Energy Transfer Among Like and Unlike Molecules in Solution VI. Effect of the Mediation of Donor Molecules Upon the Electronic Excitation Energy Transfer in Binary Systems *

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The effect of an interdonor energy transfer is investigated on the following donor-acceptor systems in thin rigid cellulose acetate films: anthracene and tetracene (I), 9-methylanthracene and 2-aminobenzophenone (II), 9,10-diphenylanthracene and 2-aminobenzophenone (III). The donor quantum yield and fluorescence anisotropy in systems I–III are in good agreement with theoretical predictions for a model of a multi-step excitation energy transfer process. In mixed two-component solutions the donor fluorescence anisotropy is higher than in single-component solutions, indicating an interdonor excitation transfer preceding the donor-acceptor transfer in these binary systems.

1. Introduction

In mixed solutions of luminescent molecules, radiationless electronic excitation energy transfer occurs between identical and different molecules as well [1–6]. In the present paper the fluorescence quantum yield and concentration depolarization of a donor is studied in order to obtain information about the interdonor energy migration preceding the donor-acceptor energy transfer.

2. Experimental

The fluorescent molecular systems

(I) Anthracene (A) and tetracene (T),

(II) 9-methylanthracene (9MA) and 2-aminobenzophenone (2ABP),

(III) 9,10-diphenylanthracene (9,10DPA) and 2-aminobenzophenone (2ABP),

were investigated in thin rigid cellulose acetate films obtained by dissolving acetylcellulose (Fluka AG) in acetone, which was subsequently evaporated. The best films were obtained by dissolving 20 g of acetylcellulose in 1 litre of acetone. The evaporation time varied from two to ten days, depending upon the amount of solution. It was found that during the evaporation of acetone the dissolved luminescent molecules also partly vaporized. Therefore the concentration of the luminescent molecules in the films was determined spectroscopically by measuring the absorption.

The extinction coefficient, $\varepsilon(\tilde{\nu})$, of the mixed solutions was found to be additive:

$$\varepsilon(\tilde{\nu}) = \varepsilon_{\mathrm{D}}(\tilde{\nu}) + \varepsilon_{\mathrm{A}}(\tilde{\nu}),$$

with ε_{D} and ε_{A} the donor and acceptor extinction coefficients, indicating that in the ground state neither complexes of donor, nor of acceptor molecules are created.

To repress reabsorption and secondary fluorescence effects the investigations were carried out at low optical densities [7]:

$$\varepsilon_{\max}(\tilde{\nu})\, C\, d \leqq 0.1,$$

where $\varepsilon_{\max}(\tilde{\nu})$ denotes the decimal molar extinction coefficient, C the molar concentration (10^{-2} to $5 \cdot 10^{-2}$ M), and d the thickness of the cellulose acetate film, ($\approx 3 \cdot 10^{-6}$ m, measured by means of an interference-polarizing microscope).

The absorption spectra were measured with Zeiss Specord UV VIS and Beckman Model 25 spectrophotometers. The fluorescence spectra and relative donor quantum yield were obtained with a method described previously [7, 8] and the fluorescence anisotropy was measured with a self-recording polarimeter [9–12]. For high concentrations, the

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fluorescence anisotropy was corrected for self-quenching [13]. The samples were excited by light with a wavenumber of $\tilde{\nu}_{exc} = \tilde{\nu}_{0-0}$.

3. Results and Discussion

a) *Donor Fluorescence Quantum Yield in Excitation Energy Transfer*

Excitation energy transfer in donor-acceptor systems appears as sensitized fluorescence of the acceptor molecules, accompanied by a drop in the donor fluorescence quantum yield. The older Förster theory [14] assumes no energy migration between the donor molecules, which holds if

$$(C_D/C_{0D}) \ll (C_A/C_{0A}) \tag{1}$$

(C_D, C_{0D} and C_A, C_{0A} are the concentrations and critical transfer concentrations of donor and acceptor, respectively), which corresponds to a one-step radiationless energy transfer from the donor to the acceptor molecules according to the scheme

$$D^* + A \xrightarrow{k_{DA}} D + A^*. \tag{2}$$

When condition (1) does not hold, an interdonor energy migration will occur with the probability k_{DD} according to the scheme

$$\begin{aligned} &D^* + D + \cdots + D + A \\ &\xrightarrow{k_{DD}} D + D^* + \cdots + D + A \xrightarrow{k_{DD}} \cdots, \\ &D + D + \cdots + D^* + A \\ &\xrightarrow{k_{DA}} D + D + \cdots + D + A^*. \end{aligned} \tag{3}$$

Then the donor fluorescence quantum yield depends on the donor concentration in the solution.

According to a theory of Bojarski and Domsta [15, 16] on multi-step energy transfer from donor to acceptor molecules, the following expression holds for the donor fluorescence quantum yield:

$$\frac{\eta}{\eta_0} = \frac{1 - f(\gamma)}{1 - \alpha f(\gamma)}, \tag{4}$$

where

$$f(\gamma) = \sqrt{\pi}\,\gamma \exp(\gamma^2)[1 - \operatorname{erf}(\gamma)], \tag{5}$$

$$\operatorname{erf}(\gamma) = \frac{2}{\sqrt{\pi}} \int_0^{\gamma} e^{-t^2} dt,$$

$$\gamma = \gamma_D + \gamma_A = \frac{\sqrt{\pi\,\eta_0}}{2}\left(\frac{C_D}{C_{0D}} + \frac{C_A}{C_{0A}}\right), \tag{6}$$

$$\alpha = \frac{\gamma_D}{\gamma_D + \gamma_A} = \frac{y}{1 + y}. \tag{7}$$

The participation of interdonor migration in the energy transfer to the acceptor molecules will therefore depend on the ratio of the reduced donor and acceptor concentrations:

$$y = \frac{\gamma_D}{\gamma_A} = \frac{C_D}{C_A}\frac{C_{0A}}{C_{0D}} = \frac{C_D}{C_A}\left(\frac{J_{\tilde{\nu}}(D,D)}{J_{\tilde{\nu}}(D,A)}\right)^{1/2}, \tag{8}$$

where $J_{\tilde{\nu}}(D, D)$ and $J_{\tilde{\nu}}(D, A)$ are the donor-donor and donor-acceptor overlap integrals, respectively.

Table 1 summarizes the parameters characterizing the molecular systems under investigation, determined from the absorption and fluorescence spectral overlap, and absolute donor quantum yields (η_0)[1].

Figure 1 shows the results obtained from the measurements of the relative fluorescence quantum yield of systems I—III, for different values of the parameter y according to (8), and theoretical curves calculated from (4). It can be seen that the empirical results obtained are in good agreement with the predictions of the Bojarski and Domsta theory [16]

[1] Respective formulas can be found in previous parts of the present series of papers [17—18]. The value of the refractive index for each system was the same and equal to 1.479. The value of the orientation factor $\langle \varkappa^2 \rangle$ describing the angular dependence of the dipole-dipole interaction, was assumed as 0.476 [19]. $C_0 = 3000/4\pi R_0^3 \cdot N$ is the critical concentration; R_0 is the Förster critical distance for the excitation energy transfer, determined from the spectral overlap; N is the Avogadro number.

Table 1.

Molecular System		$\eta_0 \equiv \eta_{0D}$	$J_{\tilde{\nu}}$ $\left(10^{-15}\,\frac{cm^6}{mM}\right)$	R_0 (Å)	C_0 (10^{-2} M)
I	A — A	0.36	1.752	28.63	1.69
	A — T		25.492	44.73	0.443
II	9MA — 9MA	0.44	1.731	28.57	0.170
	9MA — 2ABP		4.116	33.03	1.10
III	9,10DPA — 9,10DPA	1.00	1.262	33.68	1.07
	9,10DPA — 2ABP		0.906	30.41	1.41

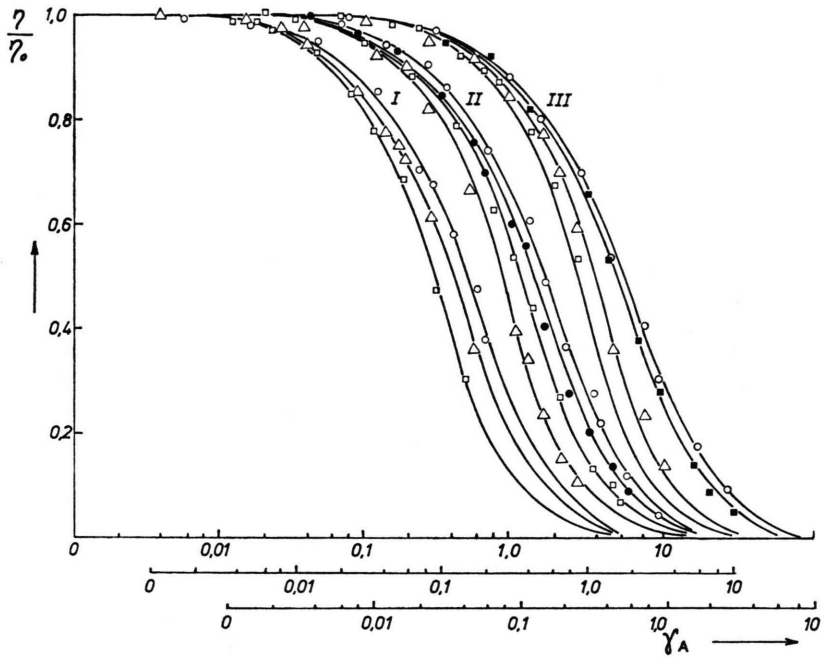

Fig. 1. Relative donor fluorescence quantum yield η/η_0 quenched by the acceptor molecules in cellulose acetate film for different values of y in the systems

(I) A + T
(○ $\beta = 0$, $y = 0$;
△ $\beta = 3.6$, $y = 1.54$;
□ $\beta = 15$, $y = 3.93$).

(II) 9MA + 2ABP
(○ $\beta = 0$, $y = 0$;
● $\beta = 1.0$, $y = 0.65$;
□ $\beta = 4.0$, $y = 2.6$;
△ $\beta = 10$, $y = 6.5$).

(III) 9,10DPA + 2ABP
(○ $\beta = 0$, $y = 0$;
■ $\beta = 0.5$, $y = 0.59$;
△ $\beta = 4.0$, $y = 4.72$;
□ $\beta = 10$, $y = 11.8$).

which takes into account the interdonor migration in the excitation transfer to the acceptor.

The contribution of the interdonor energy migration can be represented by half-concentrations, C_A^H[M], at which $\eta/\eta_0 = 0.5$, together with respective critical distances

$$R_0' = (194.32/C_A^H)^{1/3}[\text{Å}], \qquad (9)$$

(cf. [6]).

The ratio of R_0' to $(R_0')_{y=0}$, i.e. for constant but very low donor concentrations, is independent of the donor-acceptor system chosen (cf. Table 2 and Figure 2).

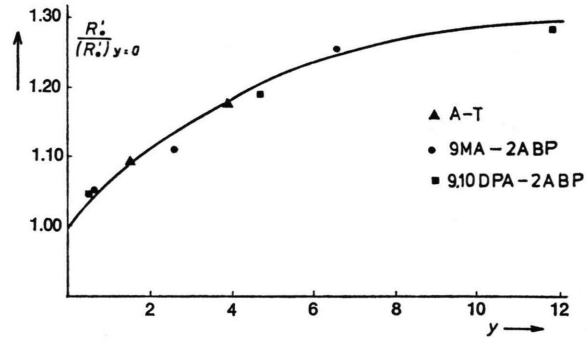

Fig. 2. Relative increment in the critical distance $R_0'/(R_0')_{y=0}$ for excitation energy transfer as a function of parameter y (according to Table 2).

Table 2.

Donor-Acceptor	$\beta = \frac{C_D}{C_A}$	$y = \frac{\gamma_D}{\gamma_A}$	C_A^H (10^{-3} M)	R_0' (Å) Eq. (9)	$\frac{R_0'}{(R_0')_{y=0}}$
A – T	0	0	2.0	45.97	1.0
	3.6	1.54	1.52	50.37	1.096
	15.0	3.93	1.23	54.05	1.176
9MA – 2ABP	0	0	5.6	32.62	1.0
	1.0	0.65	4.8	34.33	1.052
	4.0	2.60	4.1	36.19	1.110
	10.0	6.50	2.85	40.85	1.252
9,10DPA – 2ABP	0	0	7.8	29.20	1.0
	0.5	0.59	6.8	30.57	1.047
	4.0	4.72	4.6	34.83	1.193
	10.0	11.80	3.7	37.45	1.282

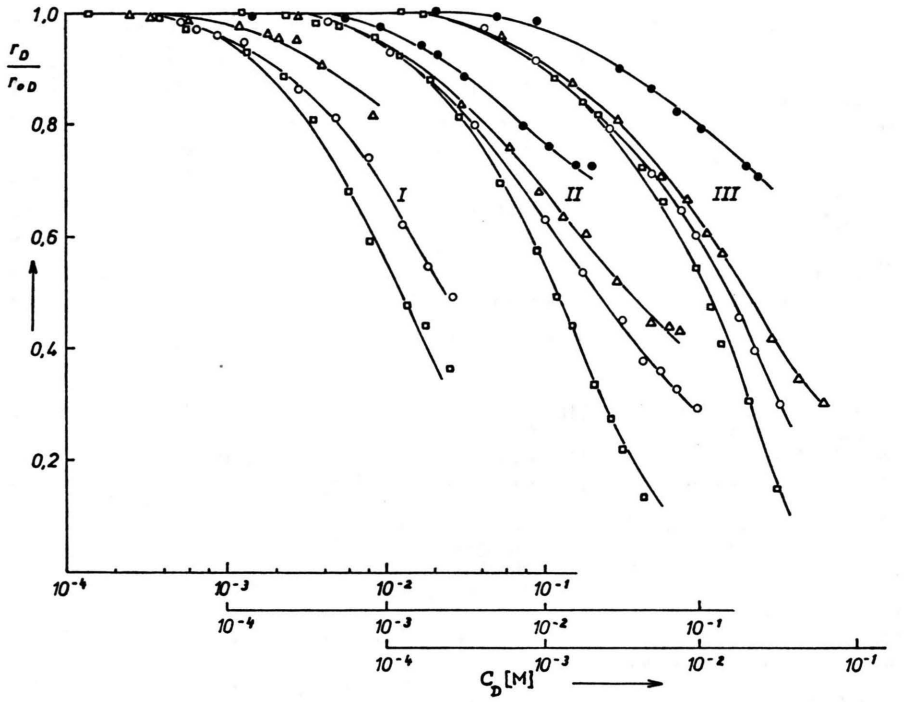

Fig. 3. Relative donor fluorescence anisotropy r_D/r_{0D} versus donor concentration C_D for different values of y in unary (A, 9MA, 9,10DPA) and binary systems: (I) A + T (□ $C_A=0$; ○ $\beta=15$, $y=3.91$; △ $\beta=3.6$, $y=1.54$). (II) 9MA + 2ABP (□ $C_A=0$; ○ $\beta=10$, $y=6.5$; △ $\beta=4.0$, $y=2.6$; ● $\beta=1.0$, $y=0.65$). (III) 9,10DPA + 2ABP (□ $C_A=0$; ○ $\beta=10$, $y=11.8$; △ $\beta=4.0$, $y=4.72$; ● $\beta=0.5$, $y=0.59$).

b) *Donor Fluorescence Anisotropy and the Migration of the Excitation Energy*

The effect of the interdonor migration upon the fluorescence anisotropy was also investigated for the systems under study. According to qualitative theoretical considerations in our previous paper [6], one can anticipate different effects of the donor fluorescence anisotropy in unary and binary solutions. If migration and transfer of the excitation energy are assumed to occur from the lowest vibrational levels of the electronic excited states, the effectiveness of both processes will depend only on the value of y. With y fixed ($y>0$) the concentration depolarization of the donor fluorescence will be accompanied also by the acceptor of the second component.

Figure 3 shows relative fluorescence anisotropies for unary (anthracene, 9-methylanthracene, 9,10-diphenylanthracene) and binary (systems I—III) films versus the donor concentration for different values of $\beta = C_D/C_A$ and y. As the acceptor concentration grows (or y decreases), the decrease of the emission anisotropy with donor concentration dimin-

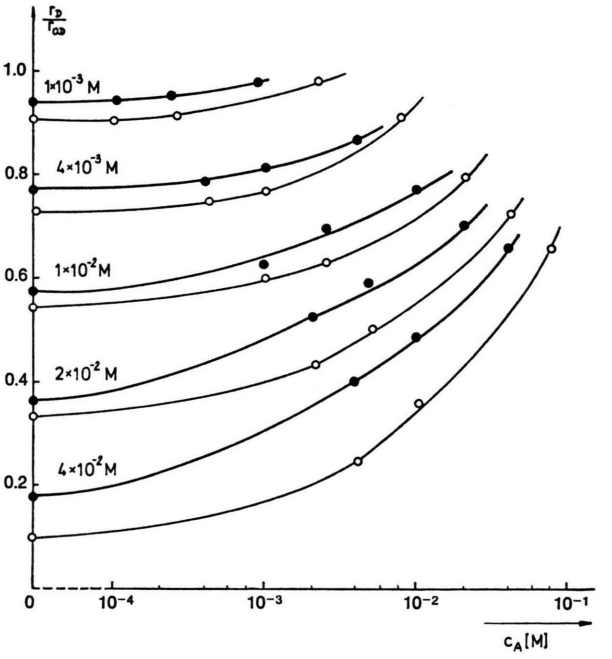

Fig. 4. Relative donor fluorescence anisotropy r_D/r_{0D} of 9MA (●) and 9,10DPA (○) versus the concentration of 2ABP (acceptor) at fixed donor concentrations.

ishes, indicated by the enhancement in the half-concentration.

The dependence of the relative fluorescence anisotropy on the acceptor concentration for selected donor concentrations is shown in Figure 4. Good agreement is found with the discussion of equation (3) with (5) in our previous paper [6].

For low donor concentrations (e.g., $C_D = 10^{-3}$ M for 9-methylanthracene) $r_D/r_{0D} = f(C_A)$ is close to unity, and in principle does not depend on the acceptor concentration, which is confirmed by our previous experiments with other donor-acceptor systems [6]. Moreover, it can be inferred from Fig. 4 that the enhancement in the donor fluorescence anisotropy due to the quenching by the acceptor molecules strongly depends upon the chosen concentration, C_D, of donor molecules. This proves that interdonor migration preceding donor-acceptor transfer grows with the donor concentration in accordance with the theories of Jabłoński [4] and Bojarski and Domsta [16].

[1] A. Kawski, Energy Transfer in Solutions, in Acoustics and Spectroscopy ed. A. Kawski and A. Śliwiński, Ossolineum Gdańsk 1979, p. 185–198.
[2] A. Jabłoński, Bull. Acad. Polon. Sci., Ser. Sci. Math. Astro. Phys. **19**, 171 (1971).
[3] R. K. Bauer and H. Cherek, Bull. Acad. Polon. Sci. Ser. Sci. Math. Astro. Phys. **20**, 961 (1972).
[4] A. Jabłoński, Acta Phys. et Chem. Szeged **20**, 223 (1974).
[5] H. Cherek, Bull. Acad. Polon. Sci. Ser. Sci. Math. Astro. Phys. **24**, 135 (1976).
[6] A. Kawski and H. Szmaciński, Z. Naturforsch. **35a**, 697 (1980).
[7] A. Kawski, J. Kamiński, and E. Kuteń, J. Phys. B: Atom. Molec. Phys. **4**, 609 (1971).
[8] D. Gloyna, A. Kawski, and I. Gryczyński, Z. Naturforsch. **35a**, 1192 (1980).
[9] A. Kawski, Z. Kojro, and M. Alicka, Z. Naturforsch. **35a**, 1197 (1980).
[10] R. K. Bauer and M. Rozwadowski, Optik, **18**, 37 (1961).
[11] R. K. Bauer, J. Phys. E. Sci. Instrum. **3**, 965 (1970).
[12] R. K. Bauer, A. Kowalczyk, A. Balter, H. Cherek, and W. Roguski, Optica Applicata **12**, 43 (1975).
[13] A. Kawski, Proc. Internal. Conf. Luminescence, Budapest 1966, p. 292.
[14] Th. Förster, Z. Naturforsch. **4a**, 321 (1949).
[15] C. Bojarski and J. Domsta, Z. Naturforsch. **25a**, 1760 (1970).
[16] C. Bojarski and J. Domsta, Acta Phys. Hung. **30**, 145 (1971).
[17] A. Kawski and J. Kamiński, Z. Naturforsch. **29a**, 452 (1974); **30a**, 15 (1975).
[18] A. Kawski and M. Stoń, Z. Naturforsch. **30a**, 1611 (1975); **34a**, 708 (1979).
[19] M. Z. Maksimov and J. M. Rozman, Opt. Spectrosc. **12**, 606 (1962).