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# ON THE SELF-DEPOLARIZATION AND DECAY OF PHOTOLUMINESCENCE OF SOLUTIONS*,**

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A further attempt to improve the "active sphere" model is proposed. The excited centre is assumed to consist of an excited luminescent molecule (donor) surrounded by an "active shell" (whose radius are: "$a$" at which the Foerster interaction brings the largest contribution to the energy migration process, and "$R_s$" the reach of Foerster interaction), which may contain unexcited luminescent molecules (acceptors) of the same kind. The probability distribution of different centres is given by Poisson statistics for a random distribution of acceptor molecules. It was shown that the Jabłoński expression for concentration depolarization is henceforth equitable. In this model an average probability of the excitation energy transfer from donor to any acceptor molecules present in the shell was calculated for two cases: (*i*) three-dimensional system and (*ii*) two-dimensional system. From these calculations the mean number of acceptor molecules in the considered "shell", which depends on the "critical distance" $R_0$ and on the mutual orientations of molecular axes of acceptor and donor of dipole-dipole interaction was obtained. The theoretical expression for the concentration-dependent depolarization was compared with experimental results of different authors. The determined values $R_0$ for all investigated compounds are in good agreement with the values $R_{0F}$ from the spectra measurements.

## 1. *Introduction*

In the theory of self-depolarization (concentration depolarization) for three-dimensional solutions given by Jabłoński [1], a simplified model of a luminescent centre is assumed, which consists of the primarily excited donor[1] molecules surrounded by the so called "active sphere". The latter may contain acceptor molecules. All the centres of a rigid solution are devided in groups according to the number of unexcited acceptor molecules belonging to a centre. A centre is ascribed to the group $k$ if it consists of one excited donor

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[1] Luminescent molecules, primarily excited by absorption of the exciting light, are called donors (D), and those primarily unexcited (excited only by excitation transfer) — acceptors (A).

and $k-1$ unexcited acceptor molecules. The probability distribution of different $k$'s in this model is that given by Poisson statistics for a random distribution of acceptor molecules.

In Jabłoński's theory [1] the following simplifying assumptions were made: (*i*) The probability of radiationless energy transfer from donor to acceptor is the same for all acceptor molecules inside the active sphere, independently of the mutual distance between donor and acceptor, but equals zero for acceptors outside the active sphere. (*ii*) Neither the influence of mutual orientations of molecular axes of acceptors and donor molecules nor any specific form assumed of the dependence of migration probability on the distance of acceptor from donor molecules were taken into account. In [2, 3] Jabłoński gave a new improved version of his formerly proposed theory, and some of the most drastic simplifications were partially relaxed.

The simplifying assumption (*i*) leads to much larger critical distances $R_0$ in comparison with the Foerster critical distances $R_{0F}$, determined from the overlap of the absorption and fluorescence spectra [4].

The other improved theories [5–10] were based on a model of a "multi-layer" luminescence centre, in order to take into account the possibility of energy migration to acceptor molecules outside the active sphere. It leads to slightly different values of $R_0$ and $R_{0F}$. It was also shown that on the basis of multilayer model one obtaines the Foerster expression for the relative quantum yield of donor emission quenched by foreign molecules [9]. In this paper a further attempt to improve the "active sphere" model will be given.

## 2. *Assumptions*

We assume that a luminescent centre in a solution consists of an excited luminescent molecule (donor) enveloped by a "shell" whose volume is

$$V = \tfrac{4}{3}\pi(R_s^3 - a^3), \tag{1}$$

where $a$ is the distance at which the Foerster interaction brings the largest contribution to the energy migration process, and $R_s$ — the reach of Foerster interaction. In the shell unexcited molecules (acceptors) are present. A centre containing one donor and $k-1$ acceptors in the shell will be called $k$-centre (as used by Jabłoński in [1]). The probability distribution of different $k$'s in this model is given by the Poisson statistics for a random distribution of acceptor molecules

$$P_{\nu k} = \frac{\nu^{k-1}}{(k-1)!}e^{-\nu}, \tag{2}$$

where $\nu = Vn$ is the average number of molecules in a volume $V$ given by formula (1) and $n$ — the concentration[2] of acceptor molecules in 1 cm$^3$.

[2] Which is almost always the same as the total concentration of all luminescent molecules, when the intensity of the exciting light is not too high. No centres containing more than one donor appear.

We assume, besides, that the probability of the energy transfer $\mu$ from donor to different acceptors in the shell depends on the mutual distance between the molecules of donor and acceptor and on the mutual orientations of molecular axes of acceptor and donor of dipole-dipole interaction. According to Foerster [11] the rate constant $\mu$ of the transfer process is

$$\mu = \frac{\langle\kappa^2\rangle}{\tau_0}\left(\frac{R_0}{R}\right)^6 = \frac{1}{\tau_0}\left(\frac{R_{0F}}{R}\right)^6, \tag{3}$$

where for fast Brownian rotation of both molecules $\langle\kappa^2\rangle = \frac{2}{3}$ [12] and for random but rigid solutions $\langle\kappa^2\rangle = 0.476 \approx \frac{1}{2}$ [13, 9]. Here, $\tau_0$ is the actual mean lifetime of the excited donor and $R_{0F}$ is the critical transfer distance for which excitation transfer and spontaneous deactivation of the donor are of equal probability.

In this "shell model" it is assumed that the excitation energy can migrate between donor and acceptor molecules present in the shell, and the probability of transfer of energy is not the same for all pairs (donor-acceptor) as in the "active sphere" model. We assume, for the probability of excitation energy transfer, an average value of (3) in the shell volume. This problem will be considered in the following Section.

## 3. *Emission anisotropy*

The time-dependent emission anisotropy as was already shown [10] is given by

$$r(t) = r_0\langle W_k(t)\rangle_k, \tag{4}$$

where $r_0$ is the fundamental emission anisotropy and

$$\langle W_k(t)\rangle_k = \sum_{k=1}^{\infty} W_k(t)P_{\nu k} = e^{-\nu(1-e^{-\langle\mu\rangle t})} + \frac{1-\{1+\nu(1-e^{-\langle\mu\rangle t})\}e^{-\nu(1-e^{-\langle\mu\rangle t})}}{\nu}. \tag{5}$$

The first term on the right-hand side of Eq. (5) describes the case when the re-excitation by energy migration of each initially excited molecule is neglected.

The time average of Eq. (4) and (5) gives

$$\left\langle\frac{r}{r_0}\right\rangle_{RM} = \frac{1}{\tau_0}\int_0^{\infty}\left\{\frac{1}{\nu} + \left(e^{-\langle\mu\rangle t} - \frac{1}{\nu}\right)e^{-\nu(1-e^{-\langle\mu\rangle t})}\right\}e^{-\frac{t}{\tau_0}}dt. \tag{6}$$

When the remigration effect is neglected we obtain

$$\left\langle\frac{r}{r_0}\right\rangle_{M} = \frac{1}{\tau_0}\int_0^{\infty}\{e^{-\nu(1-e^{-\langle\mu\rangle t})}\}e^{-\frac{t}{\tau_0}}dt. \tag{7}$$

With the assumption that

$$\frac{1}{\tau_0} = b\langle\mu\rangle \tag{8}$$

(the volume $V$ of the "active shell" depends on the adopted value of the probability of migration $\langle\mu\rangle$) we get from Eqs (6) and (7) the following expressions

$$\left\langle\frac{r}{r_0}\right\rangle_{\mathrm{RM}} = \frac{b+1}{v} - \frac{b(b+1)e^{-v+1}}{v^{b+1}} \sum_{m=1}^{\infty} \binom{b-1}{m-1} F(v-1, m-1), \tag{9}$$

and

$$\left\langle\frac{r}{r_0}\right\rangle_{\mathrm{M}} = \frac{be^{-v+1}}{v^b} \sum_{m=1}^{\infty} \binom{b-1}{m-1} F(v-1, m-1), \tag{10}$$

where

$$F(v-1, m-1) = \int_{-1}^{v-1} y^{m-1} e^y dy \tag{11}$$

($m$ is an integer). Between Eqs. (9) and (10) there exists the following relationship

$$\left\langle\frac{r}{r_0}\right\rangle_{\mathrm{RM}} = \frac{b+1}{v}\left\{1-\left\langle\frac{r}{r_0}\right\rangle_{\mathrm{M}}\right\}, \qquad b > 0. \tag{12}$$

The connection (Eq. (12)) allows one to find the influence of the remigration effect on the shape of the concentration depolarization curve as a function of $b$ and $v$.

Putting $b = 1$ we obtain from Eqs. (9) and (10) the well-known Jabłoński (cf. [1] and [14]) equations

$$\left\langle\frac{r}{r_0}\right\rangle_{\mathrm{RM}} = \frac{2(v-1+e^{-v})}{v^2}, \tag{13}$$

and

$$\left\langle\frac{r}{r_0}\right\rangle_{\mathrm{M}} = \frac{1-e^{-v}}{v}, \tag{14}$$

where $v$ is the average number of molecules in a shell volume (or on unit area in the two--dimensional solution).

Before proceeding we should like to point out the generality of formulae (13) and (14). They hold even if three-dimensional systems and two-dimensional systems are considered.

### a. Three-dimensional systems

The mean probability of the excitation energy transfer from donor to any acceptor molecules present in the shell with a volume given by Eq. (1) is

$$\langle\mu\rangle = \frac{\dfrac{1}{\tau_0}\displaystyle\int_a^{R_s} 4\pi R^2 n\langle\kappa^2\rangle\left(\frac{R_0}{R}\right)^6 dR}{\displaystyle\int_a^{R_s} 4\pi R^2 n dR}. \tag{15}$$

With the assumption of Eq. (8) we get from Eq. (15) the following relationship

$$a^3 = b\langle\kappa^2\rangle \frac{R_0^6}{R_s^3}. \tag{16}$$

The mean number of acceptor molecules in the considered "shell", for $b = 1$, is

$$\nu = \tfrac{4}{3}\pi R_s^3 \left[1 - \langle\kappa^2\rangle \left(\frac{R_0}{R_s}\right)^6\right] n. \tag{17}$$

The ratio of $\frac{R_0}{R_s}$ will be deteımined later.

b. Two-dimensional systems

In a two-dimensional non-active medium, the mean probability $\langle\mu\rangle$ of the excitation energy transfer from donor to any acceptor molecules present in the ring with an area $\pi(R_s^2 - a^2)$ is

$$\langle\mu\rangle = \frac{\frac{1}{\tau_0}\int\limits_a^{R_s} 2\pi R n \langle\kappa^2\rangle \left(\frac{R_0}{R}\right)^6 dR}{\int\limits_a^{R_s} 2\pi R n dR}. \tag{18}$$

The assumption $\langle\mu\rangle = \frac{1}{\tau_0}$ in Eq (18) leads to

$$\nu = \pi R_s^2 \left\{1 - \frac{R_0^3\langle\kappa^2\rangle}{6R_s^6}\left[\frac{R_0^3}{2} + \left(\frac{R_0^6}{4} + \frac{2R_s^6}{\langle\kappa^2\rangle}\right)^{1/2}\right]\right\}. \tag{19}$$

## 4. *Discussion of the theoretical curves*

Eqs (4) and (5) (when two terms or only the first term are taken into account) give the time-dependent emission anisotropy as affected by energy migration. The exciting light is of a sufficiently short duration ($\delta$-function excitation) for the random distribution of acceptors in a centre not to be destroyed by energy migration during the excitation period. The quantities $\left(\frac{r}{r_0}\right)_{RM}$ and $\left(\frac{r}{r_0}\right)_M$ (Eqs (4) and (5)) are plotted in Fig. 1 for different values of $b$ nad $\nu$. It is seen that the decay of the fluorescence polarization anisotropy becomes non-exponential at larger values of $\nu$. At low concentrations ($\nu = 0.01$) the decay of $r(t)$ is exponential because it is no energy transfer.

Fig. 2 shows a set of curves of calculated relative mean values $\left\langle\frac{r}{r_0}\right\rangle_{RM,M}$ (Eqs (9) and (10)) as function of logarithm of $\nu$ for different values of $b$. "$b$" stipulated the dimen-

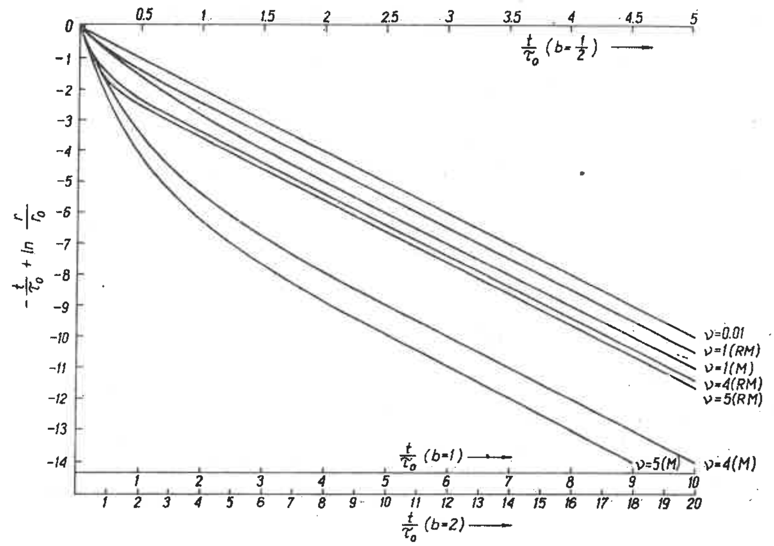


Fig. 1. Time dependence of the emission anisotropy of the donor with increasing acceptor concentration

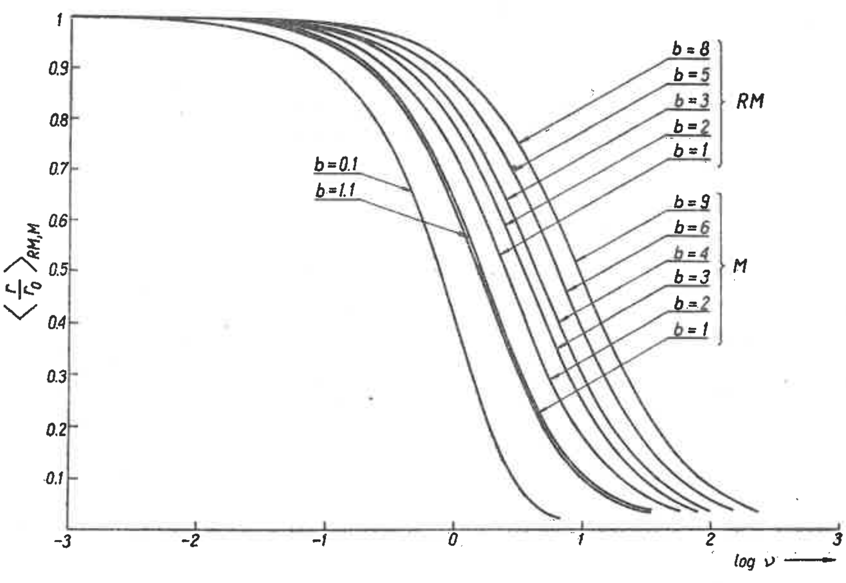


Fig. 2. Theoretical curves for the steady-state emission anisotropy $\left\langle \frac{r}{r_0} \right\rangle_{RM,\,M}$ for different values of $b$, calculated from Eqs. (9) and (10)

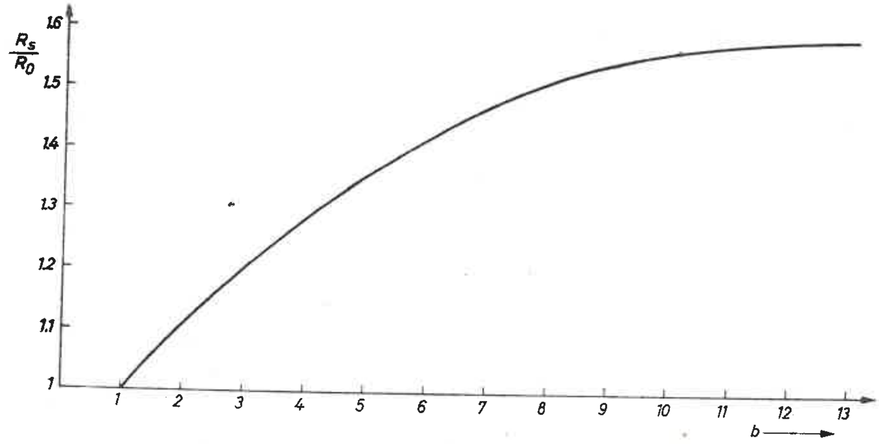


Fig. 3. The ratio of $\frac{R_b}{R_0}$ as a function of $b$, in the case when the remigration effect is not neglected

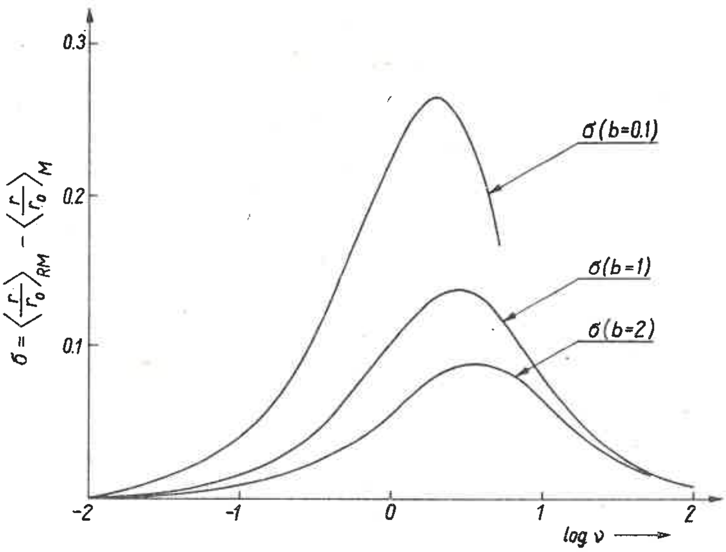


Fig. 4. The re-excitation effect as a function of the acceptor concentration $\nu$

sion of "active shell" and for $b = 1$ we have a radius of $R_0$; for $b = 2$ the active radius is determined by the condition $\frac{1}{\tau_0} = 2\langle\mu\rangle$ and so on. Interesting is the relationship given by Eq. (12) between $\left\langle \frac{r}{r_0} \right\rangle_{RM} (\nu, b)$ and $\left\langle \frac{r}{r_0} \right\rangle_M (\nu, b+1)$, what is seen in Fig. 2. For larger values of $b$ the theoretical curves are situated near one another and for $b > 12$ they follow one curve. For these curves the ratio of $R_s/R_0$ was determined, as may be seen in Fig. 3. The approximate values of $R_s/R_0$ are:

$$\left(\frac{R_s}{R_0}\right)_{\mathrm{RM}} \approx 1.6, \quad (\text{for } s = b > 12), \tag{20}$$

and

$$\left(\frac{R_s}{R_0}\right)_{\mathrm{M}} \approx 1.9, \quad (\text{for } s = b > 12). \tag{21}$$

The difference $\sigma$ between Eqs. (9) and (10) (or Eqs. (13) and (14)) gives the re-excitation effect. This effect is shown in Fig. 4. For small effective radius ($b = 0.1$) the remigration effect is large. At the same time the remigration maximum will be sharp and is shifted in direction of small values (see Fig. 4).

## 5. *Comparison of theory with experiment*

In order to evaluate the theoretical results concerning the concentration depolarization described above, we compare them with the experimental results of Kamiński and Kawski [10], Deale and Bauer [15], and Bojarski et al. [16] for three-dimensional solutions

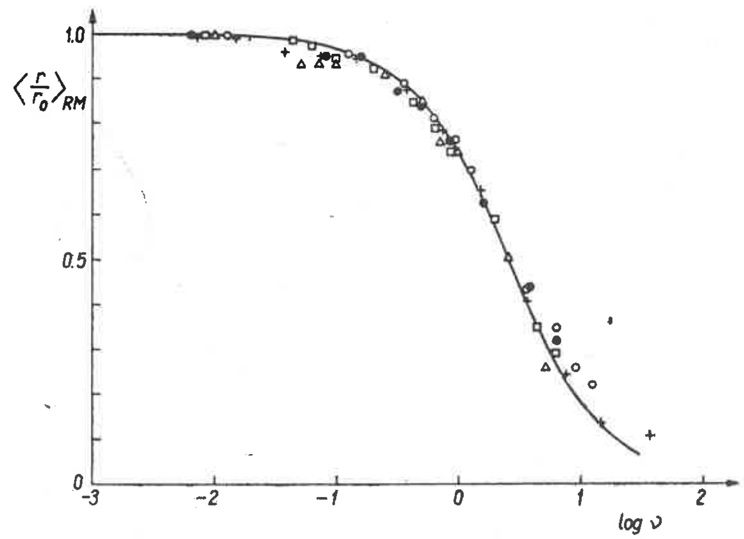


Fig. 5. A comparison of the theoretical curve $\left\langle \frac{r}{r_0} \right\rangle_{\mathrm{RM}}$ (Eq. (13), (17) and (20)) with the experimental data of concentration depolarization; ○ — rhodamine B, □ — 2-methylanthracene and ● — 5-methyl-2 phenylindole in cellulose acetate [10], + — fluorescein in glycerol-water solution [15]

and the results of Trosper et al. [17] for two-dimensional solutions. In Fig. 5 five sets of experimental data of concentration depolarization $\left\langle \frac{r}{r_0} \right\rangle$ of rhodamine B, anthracene, 2-methylanthracene and 5-methyl-2-phenylindole in cellulose acetate [10] and fluorescein in glicerol-water solutions [15] versus log $\nu$ are plotted and compared with the theoretical results (Eq. (13) with (17) and (20)). These experimental data cover a wide range of concentrations and are in good agreement with the theoretical Jabłoński curve. Table I shows the critical distance values $R_0$ determined from Eq. (17) for $\langle\kappa^2\rangle = 0.476$, $\nu_H = 2.55693$ and $n_H = C_H N'$ (where $C_H$ in mole $l^{-1}$ is the half-value concentration determined

TABLE I

Critical distances $R_0$ and $R_{0F}$ for some luminescent substances in three-dimensional solutions

| Substance and solvent | $C_H$ [mol/l] | $a$ (Å) [Eq. (16) and (20)] $b = 1$ | $R_0$ (Å) [Eq. (13) and (17)] | $R_{0F}$ (Å) (from spectra) |
|---|---|---|---|---|
| | | $\langle\kappa^2\rangle = 0.476$ | | |
| Rhodamine B in cellulose acetate [10] | $2\times10^{-3}$ | 24.5 | $50.3\pm1.0$ | $49.0\pm1.0$ |
| Rhodamine B in glycerol-water 740 cp [16] | $2\times10^{-3}$ | 24.5 | 50.3 | 50.5 |
| Fluorescein in glycerol-water containing 5% (v/v) water [15] | $3.5\times10^{-3}$ | 20.4 | 41.8 | 43.0 |
| Anthracene in cellulose acetate [10] | $2.5\times10^{-2}$ | 10.6 | $21.7\pm0.5$ | $19.9\pm1.0$ |
| 2-Methylanthracene in cellulose acetate [10] | $3\times10^{-2}$ | 10.0 | $20.4\pm0.5$ | $19.7\pm0.5$ |
| 5-Methyl-2-Phenylindole in cellulose acetate [10] | $4\times10^{-2}$ | 9.0 | $18.5\pm0.5$ | $17.2\pm0.5$ |

from the experimental curve, and $N'$ is the number of molecules per millimole). The theoretical half-value concentration $\nu_H$ was determined from the normalized Jabłoński curve (Eq. (13)). Therefore we have

$$R_0 = \left(\frac{254.78}{C_H}\right)^{1/3} \text{Å}. \tag{22}$$

In Table I the values of "$a$" and the Foerster critical distances $R_{0F}$ from the spectra measurements are also given. As can be seen, the values $R_0$ and $R_{0F}$ are in good agreement.

The comparison of the experimental results of Trosper et al. [17], for two-dimensional solutions of chlorophyll a in castor oil, with the theoretical curve (Eq. (13), (19) and (20)) is shown in Fig. 6. The obtained values of $R_0$ for chlorophyll a in different solvents (two--dimensional solutions) are given in Table II and compared with the values of $R_0$ determined from other theories. Our values of $R_0$ given in Table II are smaller for all systems than values $R_0$ found by other authors [17–19]. A discussion concerning the differences between the values of $R_0$ obtained by different authors [17–19] is given by Bojarski and Kolka [19].

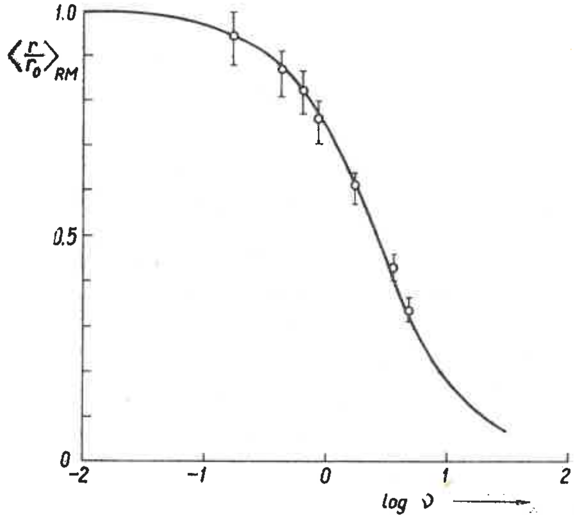


Fig. 6. A comparison of the theoretical curve $\left\langle \frac{r}{r_0} \right\rangle_{\text{RM}}$ (Eq. (13), (19) and (20)) for two-dimensional solutions of chlorophyll a in castor oil [17]

TABLE II

Critical distances $R_0$ for chlorophyll-a in two-dimensional solutions (different solvents)

| Solvent | $R_0$ (Å) | | | | $a$ (Å) [Eq. (16) and (20)] $b = 1$ |
|---|---|---|---|---|---|
| | Trosper et al. [17] | Craver [18] | Bojarski et al. [19] | Present authors [Eq. (13)] $\langle\kappa^2\rangle = 0.476$ | |
| castor oil | $57 \pm 4$ | $62 \pm 3$ | $53 \pm 4$ | $47 \pm 6$ | 23 |
| oleyl alcohol | $57 \pm 11$ | $62 \pm 11$ | $53 \pm 11$ | $53 \pm 11$ | 26 |
| sulpholipid | $78 \pm 9$ | $86 \pm 9$ | $74 \pm 9$ | $66 \pm 9$ | 32 |
| monogalacto-lipid | $88 \pm 22$ | — | — | $90 \pm 22$ | 44 |

Analizing Tweet's et al. [20] data concerning the fluorescence queching of chlorophyll a in monomolecular film by copper pheophytin a as in preceding example (at present in Eq. (14), (19) and (21)), we find $R_0 = 41.5 \pm 5.5$ Å. This agrees well with $R_{0F} = 38 \div 41$ Å obtained from the absorption and fluorescence spectra [20].

## REFERENCES


[1] A. Jabłoński, *Acta Phys. Pol.* **14**, 295 (1955); **17**, 481 (1958).
[2] A. Jabłoński, *Acta Phys. Pol.* **A38**, 453 (1970) and Errata **A39**, 87 (1971).
[3] A. Jabłoński, *Acta Phys. Pol.* **A41**, 85 (1972).
[4] A. Kawski, *Z. Naturforsch.* **18a**, 961 (1963).
[5] C. Bojarski, *Acta Phys. Pol.* **22**, 211 (1962); **34**, 853 (1968).
[6] A. Kawski, J. Kamiński, *Acta Phys. Pol.* **A37**, 591 (1970); **A41**, 775 (1972).
[7] A. Kawski, J. Kamiński, *Z. Naturforsch.* **29a**, 452 (1974).
[8] A. Kawski, J. Kamiński, *Z. Naturforsch.* **30a**, 15 (1975).
[9] J. Kamiński, A. Kawski, *Z. Naturforsch.* **32a**, 140 (1977).
[10] J. Kamiński, A. Kawski, *Z. Naturforsch.* **32a**, 1339 (1977).
[11] Th. Förster, *Ann. Phys.* (Leipzig) **2**, 55 (1948).
[12] Th. Förster, *Fluoreszenz Organischer Verbindungen*, Vandenhoeck Ruprecht, Göttingen 1951.
[13] M. Z. Maksimov, I. M. Rozman, *Opt. Spektrosk.* **12**, 606 (1962).
[14] C. Bojarski, *Bull. Acad. Pol. Sci. Ser. Sci.Math. Astron. Phys.* **6**, 719 (1958)
[15] R. E. Deale, R. K. Bauer, *Acta Phys. Pol.* **A40**, 853 (1971).
[16] C. Bojarski, A. Bujko, J. Dudkiewicz, J. Kuśba, G. Obermüller, *Acta Phys. Pol.* **A45**, 71 (1974).
[17] T. Trosper, R. B. Park, K. Sauer, *Photochem. Photobiol.* **7**, 451 (1968).
[18] F. W. Craver, *Mol. Phys.* **22**, 403 (1971).
[19] C. Bojarski, W. Kolka, *Acta Phys. Hung.* **39**, 191 (1975).
[20] A. G. Tweet, W. D. Bellamy, G. L. Gaines, *J. Chem. Phys.* **41**, 2068 (1964).