

The Influence of Rotational Depolarization on the Mechanism of Energy Transport in two-Component Systems: The Nature of Correlations¹

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The correlation effect in two-component systems of different viscosities was analyzed based on a concentration depolarization experiment. The inclusion of a correlation effect was found to be fully justified only in systems for which the localization time, τ_l , is considerably shorter than that of the rotational relaxation, τ_{rot} . On the grounds of an approximate analysis, taking into account the competition between the concentration and the rotational depolarization, it was possible to explain the concentration changes in the emission anisotropy in the systems investigated.

KEY WORDS: Emission anisotropy; rotational depolarization; concentration depolarization; correlations; energy transport.

INTRODUCTION

Recently progress has been made in understanding the nonradiative excitation energy transport in disordered systems of donor (D) and acceptor (A) molecules by taking into account the preferential return of the excitation energy to the molecule from which it has just been transferred [1–6]. Such a mechanism takes place when a correlation exists between the configurations of the donor molecules surrounding the excited D molecule before and after the transfer. Several experiments and Monte Carlo simulations were recently reported, which confirmed the influence of the correlations on the quantum yield and emission anisotropy in viscous solutions [7–10]. In the case of viscous solutions the localization time,

τ_l ⁴ [11,12], in the presence of energy transport is usually markedly shorter than that of rotational relaxation, τ_{rot} . This implies that the mutual orientations of the transition dipole moments of molecules taking part in the act of nonradiative energy transfer do not change during τ_{rot} . It is this fact that, in our opinion, leads to the increased probability of the excitation energy being transferred back to the molecule from which it has recently been received. If, however, τ_l is comparable to or distinctly longer than τ_{rot} , then the orientations of the molecules can be randomly changed during their lifetime and the non-Markovian memory effect of correlations should disappear. This is likely to take place in liquid solutions, although in this case the two competing processes, i.e., rotational

⁴ The localization time, τ_l , is defined as follows: $\tau_l = \left[\sum_D k_{DD} + \sum_A k_{DA} + k_F + k_q \right]^{-1}$, where k_{DD} and k_{DA} denote the rate constants for nonradiative donor-to-donor and donor-to-acceptor transfer, respectively, k_F is the rate constant for emission, and k_q is the rate constant for nonradiative internal transition.

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and concentration depolarization, should be considered simultaneously. Several papers dealing with this problem have been published [11,13–19]. However, the results reported do not allow a general comparison between the theory and the experimental data. Although no coherent statistical theory of the two competing processes has been formulated so far, it is possible to analyze approximately the nature of correlations based on the existing theories of rotational and concentration depolarization.

In this paper the results of concentration depolarization studies of several two-component systems with different solvent viscosities are reported. A preliminary analysis of the correlations and conditions under which they should occur is presented based on the results obtained.

THEORETICAL BASIS

Up to the present no coherent theoretical analysis of nonradiative energy transport and rotational diffusion allowing interpretation of experimental data has been carried out. The main difficulty is connected inseparably with accurate consideration of the competition between the above-mentioned phenomena in the excited-state lifetime scale. For this reason a heuristic approximate approach, presented below, could be of practical value.

Let us consider Perrin's formula for relative emission anisotropy [20]:

$$\frac{r}{r_0} = \frac{1}{1 + \frac{kT}{V\eta'} \tau_1} \quad (1)$$

where r_0 is the limiting emission anisotropy, $\tau_{\text{rot}} = V\eta'/kT$ (V is the effective volume of the luminescent molecule and η' denotes the solvent viscosity), and τ_1 denotes the mean localization time in the presence of energy transport. This expression can be rewritten in the following form:

$$\frac{r}{r_0} = \frac{1}{1 + (\tau_0/\tau_{\text{rot}}) \cdot (\tau_1/\tau_0)} = \frac{1}{1 + b (\tau_1/\tau_0)} \quad (2)$$

where $b = \tau_0/\tau_{\text{rot}}$ and τ_0 denotes the mean fluorescence lifetime of donor molecules in the absence of energy transport. At low donor concentrations, C_D , and in the absence of acceptors, $\tau_1 = \tau_0$. In this case the observed

emission anisotropy is equal to r' measured for a given solvent viscosity and the following relation is fulfilled:

$$\frac{r'}{r_0} = \frac{1}{1 + b} \quad (3)$$

Hence, for the measured r_0 and r' , one can determine the value of parameter b . Either by measuring or by taking the literature value of τ_0 , the value of τ_{rot} can easily be found (even without determining the effective volume and solvent viscosity).

The localization time, τ_1 , decreasing with the increase in concentration due to energy transport, is given by the formula [11]

$$\tau_1 = \tau_0 \cdot \frac{1 + \gamma^2 - (1.5 + \gamma^2)f}{1 - f} \quad (4)$$

where

$$\gamma = \frac{\sqrt{\pi}}{2} \cdot \left(\frac{C_D}{C_{\text{ODD}}} + \frac{C_A}{C_{\text{ODA}}} \right) \quad (5)$$

$$f(\gamma) = \sqrt{\pi} \gamma \exp(\gamma^2) [1 - \text{erf}(\gamma)] \quad (6)$$

C_D and C_A denote the donor and acceptor concentration, respectively, and C_{ODD} and C_{ODA} are the critical concentrations for energy transfer between a donor–donor pair and a donor–acceptor pair, respectively.

The concentration depolarization occurring due to excitation energy transport can be determined from the following expressions [5,21]:

$$\left[\frac{r}{r_0} \right]_1 = 1 - \alpha' f(\gamma') \quad (7)$$

$$\left[\frac{r}{r_0} \right]_2 = 1 - \alpha f(\gamma) \quad (8)$$

where

$$\alpha = \frac{\gamma_D}{\gamma}, \quad \alpha' = \frac{\gamma'_D}{\gamma'}, \quad \gamma_D = \frac{\sqrt{\pi}}{2} \frac{C_D}{C_{\text{ODD}}}, \quad (9)$$

$$\gamma'_D = \frac{\sqrt{\pi}}{2} \frac{C_D}{\sqrt{2}C_{\text{ODD}}}$$

$$\gamma' = \frac{\sqrt{\pi}}{2} \cdot \left(\frac{C_D}{\sqrt{2}C_{\text{ODD}}} + \frac{C_A}{C_{\text{ODA}}} \right) \quad (10)$$

Expressions (7) and (8) apply to the cases in which correlations were taken into account and neglected, respectively.

The approximate formulas describing the influence of rotational depolarization on concentration depolarization can be obtained by multiplying expression (2) by Eqs. (7) and (8), respectively:

$$\left[\frac{r}{r_0} \right]_1 = (1 - \alpha'f(\gamma')) \cdot \left[1 + b \frac{\tau_1}{\tau_0} \right]^{-1} \quad (11)$$

$$\left[\frac{r}{r_0} \right]_2 = (1 - \alpha f(\gamma)) \cdot \left[1 + b \frac{\tau_1}{\tau_0} \right]^{-1} \quad (12)$$

The interrelation between these processes is represented by τ_1 , which is a function of the reduced concentration of fluorescent molecules [Eq. (4)]. In expression (11), obtained based on (7), the correlations are taken into account, while in (12) they are neglected.

By measuring the emission anisotropy for different concentrations and solvent viscosities, it should be possible to estimate the applicability range of each formula and to distinguish under experimental conditions between the Markov and the non-Markov mechanism of energy transport.

EXPERIMENTAL

To verify the approach presented above and discuss the nature of correlations, two systems [Na-fluorescein (donor) and rhodamine B (acceptor), system I; and rhodamine B (donor) and malachite green (acceptor), system II] were prepared in solvents of different viscosities. Analytically pure dyes (Aldrich) were further purified by multiple recrystallization. For each series of solutions the donor and acceptor concentration ratio was constant, $C_D/C_A = 2:1$, thus ensuring that the emission anisotropy approaches, for increasing concentrations, a C_D/C_A -dependent constant limiting value. As shown in Refs. 7 and 8, such a choice (weak migration and strong quenching) offers the best opportunity to investigate the correlation effect.

For the systems considered four subsystems, each with a different viscosity, were prepared. Mixtures of anhydrous glycerol and ethyl alcohol served as solvents. The viscosity, differing for particular subsystems, allows control of the rotational depolarization and, hence, the contribution of the correlation effect to the energy transport process.

Mention should be made that the viscosity range in the experiment described should be carefully selected to ensure high dynamics in the anisotropy changes.

The donor concentrations ranged from 10^{-5} to about 10^{-1} M. For low and medium donor concentrations (up

to 10^{-2} M), the thickness d of the cuvette was in each case adjusted so that relation (13) was valid:

$$2.3\epsilon_D^{\max} C_D d \leq 0.1 \quad (13)$$

where ϵ_D^{\max} is the maximum value of the donor extinction coefficient. Under this condition, the secondary effects in the concentration range considered may be neglected [24].

For the systems investigated, $\epsilon_D^{\max} = 10^5$ L/mol cm. To satisfy relation (13) at concentrations exceeding 10^{-2} M, cuvettes with a thickness $d < 1$ μ m should be used. However, as has been shown recently [25], the absorption of dye molecules and their increased concentration in the surface layer can influence the measurement results. Therefore, at concentrations $C_D > 10^{-2}$ M, the emission anisotropy measurements were carried out in a cuvette with sufficiently large thickness, $d = 5$ μ m, allowing the above mentioned effect to be neglected.

The corrections for the reabsorption and the secondary emission were introduced as in Ref. 26. These corrections were insignificant for high donor concentrations ($C_D \geq 10^{-2}$ M).

Since the dyes used in the experiment adopt different ionic forms, a 0.1 N solution of NaOH was added to system I, and a trace of HCl to system II. The maxima and the profiles of the spectra were found to be unchanged over a wide concentration range.

The parameters characterizing the systems investigated are summarized in Tables I and II.

The fluorescence spectra were measured upon frontal excitation and observation of the sample and corrected for the spectral sensitivity of the photomultiplier. For the absorption measurements, a Specord M-40 spectrophotometer was employed. The fluorescence anisotropy was measured by the single-photon counting technique with an accuracy of 0.002 using the apparatus described in Refs. 22 and 23.

RESULTS AND DISCUSSION

Figures 1a-d and 2a-d show the experimental values of the relative emission anisotropy, r/r_0 , versus the reduced donor concentration. The same results sorted out according to the solvent viscosity are shown in Fig. 3.

At moderate concentrations a drop in anisotropy was observed. After attaining its minimum the anisotropy increased, and finally, at very high concentrations, an approximately constant value of the emission anisotropy can be seen.

The results obtained can be explained based on the

Table I. Data Characterizing the Subsystems Examined

System	C_D/C_A	Solvent	Percentage ethanol
I. Na-fluorescein + rhodamine B	2:1	Glycerol + ethanol + NaOH	
a			80
b			60
c			50
d			40
II. Rhodamine B + malachite green	2:1	Glycerol + ethanol + HCl	
a			80
b			60
c			50
d			40

Table II. Values of Physical Parameters for the Systems Investigated

System	C_{ODD} (M)	C_{ODA} (M)	r_0 (λ_{exc})	λ_{exc} (nm)	λ_{obs} (nm)	τ_{rot} (ns)	r'
I							
a						1.27	0.100
b						2.75	0.167
c	$4.39 \cdot 10^{-3}$	$2.2 \cdot 10^{-3}$	0.391 ^a	480	510	4.60	0.217
d						7.49	0.262
II							
a						1.72	0.109
b						3.73	0.179
c	$2.85 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$	0.394 ^a	540	580	5.80	0.222
d						9.43	0.267

^aMeasured in anhydrous glycerol at 288 K.

following argument. Let us assume that for low donor concentrations, the mean fluorescence lifetime of the donor is τ_0 . In this case the concentration depolarization is negligible, and for the value of the emission anisotropy observed in a given system, only the rotational depolarization conditioned by the solvent viscosity is responsible (Fig. 3). With an increase in the donor concentration, the molecules start transferring energy, which at medium concentrations enhances the fluorescence depolarization. Simultaneously, the time of energy localization on a given donor molecule begins to decrease, since the energy transport opens a new deactivation channel for the energy transfer. As a result of the decrease in localization time, the angles of revolution of the donor molecules during this time become, on average, smaller. At a certain concentration, for which the contraction of the localization time is sufficiently large, the emission anisotropy starts to increase. With a further increase in the concentration, the localization time may become much shorter

than that of the rotational relaxation. In this time scale the system under consideration will exhibit features of a solid solution. For solid systems with a constant ratio of donor to acceptor concentration, the emission anisotropy approaches a constant limiting value in the high concentration range.

This qualitative explanation is reflected by the proposed approximate quantitative approach [Eqs. (11) and (12)]. The curves corresponding to Eqs. (11) and (12) are presented in Figs. 1 and 2 and compared with the experimental data.

As shown in Figs. 1a and 2a in the case of the systems with the lowest viscosity, the experimental data are best described by the curve corresponding to Eq. (12) (correlations neglected) and deviate distinctly from curves obtained taking correlations into account.

With increasing viscosity (Figs. 1b–d and 2b–d) the experimental points in the high concentration interval progressively deviate from the dotted curves and draw

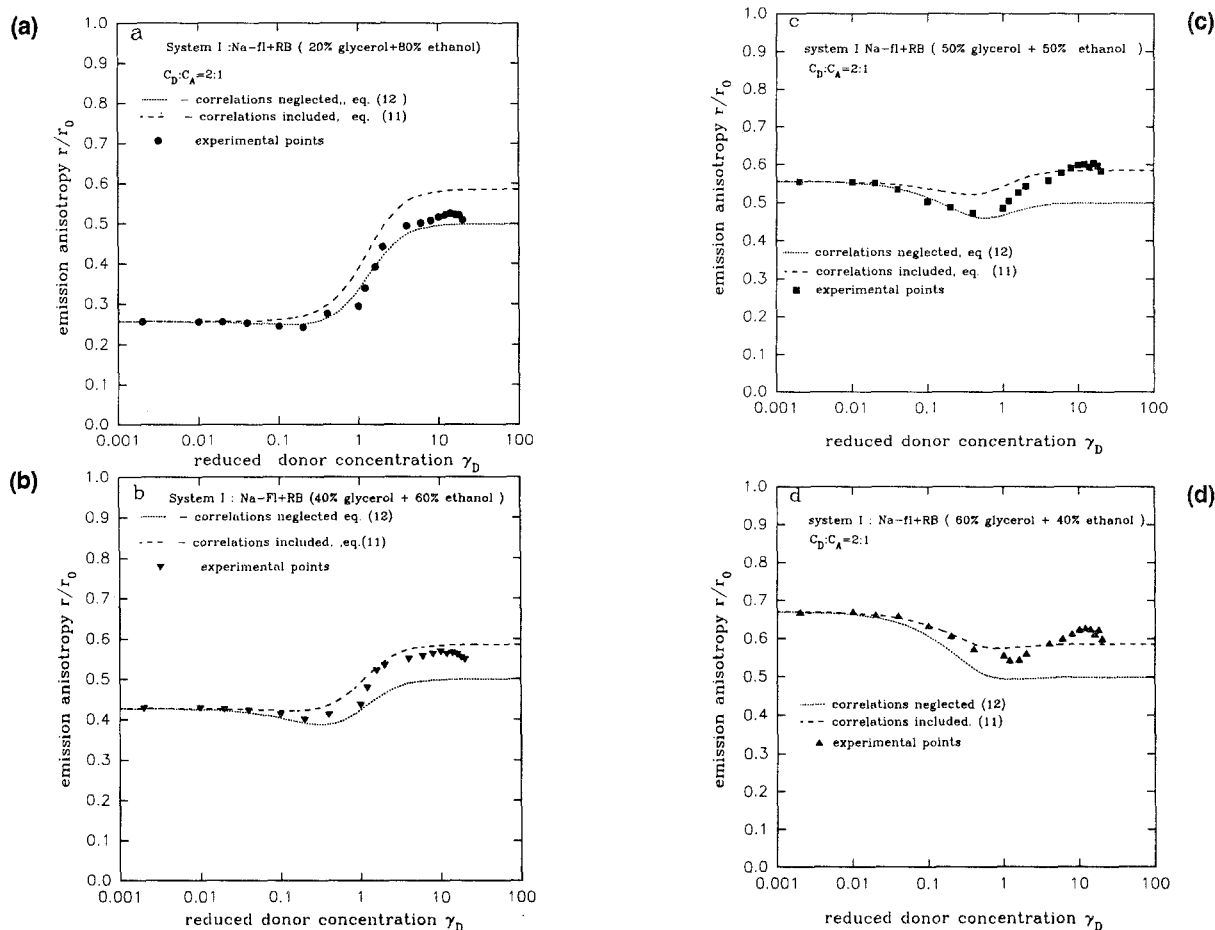


Fig. 1. Concentration changes in emission anisotropy in the presence of rotational depolarization for system I with a constant donor-to-acceptor concentration ratio. Experimental points for subsystems with different viscosities are shown in a-d.

near the dashed curves [Eq. (11), correlations included]. It can be seen that over the whole concentration range, these curves do not fully describe the experimental results.

One of the reasons for this may be the approximate character of the method applied. The formation of aggregates in the high concentration region may be another reason. As is known, in the case of a fixed donor-to-acceptor concentration ratio, the emission anisotropy approaches a constant value in the limit of high concentrations. Slight deviations of the experimental points from this regularity can be seen in Figs. 1 and 2. This may just be due to aggregate formation. Aggregates may be present in the set of both donors and acceptors. Assuming that nonluminescent dimers play the role of aggregates, one can estimate their fraction in the high concentration range based on the law of mass action and the values of dimerization constants given in the litera-

ture. The dimerization constant for Na-fluorescein in glycerol-ethanol mixture is very small, $K = 0.21$ L/mol [9], whereas that for rhodamine B is about three times higher, $K = 0.71$ L/mol. The values of the dimer concentrations obtained for several samples with the highest concentrations are shown in Table III. These values were obtained based on the law of mass action:

$$K = \frac{C_{\text{DIM}}}{C_{\text{MON}}^2}, \quad C_{\text{MON}} + 2C_{\text{DIM}} = C \quad (14)$$

where C_{MON} , C_{DIM} , and C (C_D, C_A) denote the monomer, the dimer, and the donor or acceptor concentration, respectively. For example, the data in Table III show that in the case of system I, the dimer fraction even at the highest concentration is insignificant and does not exceed 2% for Na-fluorescein and 4.2% for rhodamine B. In the bottom row in Table III the values of the reduced concentration ratio of monomers and all traps present in

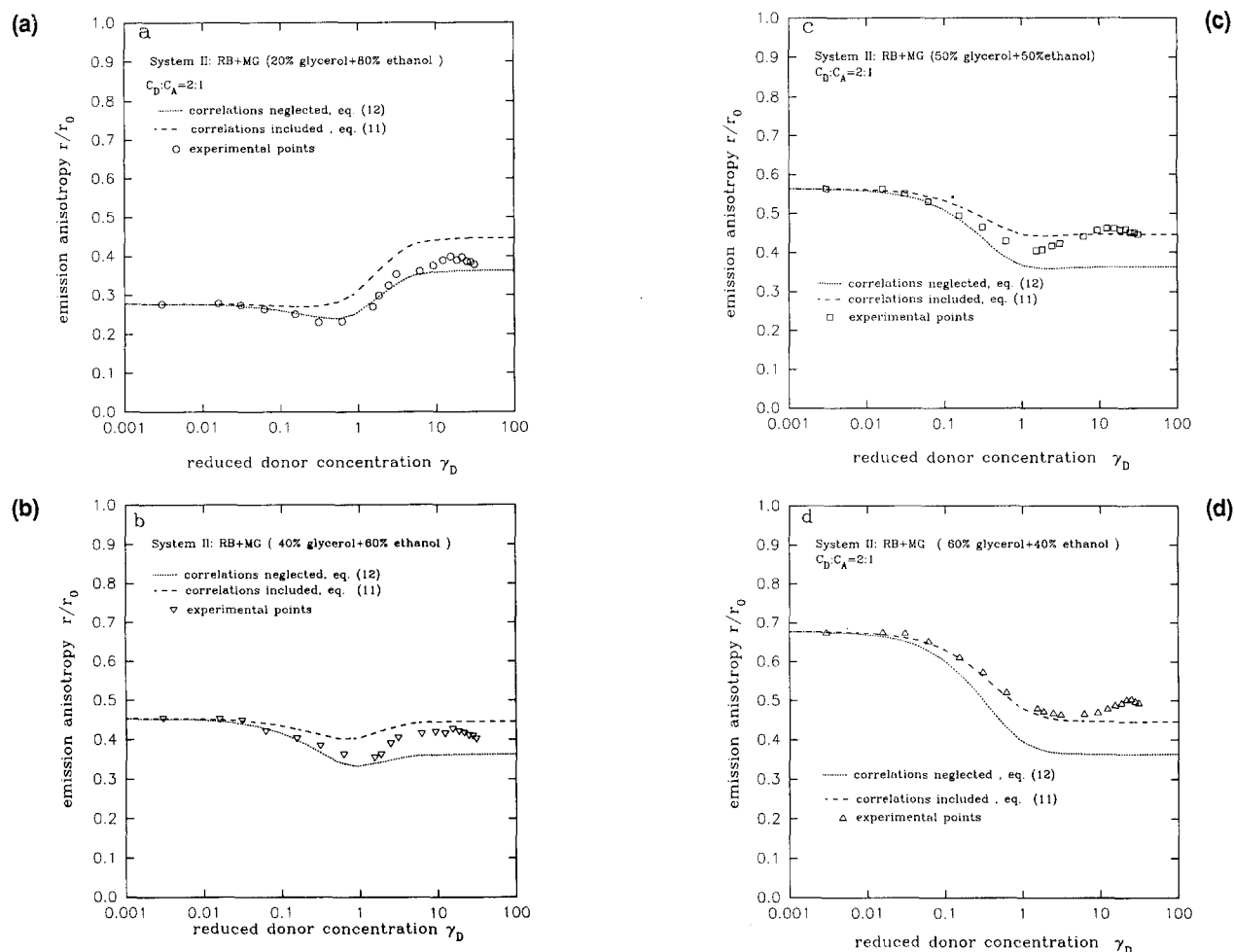


Fig. 2. Concentration changes in emission anisotropy in the presence of rotational depolarization for system II with a constant donor-to-acceptor concentration ratio. Experimental points for subsystems with different viscosities are shown in a–d.

the system considered are given (traps are understood herein as both acceptor molecules and dimers which are present in donor as well as acceptor sets). The values of $\gamma_{\text{MON}}/\gamma_{\text{TRAP}}$ were calculated according to the formula:

$$\frac{\gamma_{\text{MON}}}{\gamma_{\text{TRAP}}} = \frac{C_D^{\text{MON}}/C_{\text{ODD}}}{(C_A^{\text{MON}}/C_{\text{ODA}}) + (C_B^{\text{DIM}}/C_{\text{ODDIMD}}) - (C_A^{\text{DIM}}/2C_{\text{ODDIMA}})} \quad (15)$$

where C_D^{MON} and C_A^{MON} denote the monomer concentrations in the set of donors and acceptors, respectively; C_D^{DIM} and C_A^{DIM} are the dimer concentrations in the donor and acceptor set, respectively; and finally, C_{ODDIMD} and C_{ODDIMA} denote the critical concentrations for energy transfer from a donor to a donor dimer and from a donor to an acceptor dimer, respectively.

The values of critical concentrations $C_{\text{ODDIMD}} = 3.26 \cdot 10^{-3} M$ and $C_{\text{ODDIMA}} = 4.4 \cdot 10^{-3} M$ and

are taken from Refs. 9 and 14. From the data presented here, one can conclude that in the high concentration range, the ratio $\gamma_{\text{MON}}/\gamma_{\text{TRAP}}$ decreases (the effective number of traps increases) up to a donor concentration of $5 \times 10^{-2} M$, which can slightly increase the emission anisotropy values in this concentration range. Then the ratio $\gamma_{\text{MON}}/\gamma_{\text{TRAP}}$ increases (the effective number of traps decreases), which can slightly lower anisotropy at the highest concentrations.

In the high concentration range, apart from dimers there may also exist other fluorescence depolarizing factors, for example, a very weak dimer fluorescence recently reported in Refs. 27 and 29 or higher-order aggregate formation. These factors could additionally add to the anisotropy changes observed at the highest concentrations. These hypotheses, however, require further

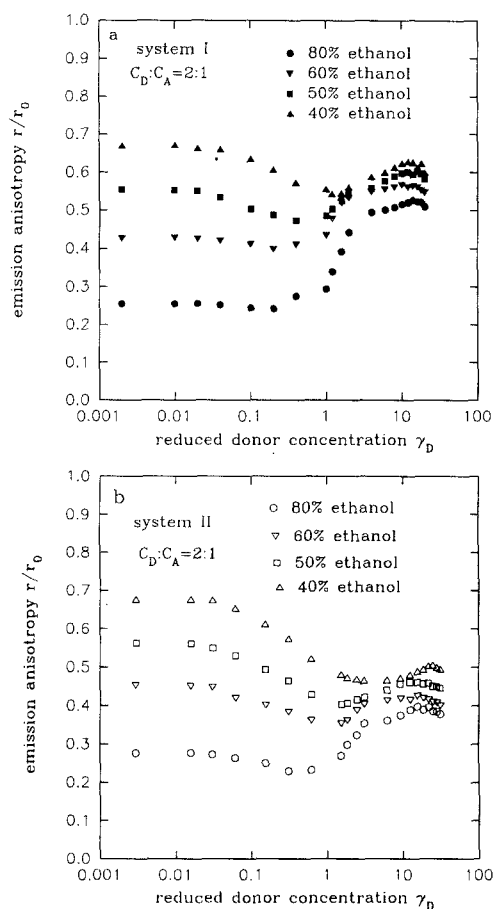


Fig. 3. Experimental results of concentration changes in emission anisotropy in the presence of rotational depolarization for different solvent viscosities.

detailed examination. A similar analysis can be performed for system II.

The probability of energy transfer depends not only on the distance between the molecules exchanging the energy (distance correlation) but also on the angle be-

tween the transition dipole moments (orientation correlation).

The effect of the orientation correlations may play a significant role at such concentrations at which the localization time is not much shorter than that of the rotational relaxation. The influence of the relative changes in the orientations of dipoles taking part in nonradiative energy transfer on the luminescent observables can be estimated by taking into account the changes in the orientation factor with increasing concentrations of luminescent molecules in the systems investigated.

According to Ref. 11, the average value of the orientation factor in the presence of energy transport can be expressed approximately as

$$\langle \kappa^2(\gamma) \rangle = \langle \kappa^2 \rangle_d \frac{F(\gamma)}{F(\gamma) + a} + \langle \kappa^2 \rangle_s \frac{a}{F(\gamma) + a} \quad (16)$$

where

$$F(\gamma) = \frac{1 + \gamma^2 - (1.5 + \gamma^2)f(\gamma)}{1 - f(\gamma)}, \quad a = \frac{\tau_{\text{rot}}}{\tau_0} \quad (17)$$

and $\langle \kappa^2 \rangle_s = 0.476$ and $\langle \kappa^2 \rangle_d = 2/3$ denote the average values of the orientation factor in the static and dynamic regime, respectively. Figure 4 shows the changes in the orientation factor versus the reduced concentration for the systems investigated.

It is clear that the changes in the orientation factor values are significant and that the dynamics of these changes is the biggest for moderate concentrations. The values of τ_0 for Na-fluorescein ($\tau_0 = 3.69$ ns) and rhodamine B ($\tau_0 = 4.5$ ns) have been taken from Ref. 30. Table II summarizes the values of the rotational relaxation time calculated from Eq. (3) for individual subsystems. These values vary from 1.27 to 7.49 ns. However, the localization time calculated from Eq. (4) attains, for a high concentration ($\gamma = 10$, system I), $\tau_1 = 53$ ps and is much shorter than that of the rotational relaxation. This implies that the energy transport in the systems investigated is, in the high concentration range,

Table III. Dimer Fractions for Samples with the Highest Concentrations

C_D (10^{-2} M)	10	8	5	4	2	1
C_D^{DIM} (10^{-5} M)	200	100	50.40	32.52	8.26	2.08
C_A (10^{-2} M)	5	4	2.5	2	1	0.5
C_A^{DIM} (10^{-5} M)	200	100	40.93	26.5	6.81	1.72
$C_D^{\text{DIM}}/C_D^{\text{MON}}$ (%)	2	1.3	1	0.8	0.4	0.2
$C_A^{\text{DIM}}/C_A^{\text{MON}}$ (%)	4.2	2.6	1.7	1.3	0.7	0.3
$\gamma_{\text{MON}}/\gamma_{\text{TRAP}}$	1.005	1.004	0.999	1.000	1.001	1.002

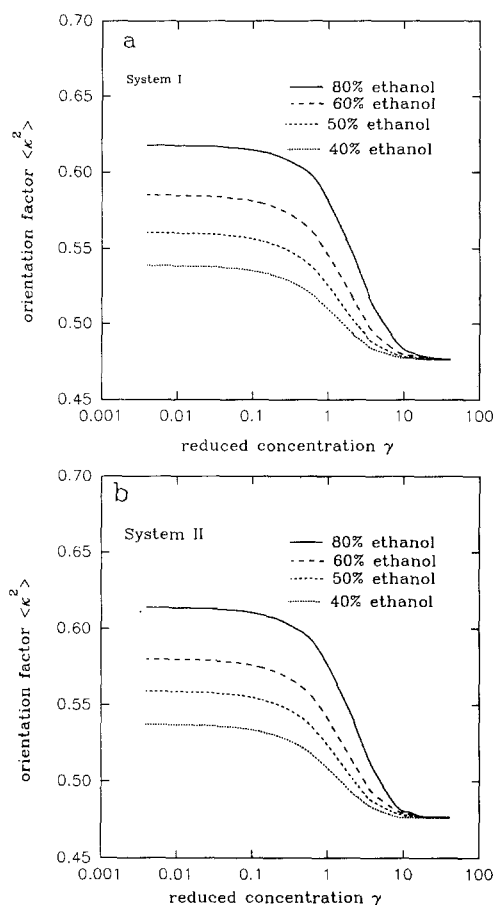


Fig. 4. Concentration changes in the averaged orientation factor $\langle \kappa^2 \rangle$ for the systems investigated.

a much faster process than the rotational relaxation. The fact that the ratio τ_1/τ_{rot} decreases with increases in concentration can even lead to a change in the mechanism of the energy transport (from a non-Markov to a Markov mechanism) in a subsystem with a given viscosity. This is well illustrated in Figs. 1b and c and 2b and c, in which, for low and moderate concentrations, the experimental points are better described by the dotted curves, whereas for high concentrations the experimental points are closer to the dashed curves.

A certain measure of the dynamics of the emission anisotropy changes may be the difference in the emission anisotropy $\Delta(r/r_0)$, which can be observed for the subsystems with maximum and minimum viscosity (Fig. 3). It is readily seen that this difference diminishes distinctly with an increase in the reduced concentration. This implies a diminishing influence of the rotational depolarization on the energy transport for increasing concentrations.

CONCLUSIONS

In the present paper the nature of correlations between the configurations of molecules taking part in the act of nonradiative energy transfer has been analyzed for the first time. The discussion was based on emission anisotropy measurements in systems of different solvent viscosities.

We found that the inclusion of the correlation effect in the description of the energy transport mechanism is fully justified for systems in which $\tau_1 < \tau_{\text{rot}}$.

Based on the approximate quantitative analysis taking into account the competition between rotational and concentration depolarization, we managed to explain the concentration emission anisotropy changes in the systems investigated. The source of this analysis is the fact that the localization time decreases with increasing concentrations since the energy transport opens a new deactivation path for excitation.

Strict analysis of the influence of the rotational diffusion on the concentration depolarization of fluorescence requires a coherent statistical theory to be elaborated. Further investigations in this field, both theoretical and experimental, seem useful and advisable.

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REFERENCES

1. D. L. Huber, D. S. Hamilton, and D. Barnett (1977) *Phys. Rev. B* **16**, 4642-4650.
2. C. R. Gochanour, H. C. Andersen, and M. D. Fayer (1979) *J. Chem. Phys.* **70**, 4254-4271.
3. R. F. Loring, H. C. Andersen, and M. D. Fayer (1982) *J. Chem. Phys.* **76**, 2015-2027.
4. R. Twardowski and C. Bojarski (1985) *J. Luminesc.* **33**, 79-85.
5. A. I. Burstein (1985) *J. Lumin.* **34**, 201-209.
6. C. Bojarski and K. Sienicki (1990) in J. F. Rabek (Ed.), *Photochemistry and Photophysics, Vol. 1*, CRC Press, Boca Raton, FL, pp. 1-57.
7. C. Bojarski, A. Kawski, A. Kubicki, and G. Żurkowska (1988) *Z. Naturforsch.* **43a**, 297-301.
8. A. Kawski, P. Bojarski, A. Kubicki, and C. Bojarski (1991) *J. Luminesc.* **50**, 61-68.
9. C. Bojarski, J. Grabowska, L. Kulak, and J. Kuśba (1991) *J. Fluoresc.* **3**, 183-191.
10. S. Błoński and C. Bojarski (1989) *Z. Naturforsch.* **44a**, 257-261.
11. C. Bojarski and J. Dudkiewicz (1979) *Chem. Phys. Lett.* **67**, 450-454.
12. R. Twardowski and C. Bojarski (1980) *Z. Naturforsch. A* **35**, 345-349.
13. J. Dudkiewicz and C. Bojarski (1981) *Acta Phys. Hung.* **50**, 201-206.

14. J. Dudkiewicz (1984) *Acta Phys. Pol.* **A65**, 325–336.
15. J. Knoester and J. E. Van Himbergen (1984) *J. Chem. Phys.* **81**, 4380–4388.
16. G. H. Fredrickson (1988) *J. Chem. Phys.* **88**, 5291–5299.
17. M. Berberan-Santos and M. J. E. Prieto (1988) *J. Chem. Phys.* **88**, 6341–6349.
18. S. Engstrom, M. Lindberg, and L. B. A. Johansson (1992) *J. Chem. Phys.* **96**, 7528–7534.
19. H. Grajek, C. Bojarski, G. Żurkowska, and R. Drabent (1992), *Photochem. Photobiol.* **55**, 381–387.
20. F. Perrin (1929) *C.R. Hebd. Seances Acad. Sci.* **181**, 169–275.
21. C. Bojarski and J. Domsta (1971) *Acta Phys. Acad. Sci. Hung.* **30**, 145–166.
22. A. Kubicki (1989) *Exp. Tech. Phys.* **37**, 329–333.
23. P. Bojarski and A. Kowski (1992) *J. Fluoresc.* **2(2)**, 133–139.
24. I. Ketskemety, J. Dombi, R. Horvai, J. Hevesi, and L. Kozma (1961) *Acta Phys. Chem. (Szeged)* **7**, 17–24.
25. B. D. Ryshikov, N. R. Senatorova, and G. W. Simonov (1986) *Opt. Spektrosk.* **61**, 497–504.
26. A. Budó and I. Ketskemeéty (1957) *Acta Phys. Hung.*, **7**, 207–223; A. Budó and I. Ketskemeéty (1962) *Acta Phys. Hung.* **14**, 167–176.
27. V. I. Yushakov and N. V. Abrosimova (1981) *J. Phys. Chem.* **55**, 630–634.
28. A. S. Prishchepov, B. D. Zaripov, and S. Astanov (1989) *Opt. Spektrosk.* **66**, 1311–1315.
29. A. Zuani, L. V. Levshin, and A. M. Saletskij (1989) *Opt. Spektrosk.* **66**, 301–304.
30. R. E. Dale and R. K. Bauer (1971) *Acta Phys. Pol.* **A40**, 853–882.