

SELF—DEPOLARIZATION IN FLUORESCENT LIQUID SOLUTIONS

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The theory of concentrational depolarization of photoluminescence as formulated by BOJARSKI has been extended over liquid solutions. The effect of strong repolarization within the region of high concentrations of more liquid solutions can be explained by the rise of the degree of association of luminescent molecules and significant restriction of their effective rotational motion due to the shortening of the lifetime molecules in the excited state.

Introduction

The concentrational depolarization of photoluminescence (CDPL) of solutions is a result of nonradiative electronic excitation energy transfer [1] between active molecules of different mutual orientation [2, 3]. A number of theories have been formulated to explain this phenomenon. Critical reviews of these theories can be found in [4—7]. All of them concern, in principle, rigid solutions *i.e.* solutions in which active molecules do not change their positions and orientations of the transition moments during their excited state lifetime.

In recent years more and more attention has been paid to luminescent systems in which restricted rotations of molecules can occur for various reasons. This was stimulated by the application of luminescence methods, and among them polarization ones, to the investigations of biological systems and their dynamic structure [8, 9]. The above mentioned theories were applied in some causes to interpret polarization data on such systems despite the fact that these systems do not have identical properties with rigid solutions.

Dye molecules in real solutions have, as a rule, some freedom of translational and rotational motion. The state of polarization of a system depends significantly on the rotation of molecules, which is one of the principal factors responsible for the fluorescence depolarization. This problem has been dealt with in many works [7, 10—13], while more detailed analyses of the problem in which the concentrational depolarization has been taken into account can be found in few papers only [14—16].

Theoretical considerations

The influence of Brownian rotational motion of the luminescent molecules on CDPL is analysed on the basis of the CDPL theory as formulated by BOJARSKI [17]. This theory is especially useful for self-depolarization investigations for it explains the effect of repolarization observed for highly concentrated solutions [16, 18].

The theory is valid for solutions containing two kinds of rigid molecules — donor (D) and acceptor molecules (A) — distributed randomly, between which manifold acts of excitation energy transfer of the type $D^* + D \rightarrow D + D^*$, as well as single transfer acts of the type $D^* + A \rightarrow D + A^*$ can occur. In the frame of this theory the following relation for the emission anisotropy (EA) has been obtained

$$r/r_0 = (1 - \alpha f) \left[1 + \frac{1}{2} \cdot \frac{(\alpha f)^2}{1 - \frac{3}{4}(\alpha f)^2} \right] \quad (1)$$

where

$$f \equiv f(\gamma) = \sqrt{\pi} \gamma \exp(\gamma^2) \left[1 - \frac{2}{\sqrt{\pi}} \int_0^\gamma \exp(-t^2) dt \right] \quad (2)$$

$$\alpha = \alpha_0 [\gamma_D / (\gamma_D + \gamma_A)] \quad (3)$$

$$\gamma = \gamma_D + \gamma_A = \frac{\sqrt{\pi}}{2} \left(\frac{c_D}{c_{0D}} + \frac{c_A}{c_{0A}} \right). \quad (4)$$

Here r_0 is EA of donor molecules in a solution where the donor concentration $c_D \rightarrow 0$ and the acceptor concentration $c_A = 0$; c_{0D} and c_{0A} are critical concentrations of the donor and acceptor, respectively [2, 3]; α_0 is the probability that the excitation energy will not be dissipated during the transfer.

It should be noted that the general picture of energy migration among donors and its transfer to acceptors for liquid solutions the same as for rigid ones. Thus, apparently, relation [1] should give the correct description of EA also for liquid solutions. One cannot however, neglect the effect of molecule rotation on the limit value of the donor molecule EA (*i.e.* for the case of $c_D \rightarrow 0$ and $c_A = 0$ simultaneously) and on the energy transfer efficiency associated with rotations of molecules during their excited state lifetime [3, 9].

The limit emission anisotropy r_f for a system containing isolated and isotropically oriented rotating molecules is given by [10, 12, 19]

$$r_f = r_0 \left(\frac{3}{2} \langle \cos^2 \theta \rangle - \frac{1}{2} \right) \quad (5)$$

where θ is the angle between the directions of molecule transition moments in the instants of its excitation and de-excitation; r_0 has the same meaning as in (1).

For spherical molecules — the simplest case possible — formula (5) reduces to the known Perrin—Levshin formula [11, 13]

$$r_f = r_0 \left(1 + \frac{kT}{V\eta} \tau_0 \right)^{-1} \quad (6)$$

where k is the Boltzmann constant; T is the temperature; V is the volume of the rotating molecule; η is the solution viscosity; and τ_0 is the fluorescence decay lifetime.

The mean time in which a molecule is in the excited state τ_i , also called the localization time, is for concentrated solutions shorter than τ_0 , which is caused by intermolecular energy transfer acts competing with the fluorescence emission acts.

Denote by r'_{fD} EA of donor molecules in a liquid solution which are excited directly by an external radiation. Then the Perrin—Levshin formula (6) can be written as

$$r'_{fD} = r_0 \left[1 + \left(\frac{kT}{V\eta} \tau_0 \right) \frac{\tau_i}{\tau_0} \right]^{-1} \quad (7)$$

According to the assumptions of the theory [17] as well as other theories [2—7] those molecules only which have been excited by the external radiation contribute substantially to the polarization. For this reason r'_{fD} in a concentrated liquid solution corresponds to r_0 in a rigid solution.

Thus the relation for the emission anisotropy in liquid solutions will be obtained when r_0 in formula (1) is substituted with r'_{fD} . Then the concentration dependence of EA for liquid solution, will be given by

$$r_D/r_0 = \left[1 + \left(\frac{kT}{V\eta} \tau_0 \right) \frac{\tau_i}{\tau_0} \right]^{-1} \cdot (1 - \alpha f) \left[1 + \frac{1}{2} \cdot \frac{(\alpha f)^2}{1 - \frac{3}{4} (\alpha f)^2} \right], \quad (8)$$

which for $\gamma \rightarrow 0$ (leading to $\tau_i/\tau_0 = 1$) reduces to the Perrin—Levshin formula (6). The ratio τ_i/τ_0 in (8) can be calculated from the relation [20]

$$\tau_i = \tau_0 \left[1 - \left(\frac{1}{2} \cdot \frac{f(\gamma)}{1 - f(\gamma)} - \gamma^2 \right) \right] \quad (9)$$

derived recently based on theoretical results [21] in agreement with the CDPL theory [17].

It was already mentioned that the energy transfer efficiency depends strongly on the mutual orientation of molecules [3, 9, 22]. For solutions the energy transfer efficiency will depend on the mean value of the orientation factor κ^2 , as employed in the theory of long-range electronic excitation energy transfer [1, 3]. According to our earlier work [23] changes of the excitation energy transfer efficiency caused by the rotation of luminescent molecules can be related to critical concentration variations. For three-dimensional solutions

$$\begin{aligned} c_{0D} &= \bar{c}_{0D} \cdot \sqrt{2/3} \left(\langle \sqrt{\langle \kappa_{DD}^2 \rangle} \rangle \right)^{-1} \\ c_{0A} &= \bar{c}_{0A} \cdot \sqrt{2/3} \left(\langle \sqrt{\langle \kappa_{DA}^2 \rangle} \rangle \right)^{-1} \end{aligned} \quad (10)$$

where \bar{c}_{0D} and \bar{c}_{0A} are critical concentrations of liquid solutions that contain very fast rotating molecules for which it is assumed that $\kappa_{DD}^2 = \kappa_{DA}^2 = 2/3$ [3, 22]; $\langle \sqrt{\langle \kappa_{DD}^2 \rangle} \rangle$ and $\langle \sqrt{\langle \kappa_{DA}^2 \rangle} \rangle$ are mean values of κ^2 averaged over time and the initial orientations of the transition moments of interacting molecule pairs, $D^* - D$ and $D^* - A$, respectively [23].

Results obtained recently by the author [24] which concern the course of $\langle \sqrt{\langle \kappa_{DA}^2 \rangle} \rangle$ value for arbitrary values of so-called rotational orientation factors d_D and d_A are shown in Fig. 1. These factors are defined by formulae [12, 19]

$$d_D = \frac{3}{2} \langle \cos^2 \theta_D \rangle - \frac{1}{2}; \quad d_A = \frac{3}{2} \langle \cos^2 \theta_A \rangle - \frac{1}{2} \quad (11)$$

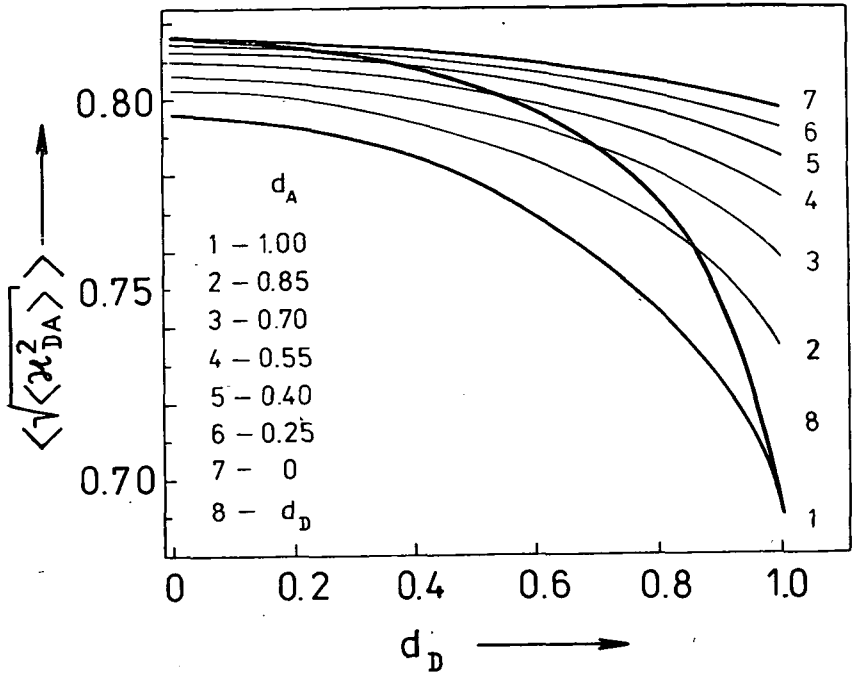


Fig. 1. Mean value of the orientation factor κ^2 , $\langle \sqrt{\langle \kappa^2 \rangle} \rangle$ plotted against values of rotation depolarization factors d_D and d_A for donor and acceptor molecules in a solution [24].

where θ_D and θ_A have the same meaning as the angle θ in formula (5), for the donor and acceptor molecules, respectively. In view of the above presented discussion the rotation depolarization factors for spherical molecules can be described by relations

$$d_D = \left[1 + \left(\frac{kT}{V_D \eta} \tau_0 \right) \frac{\tau_1}{\tau_0} \right]^{-1}; \quad d_A = \left[1 + \left(\frac{kT}{V_A \eta} \tau_0 \right) \frac{\tau_1}{\tau_0} \right]^{-1} \quad (12)$$

where V_D and V_A are volumes of donor and acceptor molecules, respectively (together with solvation envelope, if any [7]).

On grounds of formulae (4) and (7) the reduced concentration of a liquid solution is given by the relation

$$\gamma = \frac{1}{2} \sqrt{\frac{3\pi}{2}} \left[\langle \sqrt{\langle \kappa_{DD}^2 \rangle} \rangle \frac{c_D}{\bar{c}_{0D}} - \langle \sqrt{\langle \kappa_{DA}^2 \rangle} \rangle \frac{c_A}{\bar{c}_{0A}} \right] \quad (13)$$

thus depending on d_D and d_A through averaged values of κ^2 . It follows then that EA of liquid solutions is also a function of rotation depolarization factors d_D and d_A ; indeed, the results for limit cases are as expected: for complete rotations of molecules $d_D=0$ and from (8) it follows that $r_D/r_0=0$, while for a case of no rotation, i.e. for $d_D=d_A=1$ formula (8) leads to (1).

Discussion of results and conclusions

Formula (8) describing the effect of concentrational depolarization in liquid solutions can be written as a product of two depolarization factors — rotation factor d_D (Eq. (12)) and transfer depolarization factor d_t associated with the intermolecular excitation energy transfer and described by the right-hand side of relation (1). This does not mean, however, that both factors are independent of each other. It should be noted that molecule rotations result in increased energy transfer efficiency. This leads to shortening of the localization time τ_i , limiting the extent of rotational motion and reducing, in turn, the efficiency of the energy transfer. Thus rotations are responsible for two concentration — dependent effects acting in opposite directions, namely the relative decrease and increase of EA as compared to the situation in rigid solutions.

Fig. 2 shows the dependence of r/r_0 on concentration for different values of the rotation depolarization factor $d_D^{(0)}$ (equal to d_D for $c_D \rightarrow 0$) in solutions containing molecules of one species only, i.e., when molecule association does not occur (the dimerization constant $K=0$ [1/M]). It should be noted that for more liquid solutions relative changes of EA with concentration (related to appropriate limit values r_f)

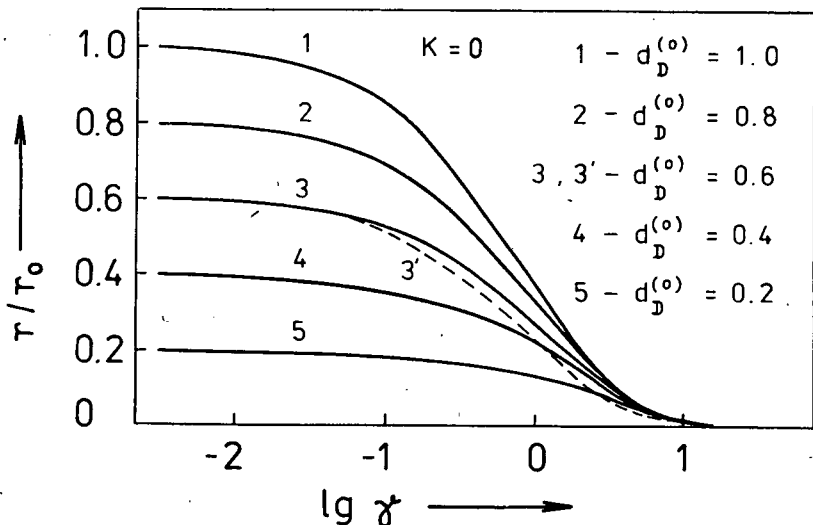


Fig. 2. Concentration dependence of EA for one-component non-dimerizing liquid solutions, obtained according to (8) for different values of rotation depolarization factors $d_D^{(0)}$. The dashed line 3' correspond to the product of values of r/r_0 taken from curve 1 and $d_D^{(0)}=0.6$.

are smaller, while at the same time at extremely high concentrations values of EA become identical independent of the solution viscosity.

This proves that the above mentioned effect of the relative rise of EA due to the shortening of τ , prevails over the effect of depolarization caused by the molecule rotation and dominates over the range of very high solution concentrations. The same is evident from curve 3 in Fig. 2, showing the product $d_B^{(0)} \cdot d_i$ for $d_B^{(0)} = 0.6$ and d_i corresponding to that in a rigid solution. The effect of concentrational depolarization of liquid solutions as predicted by formula (8) is weaker than for the concentrational and rotational depolarization regarded as mutually independent.

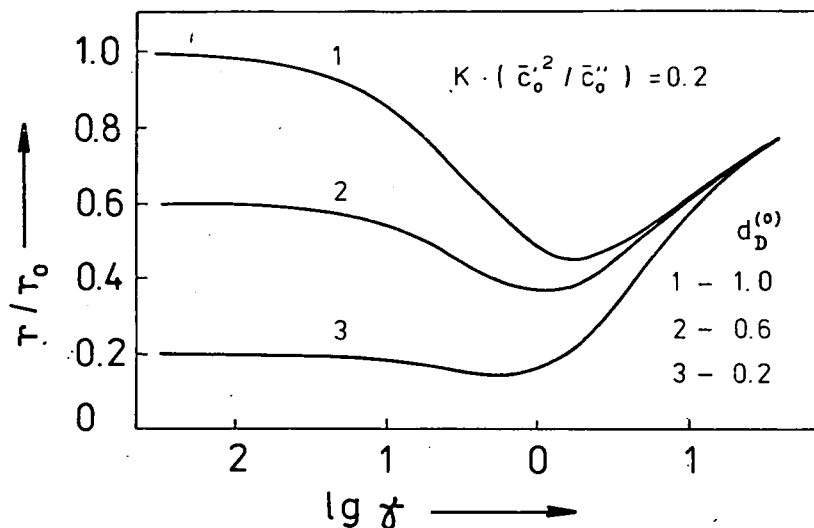


Fig. 3. Dependence of the EA on concentration, as expected in view of (8), for solutions of different viscosity and set value of $k \cdot (\bar{c}_0'' / \bar{c}_0') = 0.2$; k is the dimerization constant while \bar{c}_0' and \bar{c}_0'' denote critical concentrations with respect to the energy transfer between monomer molecules and from monomers to dimers, respectively, for the mean value of the orientation factor equal to $2/3$.

Studies of systems in which molecule association takes place lead to analogous conclusions. Fig. 3 shows theoretical results for r/r_0 obtained from (8) for solutions containing luminescent monomers and non-luminescent dimers only, and characterized by the same value of the dimerization constant K , but different values of $d_B^{(0)}$. It is evident that the presence of dimers quenching the excitation energy leads at high concentrations of solutions to the shortening of the localization time τ , for monomers, effective enough to make the behaviour of active molecules in liquid solutions identical to that in rigid ones. As a result the repolarization of luminescence is so strong that for high concentrations the values of EA can substantially exceed the limit value r_f .

Such phenomenon has also been observed in experiments among others, for solutions of low viscosity as fluorescein in a glycerin — water solvent [16]. Some results presented in that paper have been replotted in our Fig. 4 (circles) to compare

with theoretical curves given by the modified BOJARSKI theory (relation (8)) for the solutions investigated. Data presented in [16] were used for determination, based on the Perrin—Levshin formula, of the fundamental EA, equal to $r_0=0.4$, and the parameter $kT\tau_0/V_D=0.161 \text{ P}^{-1}$. Other quantities required were obtained by comparing the experimental results with theoretical ones for the most viscous system

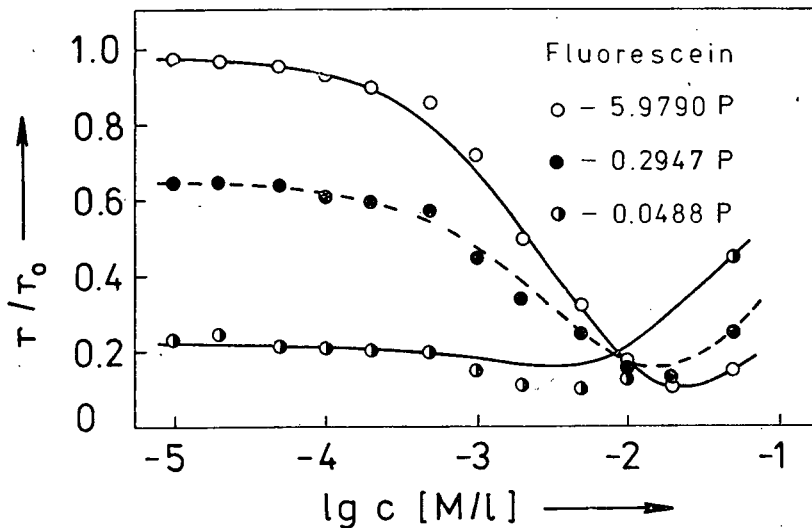


Fig. 4. Comparison of experimental values of r/r_0 from [16] with theoretical (calculated according to (8)) values of concentration dependent EA for solutions investigated.

(regarded as a rigid solution). To this end the method described in [25] was employed. As a result the dimerization constant $K=1 \text{ l/M}$ was obtained for the system mentioned, whereas such constant for the remaining two systems of lower viscosity, namely $K=2.51 \text{ l/M}$ for solutions having $\eta=0.2947 \text{ P}$ and $K=131 \text{ l/M}$ for solutions with $\eta=0.0488 \text{ P}$ were determined by fitting the theoretical curves to experimental values of r/r_0 for maximum concentrations. It was assumed additionally that for solutions under consideration the values of $\langle \sqrt{\chi_{DD}^2} \rangle$ and $\langle \sqrt{\chi_{DA}^2} \rangle$ are equal to 0.6901, which corresponds to the rigid solution case. This can be justified by the independence of r/r_0 at extremely high concentrations of the solution viscosity, as shown in Fig. 3 where r/r_0 values are determined solely by the value of the dimerization constant K .

Theoretical results obtained, shown in Fig. 4, agree well, both qualitatively and quantitatively, with the experimental points. This shows that the Bojarski theory [17], adapted to dimerizing liquid solutions by allowing for rotation of active molecules, gives correct description of the concentrational depolarization effect, at the same time explaining well the strong repolarization of liquid solutions. It seems, however, that certain differences between experimental and theoretical results for the most liquid system may be associated, at least in part, with the omission of

increased rate of intermolecular energy transfer due to the translational motion of molecules accompanying their rotations [26, 27].

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САМО-ДЕПОЛАРИЗАЦИЯ В ФЛУОРЕСЦИРУЮЩИХ ЖИДКИХ РАСТВОРАХ

Й. Дудкиевич

Распространена теория концентрационной деполяризации фотолуминесценции Боярского на жидкие растворы. Эффект сильной деполяризации в области высоких концентраций для многих жидких растворов может быть объяснен возрастанием степени ассоциации люминесцирующих молекул и значительным ограничением их эффективного вращательного движения, в результате сокращения времени возбужденного состояния молекул.