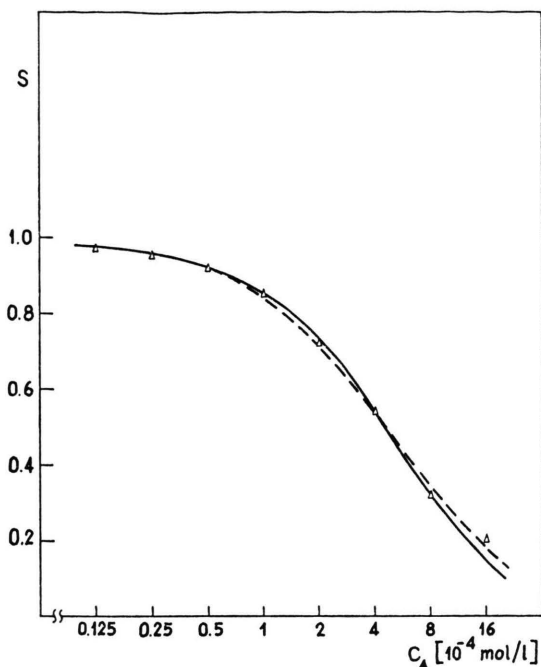


Fig. 4. Dependence of S on concentration of Rhodamine 6G as obtained from formula (27) with $C_d = 4.5 \times 10^{-2}$ mol/l, $C_D = C_A$ (see curve 2 on Figure 3). Broken line shows theoretical dependance of S on C_A with $N_d = 143$, $\alpha = 1.2$. Solid line shows theoretical dependence with $N_d = 99$, $\alpha = 2.6$.

To calculate S for different concentrations of acceptor molecules the parameter α and the number of detergent molecules in a micelle has to be known. Unfortunately, this number is not known for Triton X-100. The number of detergent molecules in one micelle found experimentally ranges from 100 to 240 molecules [3, 33, 34]. The broken curve in Fig. 4 is calculated assuming $N_d = 143$. The best fit with experimental values is obtained with $\alpha = 1.2$. This value was found by a least squares fit of the experimental and theoretical values.

The solid curve in Fig. 4, the best theoretical fit optimizing the N_d and α values gives $\alpha = 2.6$ and $N_d = 99$. The accuracy of the determination of α and N_d could be increased, if one of these quantities could be determined independently. It is possible to estimate the mean distance between donor and acceptor molecules in micelles when the value of α is known. The probability μ of transport of energy $D \rightarrow A$ by dipol-dipol interaction is given by the

formula [18, 35]:

$$\mu = \frac{9000 k^2 \ln 10}{128 \pi^5 n^4 N \tau_{0D} R^6} \int_0^\infty f_D(\tilde{\nu}) \varepsilon_A(\tilde{\nu}) \frac{d\tilde{\nu}}{\tilde{\nu}^4} \quad (33)$$

$$= \tau_D^{-1} (R_0/R)^6,$$

where $k^2 \approx \frac{2}{3}$ is the angular coefficient, n the refractive index of the solution, N the Avogadro's number, τ_{0D} the natural fluorescence decaytime, R the distance between A and D molecules, $f_D(\tilde{\nu})$ the spectral distribution of the fluorescence of donors, with the condition $\int_0^\infty f_D(\tilde{\nu}) d\tilde{\nu} = 1$, and $\varepsilon_A(\tilde{\nu})$ the decimal molar extinction of acceptors. Knowing experimental values for $f_D(\tilde{\nu})$ and $\varepsilon_A(\tilde{\nu})$ and using (33) one obtains $R_0 = \sqrt[6]{\tau_D/\tau_{0D}} \cdot 5.4$ nm and

$$\alpha = \mu \tau_D = \frac{\tau_D}{\tau_{0D}} \left(\frac{5.4}{R} \right)^6. \quad (34)$$

Assuming $\tau_D \approx \tau_{0D}$ for $\alpha = 1.2$ one gets $R = 5.2$ nm, and for $\alpha = 2.6$, $R = 4.6$ nm. These values for R are consistent with the value of the radius of a spherical micelle of Triton X-100 (according to [13, 14] equal 4.8 nm).

Taking into account the experimentally obtained radius of a micelle [13, 14] and the obtained mean distance of donor and acceptor molecules some idea about the localisation of the dye molecules in the micelles may be obtained. Presently the conception about the shape of Triton X-100 micelles is not uniform. E.g. in [3] it is claimed, that Triton X-100 micelles are of the shape of oblate ellipsoids with halfaxes 2.7 nm and 5.2 nm.

Basing on the experimental results presented in this paper and their theoretical interpretation some general conclusions may be drawn.

1. As was shown in many papers, Jabłoński's theory of concentrational quenching of luminescence [11, 12, 29, 36, 37–40] and its generalisation by Kawski [22, 41, 42] and Bojarski [43, 44] is in good agreement with experiment. In the present paper it is shown that Jabłoński's model of a luminescence centrum acquires a new meaning as a real physical object of well defined physico-chemical properties in micellar solutions. The point of interest in our approach is rather the investigation of the probability of energy transfer than the dimension of the "active spheres".

2. The concentration range for which our description of micellar solutions is in agreement with experimental data is not smaller than for homogeneous solutions, providing well developed micelles are present in the solution. An experimental remark has to be added: it is not immaterial, how water-detergent dye solutions are prepared.

3. A suitable measure of efficiency of energy transfer from donors to acceptors appeared to be the quantity S given by (25) and (27). The physical meaning of this function may be recognized in (22)

and (23):

$$S = 1 - \frac{\text{number of } D \rightarrow A \text{ energy transfer events}}{\text{number of photons absorbed in } D}$$

Because S can be obtained from experimental data using (32) and/or (24), the procedure presented in this paper gives a possibility to obtain the efficiency of energy transfer between molecules. This may be of some interest in dye laser technology.

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