PHOTOINDUCED ENERGY AND ELECTRON TRANSFER IN MICELLAR SOLUTIONS OF METHYLENE BLUE

Viktor ŘEHÁK and Yvona RYBOVÁ

Department of Polygraphy, Institute of Chemical Technology, 532 10 Pardubice

Received March 6th, 1987

In the micellar medium of sodium dodecyl sulphate the monomer–dimer equilibrium of methylene blue is shifted markedly in favour of the monomer. Methylene blue quenches the fluorescence of pyrene solvated in micelles, which is explained in terms of resonance energy transfer. Based on the theoretical model, the pyrene fluorescence quenching constant in the micelles was determined ($k_{qm} = 1{\cdot}8 \,.\, 10^6\ s^{-1}$) and the average pyrene–methylene blue interaction distance for the singlet–singlet energy transfer estimated. The $T_1 \rightarrow T_n$ absorption of methylene blue is quenched by pyrene and tetrasodium salt of ethylenediaminetetraacetic acid (EDTA); the quenching rate constants corresponding to the electron transfer are $5 \,.\, 10^6$ and $2{\cdot}05 \,.\, 10^8\ l\ mol^{-1}\ s^{-1}$, respectively.

Photochemical reactions in organized systems[1,2] (micelles, vesicles, microemulsions, polyelectrolytes, cyclodextrins) are receiving interest particularly in relation to the study of photoredox reactions modelling photobiological processes and processes associated with solar energy conversion and information storage. In this connection, attention has been paid to methylene blue (MB), which can act as an energy acceptor[3] and electron acceptor[4–7] and also as an energy donor in photooxygenation reactions[8].

In the present work, the possibility of energy and electron transfer between MB and pyrene or EDTA (tetrasodium salt of ethylenediaminetetraacetic acid) is studied in micellar medium of sodium dodecyl sulphate (SDS) in conditions of selective excitation of pyrene and MB.

EXPERIMENTAL

Chemicals

Methylene blue (Lachema, Brno) was recrystallized three times from 0·1M-HCl; the crystals were washed with pure ethanol and dried in a vacuum dessicator. The purity of the dye was checked by thin layer chromatography on Silufol plates (Kavalier, Sázava) using ethanol as eluent. Pyrene was purified by zone refining; the vibronic structure of its absorption and luminescence bands in cyclohexane at room temperature agreed with published data[9]. EDTA (Lachema, Brno) and SDS (Pierce) were used as received; the purity of the latter, as declared by the manufacturer, was 99% or better. Dodecyl pyridinium bromide (DPB) was obtained from the Technical University in Merseburg, G.D.R.

Methods and Apparatus

Micellar solutions of pyrene were prepared by sonication at 40°C in an SDS solution ($2{\cdot}5 \cdot 10^{-2}$ mol l^{-1}) accomodated in a UC 005 A31 ultrasonic bath (Tesla, Vráble). The undissolved pyrene was separated on an S4 glass filter. The concentration of the substance in the micellar solutions did not exceed 10^{-4} mol l^{-1}.

Electronic absorption spectra were scanned on a Perkin–Elmer 330 instrument at room temperature. The fractions of the monomeric and dimeric MB species were determined from spectral data in the long-wavelength absorption band region (19 000 – 14 000 cm^{-1}).

The uncorrected luminescence spectra and fluorescence lifetimes of pyrene were measured on an apparatus described previously[10]. The exicitation source for pulse measurements was a home made nitrogen laser (337 nm emission wavelength, 2·5 ns FWHM, 300 kW power, 10 Hz pulse frequency). After passing an SPM-2 monochromator (Carl Zeiss, Jena), the luminescence was detected by an RCA 1P28 photomultiplier at 395 nm and recorded on a Tektronix 466 DM44 storage oscilloscope.

Laser-flash photolysis measurements were accomplished on a homemade apparatus[10]. The excitation pulse source was Q switched ruby laser (694·3 nm emission wavelength, 15 nm FWHM, 0·9 J pulse energy; Tesla — Vakuová elektronika, Prague). The time changes in transmittance of the excited samples at a chosen wavelength were detected with an RCA 1P28 or a 65 PK 413 (Tesla — Vakuová elektronika, Prague) photomultiplier using a Tektronix 466 DM44 storage oscilloscope. The samples were freed from oxygen by 20 min nitrogen purging in quartz cells $10 \times 10 \times 40$ mm inner dimensions with a neck closed with a rubber septum; nitrogen feed and outlet were provided by syringe needles.

RESULTS AND DISCUSSION

The photophysical and photochemical properties of solutions of MB are affected considerably by the formation of dimers and higher aggregates of the dye, proceeding readily particularly in aqueous solutions. While in aqueous solutions dimers predominate at concentrations of 10^{-5} mol l^{-1} and higher[11,12], in ethanolic systems at concentrations of $10^{-5}-10^{-4}$ mol l^{-1} the monomer–dimer equilibrium is shifted appreciably in favour of the former[11]. In micellar media this equilibrium is affected by the ionic nature of the tenside[5]. For investigating the possibility of energy and electron transfer in aqueous medium, the monomeric and dimeric fractions of MB were determined in micellar media of a cationic (DPB) and anionic (SDS) tensides. The proportions of the two species are best measured on the long-wavelength spectral band of the substance; the monomer exhibits its aborption maximum at 15 250 cm^{-1}, the dimer at 16 400 cm^{-1}. The dimer-to-monomer absorbance ratios at these wavelengths (A_D/A_M) are plotted against the MB concentration in Fig. 1. In water and DPB solutions the A_D/A_M ratio varies appreciably at concentrations of 10^{-6} to 10^{-4} mol l^{-1} whereas in ethanol and SDS this ratio remains constant, the equilibrium being shifted in favour of the monomer. At $c_{SDS} = 2{\cdot}5 \cdot 10^{-2}$ mol l^{-1} the concentration of micelles, calculated as $c_m = (c_{SDS} - CMC)/AN$, where CMC is the critical micellar concentration ($8{\cdot}1 \cdot 10^{-3}$ mol l^{-1}) and AN is the aggregation number ($AN = 62$, ref.[13]), is $2{\cdot}7 \cdot 10^{-4}$ mol l^{-1}. It can be assumed that at the maximum

MB concentration used, $1 . 10^{-4}$ mol l^{-1}, and in thermodynamic equilibrium, one molecule of MB is bonded to one micelle of SDS. Owing to electrostatic attraction, the monomer of the dye is "fixed", and it is reasonable to assume that the photophysical processes associated with the energy and electron transfer will be virtually unaffected by the dimer and higher aggregates present in low concentrations.

Pyrene in solutions in polar as well as nonpolar solvents exhibits long-lived fluorescence[14], on the order of 10^{-7} s^{-1}, and in dependence on concentration the fluorescence of the singlet excimer, whose lifetime is about ten times longer[14], is also observed in addition to the fluorescence of the monomer. In anionic micellar medium, pyrene dissolves in the hydrophobic part of the micelles and undergoes easily photoionization[15] giving rise to the cation-radical ($P^{+\cdot}$) and electron, which is expelled rapidly through the Stern layer into the aqueous medium where it is hydrated. The electronic absorption spectra of MB and pyrene in the micellar medium of SDS and their luminescence spectra are shown in Fig. 2. It is clear that in the concentration conditions used, pyrene solely and MB solely can be excited with the nitrogen pulse laser and the ruby laser, respectively, owing to which the changes in the fluorescence lifetime of monomeric pyrene in dependence on the concentration of MB and, conversely, changes in the lifetime of the $T_1 \rightarrow T_n$ absorption of MB in dependence on the concentration of pyrene or EDTA can be examined.

In micellar and ethanolic media, the fluorescence of pyrene is increasingly quenched with increasing concentration of MB (Fig. 3). In the absence of MB and oxygen, the pyrene fluorescence lifetime is 271 ns in ethanol and 322 ns in SDS medium, in agreement with published data[14]. In contrast to the homogeneous medium where the two partners solvated in the solvent cage can interact by diffusion-controlled processes, in micellar medium the interaction occurs through an ionic interface, and the kinetic relationships are considerably more complex[16–20].

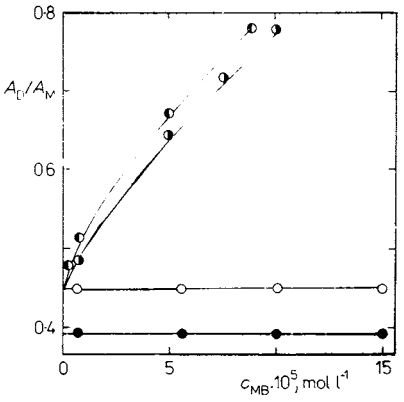

FIG. 1

Dimer-to-monomer absorbance ratio A_D/A_M in dependence on the concentration of MB in ◑ water, ◐ DPB ($2 . 10^{-2}$ mol l^{-1}), ○ SDS ($2{\cdot}5 . 10^{-2}$ mol l^{-1}), ● ethanol

The following rate constants can be used for the counterpart solvated inside the micelle (e.g., pyrene): k_f, the reciprocal fluorescence lifetime ($k_f = 1/\tau_0$, s^{-1}); k_e, referring to the entering of a molecule of quencher into the micelle ($1\ mol^{-1}\ s^{-1}$); k_a, referring to the abandoning of the micelle by a molecule of quencher (s^{-1}); and k_{qm}, referring to the quenching of the excited state of pyrene molecule by a molecule of quencher in the micelle (s^{-1}). The rates of the two last processes depend also on the number of molecules of quencher, i; they are expressed as $ik_a[P_i^*]$

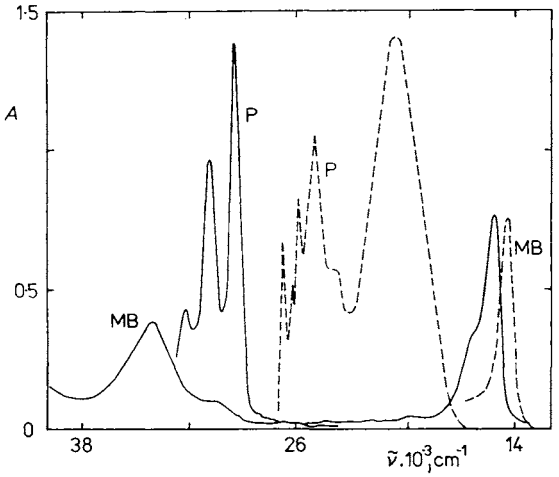

FIG. 2

Absorption ——— and uncorrected luminescence ----- spectra of pyrene ($1 . 10^{-4}$ mol l^{-1}) and MB ($1 . 10^{-5}$ mol l^{-1}) in SDS; $l = 1$ cm

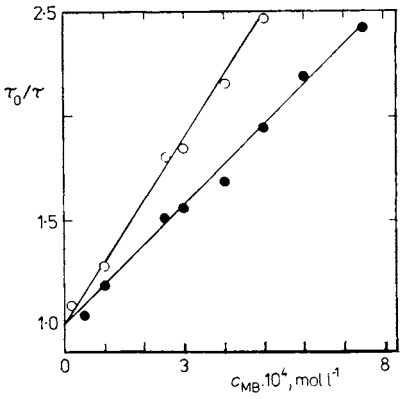

FIG. 3

Quenching of fluorescence of pyrene ($1 . . 10^{-4}$ mol l^{-1}) by MB in ● ethanol and ○ SDS

and $ik_{qm}[P_i^*]$, respectively, where $[P_i^*]$ is the concentration of micelles containing i quenchers and one molecule of P (pyrene). The rate constant for such a system then can be expressed as

$$-d[P_i^*]/dt = (1/\tau_0 + k_e[Q_w] + ik_a + ik_{qm})[P_i^*] - (i+1)k_a[P_{i+1}^*] - k_e[Q_w][P_{i-1}^*], \quad (1)$$

where $i = 0, 1, 2, \ldots$ and $[Q_w]$ is the concentration of quencher in water; $[P_{-1}^*] = 0$. The fluorescence decay curve for this case has been derived[16-8] in a more complex exponential form for excitation with a δ-pulse (Eqs (2)–(4)):

$$I_F(t) = I_F(0) \exp\{-At + B[\exp(-Ct) - 1]\} \quad (2)$$

with

$$A = 1/\tau_0 + \alpha[Q_t] \quad (3)$$

$$B = \beta[Q_t], \quad (4)$$

where $\alpha = k_{qm}k_e/[(k_{qm} + k_a)(1 + K[M])]$, $\beta = k_{qm}^2 k_e/[k_a(k_{qm} + k_a)^2(1 + K[M])]$, $K = k_e/k_a = [Q_m]/([Q_w][M])$, $C = k_{qm} + k_a$, $[M]$ is the concentration of micelles, $[Q_m]$ is the concentration of quencher in micelles and $[Q_t]$ is the total concentration of quencher, $[Q_t] = [Q_m] + [Q_w]$.

Eq. (2) describes the biexponential decay of fluorescence of P* arising basically from the nonuniform distribution of quencher inside the micelle during the lifetime of P*. This distribution is a result of competitive processes associated with the mobility of the quencher (k_e, k_a) and the quenching itself (k_{qm}). If the rates of these processes are comparable in magnitude, there are 0, 1, 2 or more quenchers bound in a micelle. With regard to the fact that MB is rather strongly bonded in the vicinity of the negatively charged Stern layer owing to electrostatic attraction, and virtually one molecule of MB comes to one SDS micelle, MB cannot be expected to leave this region within the lifetime of P*. The decay of fluorescence of pyrene is thus monoexponential over the MB concentration range used, Eq. (2) being simplified[21] to

$$I_F(t) = I_F(0) \exp A't, \quad (5)$$

where

$$A' = 1/\tau_0 + k_{qm}[Q_t]/(K^{-1} + [M]). \quad (6)$$

Quenching is the slowest process, and a steady state with respect to the mobility of MB exists during the life of P*; the solutions is "homogenized" with respect to the quencher. In such conditions, the Stern–Volmer relation (7),

$$\tau_0/\tau = 1 + \tau_0 k_{qm} K[Q_t]/(1 + K[M]) \qquad (7)$$

is obeyed.

The case where $K[M] \leqq 1$ must be examined. With metal cations as pyrene fluorescence quenchers, K is largely on the order of $10^3 - 10^4$ l mol^{-1} (ref.[21]). Owing to the fact that the positive charge in the molecule of MB can be to some extent delocalized over the π-electron system, this molecule – despite its size – can overcome the barrier of the positive Gouy–Chapman layer of Na^+ ions and bond in the negatively charged Stern layer of the micelle. In analogy to positive ions[21], K can be expected to be on the order of 10^4 l mol^{-1}. Eq. (7) combined with experimental data (Fig. 3) then gives the slope of the linear dependence $2{\cdot}9 \cdot 10^3$ and $k_{qm} = 1{\cdot}8 \cdot 10^6$ s^{-1} (for $\tau_0 = 322$ ns).

According to Almgren and coworkers[22], the thickness of the spherical layer d_s from the surface of the micelle to the aqueous medium where interaction between the metal cations and the counterpart solvated predominantly in the micelle can take place is inversely proportional to the magnitude of the positive charge. For an MB molecule (about 1·4 nm long) with a delocalized positive charge this layer thickness can be expected to be relatively high. The empirical relation[18] (*8*) for a micelle radius of 2 nm (ref.[23]),

$$d_s = (66 k_{qa}/k_{qm} + 8\,000)^{1/3} - 20\,, \qquad (8)$$

where k_{qa} is the quenching rate constant in aqueous medium, gives d_s 4·4 nm. This is a rather high value, actually more than twice as high as the micelle radius.

For the quenching of fluorescence of pyrene in micelles of SDS e.g. by Tl^+ or Eu^{3+} ions[18] (ionic radii[24] 0·136 and 0·097 nm, respectively), the calculated d_s values are 1·0 and 0·5 nm, respectively. The d_s values calculated by the empirical theory are consistent with the above concept provided that a molecule of MB fits into a sphere 1·4 nm in diameter. The calculated d_s value is the limiting distance within which energy transfer from the S_1 state of pyrene to MB can take place. The most probable is the singlet–singlet energy transfer, whose rate r_{DA} is a function[25] of the distance between the energy donor and acceptor, R_{DA}, and the Förster radius R_0:

$$r_{DA} = \tau_0^{-1}(R_0/R_{DA})^6\,, \qquad (9)$$

where

$$R_0^6 \approx q_D \int F(\tilde{\nu})\, \varepsilon(\tilde{\nu})\, \frac{d\tilde{\nu}}{4}\,, \qquad (10)$$

q_D is the quantum yield of fluorescence of the donor, and the integral refers to the overlap of the fluorescence ($F(\tilde{\nu})$) and absorption ($\varepsilon(\tilde{\nu})$) spectra of the energy donor and acceptor.

The quantum yield of fluorescence of pyrene in deaerated SDS solutions is 0·6

(ref.[26]). Fig. 2 demonstrates that the fluorescence and absorption spectra of pyrene and MB overlap. The molar absorptivity of MB in the spectral range of fluorescence of pyrene is on the order of 10^3 l mol^{-1} cm^{-1}. By comparison with similar cases[26], R_0 is estimated to be about 1 nm. For efficient energy transfer in a micelar system, R_0 must not be considerably lower than the micelle radius, or d_s (considering the distribution of pyrene in the vicinity of the Stern layer in terms of the concept[22]). For $R_{DA} = d_s$, Eq. (9) gives $r_{DA} = 4{\cdot}3 \,.\, 10^2$ s^{-1}, whereas for $R_{DA} = 1$ nm, this value is $3 \,.\, 10^6$ s^{-1}, hence, on the same order of magnitude as k_{qm}. Thus the mean distance for energy transfer between pyrene and MB is likely to approach 1 nm; this distance is sufficient for energy transfer by the dipole–dipole interaction mechanism.

Pyrene fluorescence quenching can also be contributed to photoionization[27-29], which is appreciable particularly in the anionoid micellar medium during excitation with a pulse laser (the 2nd harmonic of the ruby laser at 347·1 nm, 250 mJ). Photoionization is a biphotonic process[27,29], strongly dependent on the excitation radiation intensity. A nitrogen pulse laser with an output energy of 1·25 mJ/pulse was used by us; this energy is considerably lower than that used by other authors[27-29]. We suppose that in our experiments, photoionization of pyrene giving rise to its cation-radical and hydrated electron virtually did not take place.

Quenching of fluorescence of pyrene by molecules of MB in a micellar medium is examined here from the point of view of its dynamic component. Static quenching, arising from interactions in the ground electronic state such as formation of CT complexes and aggregates, can also be considered. The trivial reabsorption of the pyrene fluorescence by MB molecules certainly plays a significant part in this system as well. No evidence of complex or aggregate formation was gained from spectral measurements in the homogeneous medium of ethanol or the micellar medium of SDS at various concentration ratios of the two partners. We assume that a substantial role in the pyrene fluorescence quenching is played by the dynamic singlet–singlet energy transfer, the intensity of the red fluorescence of MB in the solutions studied growing with increasing concentration of pyrene during its selective excitation.

Laser-flash photolysis measurements showed that the lifetime of the T_1 state of MB monomer (measured at 420 nm) in ethanol, 34 μs, is about twice as long as in SDS medium (19 μs). The $T_1 \rightarrow T_n$ absorption quenching[5,30] is accelerated by the presence of pyrene or EDTA in both media (Fig. 4). The effect of concentration of quencher is particularly marked in the case of EDTA. The Stern–Volmer relation is obeyed up to a concentration of about $1 \,.\, 10^3$ mol l^{-1} (Fig. 5). In agreement with published data[4,30,31] we assume that in both cases the $T_1 \rightarrow T_n$ absorption quenching is due to electron transfer from pyrene or EDTA to the T_1 state of MB. The electron transfer rate constants calculated from these measurements are $5 \,.\, 10^6$ l mol^{-1} s^{-1} for pyrene and $2 \,.\, 10^8$ l mol^{-1} s^{-1} for EDTA. For the latter, this value is an order of magnitude higher than in the homogeneous aqueous medium[32] or in a water–

-acetonitrile mixture[33]. This is rather surprising in the light of the work of Usui and Saga[4], who found that in the anionoid micellar medium of SDS the photochemical reduction of MB by the negatively charged ions of EDTA was strongly inhibited for electrostatic reasons. Based on our results we suggest that the "inhibition" is primarily due to electron back-transfer from the EDTA radical to the MB radical.

The rate constant of electron tansfer from pyrene to the T_1 state of MB is roughly two orders of magnitude lower than for EDTA. The Gibbs free energy G^0 for this redox process is 18·3 kJ mol^{-1} ($E^{ox}_{1/2}(P/P^{+\cdot}) = -1{\cdot}4$ V, $E^{red}_{1/2}(^3MB^+/MB^{\cdot}) = 1{\cdot}21$ V,

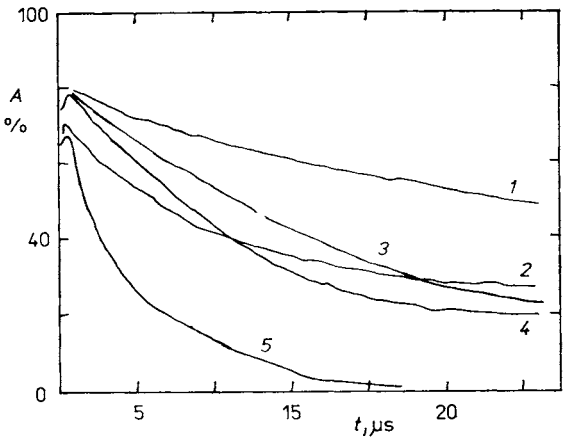

FIG. 4

Decay of the $T_1 \rightarrow T_n$ absorption of MB ($1 . 10^{-4}$ mol l^{-1}). Medium: *1* ethanol, *2* ethanol with pyrene ($1 . 10^{-4}$ mol l^{-1}), *3* SDS, *4* SDS with pyrene, *5* SDS with EDTA ($5 . 10^{-4}$ mol l^{-1})

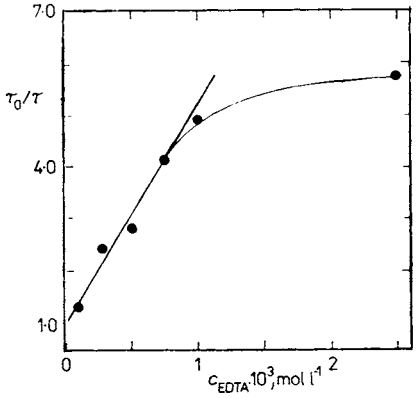

FIG. 5

Quenching of the $T_1 \rightarrow T_n$ absorption of MB in dependence on the concentration of EDTA in SDS

ref.[31]). This value is considerably higher than the limit for the diffusion-controlled exothermal process of quenching of triplet states of organic dyes by electron transfer[34] ($G^0 < -42\,\mathrm{kJ\,mol^{-1}}$). From the thermodynamic point of view this process is endothermal and it must be orders of magnitude lower than the diffusion-controlled electron transfer (rate constant on the order of $10^9 - 10^{10}\,\mathrm{l\,mol^{-1}\,s^{-1}}$).

REFERENCES

1. Turro N. J., Grätzel M., Braun A. M.: Angew. Chem. *92*, 712 (1980).
2. Fendler J. H.: J. Chem. Educ. *60*, 872 (1983).
3. Singhal G. S., Rabinovich E., Heveri J., Srinivasan V.: Photochem. Photobiol. *11*, 531 (1970).
4. Mitsuzuka M., Kikuchi K., Kokubun H., Usui Y.: J. Photochem. *29*, 363 (1985).
5. Murgia S. M., Poletti A.: Photobiochem. Photobiophys. *5*, 53 (1983).
6. Sudo Y., Toda F.: J. Chem. Soc., Chem. Commun *1979*, 1044.
7. Bagno O., Saulignac J. C., Joussot-Dubien J.: Photochem. Photobiol. *29*, 1079 (1979).
8. Gorman A. A., Lovering G., Rodgers M. A. J.: Photochem. Photobiol. *23*, 399 (1976).
9. Berlman I. B.: *Handbook of Fluorescence Spectra of Aromatic Molecules.* Academic Press, New York 1971.
10. Řehák V.: Chem. Listy *72*, 1289 (1978).
11. Bergmann K., O'Konski C. T.: J. Phys. Chem. *67*, 2169 (1963).
12. Rabinovich E., Epstein L. F.: J. Am. Chem. Soc. *63*, 69 (1941).
13. Blažej A. (Ed.): *Tenzidy.* Alfa, Bratislava 1977.
14. Birks J. B.: *Photophysics of Aromatic Molecules.* Wiley–Interscience, London 1970.
15. Grätzel M., Thomas J. K.: J. Phys. Chem. *78*, 2248 (1974).
16. Infelta P. P., Grätzel M., Thomas J. K.: J. Phys. Chem. *78*, 190 (1974).
17. Tachiya M.: Chem. Phys. Lett. *33*, 289 (1975).
18. Dederen J. C., Van der Auweraer M., De Shryver F. C.: Chem. Phys. Lett. *68*, 451 (1979).
19. Löfroth J.-E., Almgren M.: J. Phys. Chem. *86*, 1636 (1982).
20. Almgren M., Löfroth J.-E.: J. Chem. Phys. *76*, 2734 (1982).
21. Dederen J. C., Van der Auweraer M., De Shryver F. C.: J. Phys. Chem. *85*, 1198 (1981).
22. Almgren M., Grieser F., Thomas J. K.: J. Am. Chem. Soc. *101*, 2021 (1979).
23. Kratochvíl J. P.: Chem. Phys. Lett. *60*, 238 (1979).
24. Rabinovič V. A., Chavin Z. Ja.: *Stručná chemická příručka.* SNTL — Nakladatelství technické literatury, Prague 1985.
25. Förster T.: *Comprehensive Biochemistry.* Elsevier, Amsterdam 1967.
26. Koglin P. K. F., Miller D. J., Steinwandel J., Hauser M.: J. Phys. Chem. *85*, 2363 (1981).
27. Richards J. T., West G., Thomas J. K.: J. Phys. Chem. *74*, 4137 (1970).
28. Wallace S. C., Grätzel M., Thomas J. K.: Chem. Phys. Lett. *23*, 359 (1973).
29. Hall G. E.: J. Am. Chem. Soc. *100*, 8262 (1978).
30. Řehák V., Poskočil J.: Collect. Czech. Chem. Commun. *44*, 2015 (1979).
31. Ohno T., Lichtin N. N.: J. Phys. Chem. *86*, 354 (1982).
32. Vogelmann E., Kramer H. E. A.: Photochem. Photobiol. *23*, 383 (1976).
33. Becker H. G. O., Schütz R., Tillack B., Řehák V.: J. Prakt. Chem. *328*, 661 (1986).
34. Vogelmann E., Schreiber S., Rauscher W., Kramer H. E. A.: Z. Phys. Chem. (Wiesbaden) *101*, 321 (1976).

Translated by P. Adámek.