

## FLUORESCENCE SELF-QUENCHING OF THE MOLECULAR FORMS OF RHODAMINE B IN AQUEOUS AND ETHANOLIC SOLUTIONS

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The fluorescence quenching produced by the aggregates of the zwitter-ion and the cationic molecular forms of Rhodamine B in water and in ethanol is evaluated in this paper. Experimental results indicate that the quenching is higher in ethanol than in water. In ethanolic systems the trimer produces a higher fluorescence quenching than the dimer. The participation of different quenching processes is discussed on the basis of these results.

### 1. Introduction

Rhodamine B, RB, is an organic dye with a large variety of technical applications [1], which has been frequently used in photophysical and photochemical studies such as photosensitizers [2], quantum counters [3] etc. More recently, it has become very important as an active medium in tunable lasers [4] as well as in photovoltaic solar energy cells [5]. An important factor that limits its lasing and luminescent solar concentrator characteristics is the fluorescence self-quenching in concentrated dye solutions [4–7]. This phenomena is studied in this work in concentrated aqueous and ethanolic solutions of RB.

Rhodamine B has a strong tendency to aggregate in aqueous solutions [8–11]. The dimerization of RB in water was observed by absorption spectroscopy at concentrations higher than  $10^{-5}$  M, and the aggregation equilibrium constant and the dimer absorption spectrum of the zwitter-ion,  $\text{RB}^{+-}$ , and the cationic,  $\text{RBH}^+$ , molecular forms of the dye have been determined [11]. The aggregation tendency of RB in ethanol is much smaller [12]. A shift in the absorption spectrum of RB was reported in moderately concentrated solutions,

from  $10^{-6}$  to  $10^{-3}$  M, which was attributed to the displacement of the molecular equilibrium of the dye towards the cationic side [13,14] and not to the aggregation. However, dimerization of  $\text{RBH}^+$  has been reported [15,16] in very concentrated ethanolic solutions ( $> 5 \times 10^{-3}$  M). Recently, starting from vapour pressure osmometry measurements and absorption spectra we have reported [12] the existence, not only of the dimer, but also of the trimer of both molecular forms of RB in very concentrated ethanolic solutions. This is confirmed in the present paper.

The fluorescence self-quenching of RB is observed in concentrated solutions of the dye. As in Rhodamine 6G [17–19] and other xanthene dyes [20] this fluorescence quenching has been attributed to the long-range dipole–dipole energy transfer from the monomer excited state to the aggregates. This mechanism seems to be affected by excitation energy migration between monomers [10,16]. In this work, the fluorescence quenching of both molecular forms of RB is separately studied in water and in ethanol. The participation of different quenching processes [5,21,22] such as the long-range and collisional energy transfer from the monomer to the aggregates and the energy

migration between monomers is discussed as well as the effect of molecular diffusion on these processes.

## 2. Experimental

Rhodamine B was supplied by Merck (pro-analysis). It was twice recrystallized from ethanol and dried in a vacuum oven. The zwitter-ion and cationic molecular forms of the dye were generated by adding appropriate amounts of NaOH and HCl (aqueous and ethanolic solutions), respectively, to the solutions [11,18,23]. Measurements were made at dye concentrations from  $10^{-6}$  to  $7 \times 10^{-3}$  M in water and from  $10^{-6}$  to  $3 \times 10^{-2}$  M in ethanol (Merck, pro-analysis) at 20 and 50 °C.

Fluorescence spectra were recorded on a Perkin-Elmer model MPF-3 fluorimeter in a 1-mm optical pathway cell and in the front-face mode (reflection) in order to minimize the reabsorption and reemission effects [24]. The angles between the normal to the cell and the excitation and analysis beams were 30° and 60°, respectively. Fluorescence quantum yields were evaluated using the zwitter-ion molecular form of Rhodamine B in ethanol (ca.  $10^{-6}$  M) as a reference [3], being  $\phi^0 = 0.70$  at 20 °C [13].

## 3. Results and discussion

The photophysical properties of the zwitterion,  $\text{RB}^{+-}$ , and cationic,  $\text{RBH}^+$ , molecular forms of RB have been extensively studied [11–16,23,25]. The fluorescence parameters [23] used in this work

are listed in table 1. Furthermore, the aggregation of this dye has been the subject of numerous publications [8–12,15,16]. A large dimerization ( $\text{M} + \text{M} \rightleftharpoons \text{D}$ ) of both molecular forms of RB occurs by increasing the dye concentration [8–11] in water. This aggregation is observable by absorption spectroscopy for dye concentrations higher than  $10^{-5}$  M [11]. In ethanol, however, the aggregation tendency is smaller, and not only the dimer [12,15,16] but also the trimer [12] ( $\text{M} + \text{D} \rightleftharpoons \text{T}$ ) of the cationic form of RB appear in very concentrated solutions ( $> 5 \times 10^{-3}$  M). The dimerization and trimerization equilibrium constants,  $K_d$  and  $K_t$ , respectively, are included in table 1 at 20 and 50 °C [11,12]. The results obtained for the cationic form of RB have been considered for the self-association parameters of the zwitter-ion molecular form of the dye [12]. At a much higher dye concentration of Rhodamine 6G in methanol ( $> 10^{-1}$  M), the formation of so-called closely-spaced pairs by statistical random walk distribution of species has been reported [26]. The intermolecular separation between solute molecules is less than 2.5 nm in such concentrated solutions and solute–solute interactions become important at this separation distance. However, in the concentration range of the present work ( $< 3 \times 10^{-2}$  M) the intermolecular separation between solute species is too large to form the closely spaced pairs. Moreover, osmometry pressure results indicate the absence of tetramers and higher order aggregates of RB at concentration smaller than  $3 \times 10^{-2}$  M in ethanol [12] corroborating this conclusion.

The fluorescence spectrum (registered in a 1 mm cell) of RB in water and in ethanol is shifted to smaller energies when the dye concentration is

Table 1

Fluorescence quantum yield ( $\phi^0$ ) and lifetime ( $\tau^0$ , ns) of the zwitter-ion and cationic molecular forms of Rhodamine B in water and ethanol at 20 and 50 °C [23]. Dimerization ( $K_d$ ) and trimerization ( $K_t$ ) equilibrium constants (standard concentration 1 M) of Rhodamine B at 20 and 50 °C [11,12]

System	$\phi_{20}^0$	$\tau_{20}^0$	$\phi_{50}^0$	$\tau_{50}^0$	$K_d^{20}$	$K_t^{20}$	$K_d^{50}$	$K_t^{50}$
$\text{RB}^{+-}/\text{H}_2\text{O}$	0.32	1.9	0.15	0.88	2100	–	1240	–
$\text{RBH}^+/\text{H}_2\text{O}$	0.27	1.7	0.12	0.75	1400	–	775	–
$\text{RB}^{+-}/\text{EtOH}$	0.70	2.9	0.46	1.9	–	–	–	–
$\text{RBH}^+/\text{EtOH}$	0.56	2.6	0.34	1.5	1.7	24.7	2.1	18.9

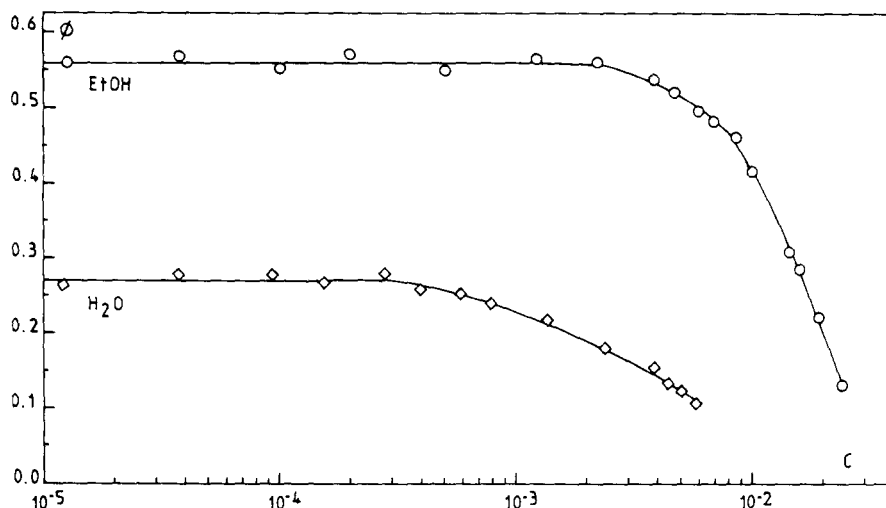


Fig. 1. Fluorescence quantum yield,  $\phi$ , of the cationic form of Rhodamine B in aqueous and ethanolic solutions at different dye concentrations (M) at 20 °C.

increased at 20 °C. However, the fluorescence spectrum of concentrated solutions recorded using a cell with a very small optical path (a RIIC cell model DC-14 Beckman of variable optical pathway was used) has the same shape as the dilute ones. These results show the lack of the emission from the aggregate excited states and indicate that the spectral shift observed with the 1 mm cell is due to reabsorption. So, following the methods of ref. [24], the fluorescence spectra are corrected not only for the reabsorption and reemission effects but also for the fluorescently inactive absorption of the aggregates.

The fluorescence quantum yield,  $\phi$ , of these systems decreases in concentrated solutions as shown in fig. 1 for the cationic form of RB in aqueous and ethanolic solutions. The value of  $\phi$  is constant up to a concentration of about  $5 \times 10^{-3}$  M in ethanol, suggesting that the fluorescence quenching is mainly produced by the aggregates rather than by the monomer, in agreement with previous results for other xanthene dyes [17–19]. Owing to the low viscosity of the solvents, the following Stern–Volmer equation has been considered:

$$\begin{aligned} \phi^0/\phi - 1 &= k_{qd}\tau^0[D] + k_{qt}\tau^0[T], \\ &= k_{qd}\tau^0K_d[M]^2 + k_{qt}\tau^0K_dK_t[M]^3, \quad (1) \end{aligned}$$

where  $k_{qd}$  and  $k_{qt}$  are the rate constants of the quenching produced by the dimer and the trimer respectively, and  $\tau^0$  is the lifetime of the unquenched excited state of the dye. The fluorescence quenching produced by the monomer has been neglected in eq. (1) according to fig. 1.

A good linear fitting of  $\phi^0/\phi$  values versus  $[M]^2$  is obtained in the aqueous systems (fig. 2). This is reasonable since the dimer is the only

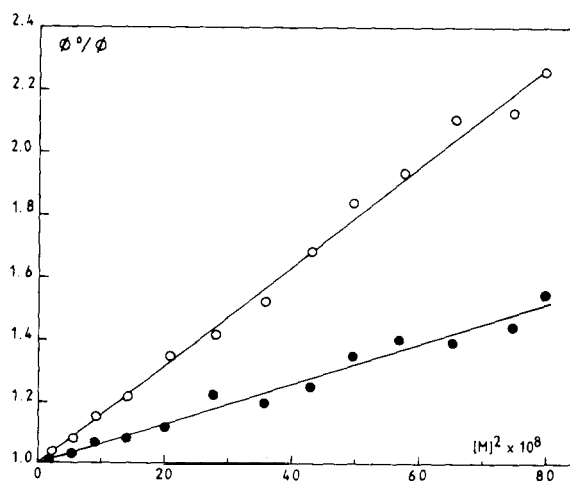


Fig. 2. Dependence of the fluorescence quantum yield of the zwitter-ion molecular form of Rhodamine B in aqueous solution on the presence of the dimer (M) at 20 °C (open symbols) and 50 °C (full symbols).

Table 2

Rate constant of the fluorescence quenching,  $k_q \pm 15\%$  (in  $10^{11} \text{ M}^{-1} \text{ s}^{-1}$ ), produced by the dimer (M-D),  $k_{qd}$ , and the trimer (M-T),  $k_{qt}$ , of the zwitter-ion,  $\text{RB}^{+-}$ , and cationic,  $\text{RBH}^+$ , molecular forms of Rhodamine B in water and ethanol at 20 and 50 °C. "Critical parameters",  $R_0$  (Å) and  $C_0$  ( $10^{-3} \text{ M}$ ), obtained from Förster theory [21] ('spc' values) and from experimental data ('app' values).

System	$k_q^{20}$	$k_q^{50}$	$R_0^{\text{spc}}$	$C_0^{\text{spc}}$	$R_0^{\text{app}}$	$C_0^{\text{app}}$	$C_0^{\text{app}}$ (dye)
RB <sup>+-</sup> /H <sub>2</sub> O							
M-M	—	—	52	2.9	—	—	3.4
M-D	4.0	6.0	48	3.7	67	1.3	
RBH <sup>+</sup> /H <sub>2</sub> O							
M-M	—	—	50	3.1	—	—	4.5
M-D	3.5	5.0	46	4.0	62	1.7	
RB <sup>+-</sup> /EtOH							
M-M	—	—	57	2.2	—	—	15
M-D	7.0	12	—	—	93	0.49	
M-T	12	19	—	—	111	0.29	
RBH <sup>+</sup> /EtOH							
M-M	—	—	58	2.0	—	—	16
M-D	6.5	11	61	1.8	87	0.59	
M-T	10	16	62	1.7	101	0.38	

aggregate formed in the concentration range of this work in aqueous systems. The rate constant  $k_{qd}$  for both molecular forms of RB in water, calculated from the slope of this linear relationship, is given in table 2. Plots of  $\phi^0/\phi$  versus  $[\text{M}]^2$  and versus  $[\text{M}]^3$  in ethanol are never linear: this may be attributed to the cooperative fluorescence quenching produced by the dimer and the trimer of the dye in this solvent. However, eq. (1) predicts a linear relation between  $(\phi^0/\phi - 1)/[\text{M}]^2$  and  $[\text{M}]$ , as is experimentally tested in fig. 3 for the  $\text{RBH}^+/\text{EtOH}$  system. The good linearity observed in figs. 2 and 3 supports the conclusion that the quenching produced by the monomer is not important. From the intercept and slope in fig. 3 values of  $k_{qd}$  and  $k_{qt}$  are determined for ethanolic solutions and are listed in table 2. These results suggest that the fluorescence quenching of RB by the aggregates is higher in ethanol than in water, and that in ethanol the trimer has a larger quenching capacity than the dimer. The rate constants listed in table 2 are of the same order of magnitude as those reported for the self-quenching of Rhodamine 6G in water and ethanol [18]. It should be pointed out that the fulfilment of eq. (1) does not imply a Stern-Volmer kinetic for the

fluorescence quenchings [21] as has been discussed earlier [18].

The large value obtained for the quenching rate constants  $k_{qd}$  and  $k_{qt}$  (table 2) suggests that the fluorescence quenching is mainly produced by the electronic energy transfer from the monomer-

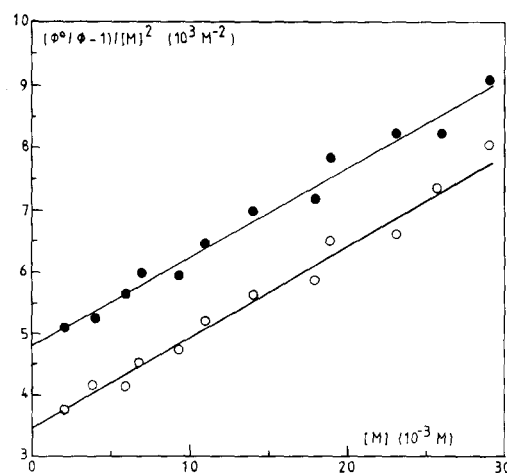


Fig. 3. Dependence of the fluorescence quantum yield of the zwitter-ion molecular form of Rhodamine B in ethanol on the presence of dimer and trimer at 20 °C (open symbols) and 50 °C (full symbols).

Table 3

Mean separation distance,  $\bar{S}$  (Å), between the molecular species at the “apparent critical dye concentration”,  $C_0^{\text{app}}$  (dye), of the systems for which there is a concentration ( $10^{-3}$  M) [M] of monomer, [D] of dimer and [T] of trimer and  $C_s$  of species (at 20 °C)

System	$C_0^{\text{app}}$ (dye)	[M]	[D]	[T]	$C_s$	$\bar{S}$
RB <sup>+-</sup> /H <sub>2</sub> O	$3.4 \times 10^{-3}$	0.79	1.31	–	2.10	115
RBH <sup>+</sup> /H <sub>2</sub> O	$4.5 \times 10^{-3}$	1.09	1.68	–	2.77	106
RB <sup>+-</sup> /EtOH	$15.0 \times 10^{-3}$	13.9	0.19	0.27	14.4	60
RBH <sup>+</sup> /EtOH	$16.0 \times 10^{-3}$	14.9	0.22	0.33	15.4	59

excited state to the aggregates. Long-range dipole–dipole energy transfer proposed by Förster [5,22], is first considered. The energy transfer efficiency of this process is usually expressed in terms of a “critical radius”,  $R_0$ , or equivalently by a “critical concentration”,  $C_0$ , defined as the donor–acceptor distance (or the acceptor concentration) at which the energy transfer and the spontaneous decay of the donor-excited state are equally probable. These critical parameters can be spectroscopically evaluated from the fluorescent properties (table 1) and absorption characteristics [11,12] of the donor and acceptor species [22]

$$R_0^6 = \frac{8.8 \times 10^{-25} K^2 \phi^0}{n^4} \int_0^\infty F_D(\nu) \epsilon_A(\nu) \frac{d\nu}{\nu^4}, \quad (2)$$

$$C_0 = \frac{4.8 \times 10^{-10} n^2}{K} \left( \phi^0 \int_0^\infty F_D(\nu) \epsilon_A(\nu) \frac{d\nu}{\nu^4} \right)^{-1/2}, \quad (3)$$

which are approximately related by

$$R_0 = 7.35(C_0)^{-1/3}, \quad (4)$$

where  $F_D(\nu)$  is the spectral distribution of the donor emission in quanta normalized to unity,  $\epsilon_A(\nu)$  is the decadic molar extinction coefficient of the acceptor,  $n$  is the refractive index of the solvent and  $K$  is an orientation factor equal to  $(2/3)^{1/2}$  for a random distribution of molecules.

The results obtained applying eqs. (2)–(4) for the monomer–monomer (M–M), monomer–dimer (M–D) and monomer–trimer (M–T) energy transfer of the systems studied are listed in table 2 as “spc” values. It should be pointed out that these values are similar to each other and independent of the solvent, in contrast with the experimental results of  $k_{\text{qd}}$  and  $k_{\text{qt}}$  (table 2). Moreover, these “spectroscopic critical parameters” are different

from the “apparent critical parameters”,  $R_0^{\text{app}}$  and  $C_0^{\text{app}}$  (table 2), determined from experimental  $\phi$  values.  $C_0^{\text{app}}$  is defined as the quencher concentration at which the fluorescence quantum yield of a species is reduced to half its unquenched value,  $\phi^0$ . The “apparent critical concentration” for the dimer and trimer were calculated by separating the terms of eq. (1) and considering  $\phi^0/\phi = 2$ , i.e. from the expressions

$$C_0^{\text{app}}(\text{M} - \text{D}) = (k_{\text{qd}}\tau^0)^{-1},$$

$$C_0^{\text{app}}(\text{M} - \text{T}) = (k_{\text{qt}}\tau^0)^{-1}. \quad (5)$$

The corresponding  $R_0^{\text{app}}$  values were calculated from eq. (4). An “apparent critical dye concentration”,  $C_0^{\text{app}}$  (dye) in table 2, is also determined as the dye concentration at which the fluorescence quantum yield falls by a factor of 2 from its unquenched value (the dye concentration at which experimental  $\phi^0/\phi = 2$  in fig. 1).

We see that the Förster treatment for the direct long-range energy transfer does not adequately explain the rate constants  $k_{\text{qd}}$  and  $k_{\text{qt}}$ , and additional processes of quenching have to be considered.

The values of  $R_0^{\text{app}}$  (M–M) listed in table 2 indicate that M–M energy migration can be efficient for these systems. This process does not produce direct fluorescence quenching as is shown in fig. 1, although it can cause fluorescence depolarization [27] and can increase the monomer–aggregate energy transfer efficiency [21]. The mean separation distance,  $\bar{S}$ , between monomers in the solution should govern the efficiency of this process. This distance can be approximately calculated by associating a sphere of radius  $\bar{R}$  with every molecule present in the solution, the sum of all spheres being equal to the total volume of the

solution. Table 3 lists the mean separation distance,  $\bar{S} = 2 \times \bar{R}$ , at the  $C_0^{\text{app}}$  (dye) of every system. In ethanol this distance should be considered as the average M–M, M–D and M–T separation distances since the number of monomer molecules in the solution is significantly higher than the number of dimers and trimers. The value  $\bar{S} = 60 \text{ \AA}$  between monomer at the  $C_0^{\text{app}}$  (dye) in ethanol (table 3) is similar to the  $R_0^{\text{spc}}$  (M–M) =  $58 \text{ \AA}$  “spectroscopic critical radius” given in table 2. Consequently, the excitation energy is expected to migrate through the solution by consecutive excitation energy transfer from monomers to monomers. The aggregates can trap this excitation energy migration [28] and, consequently, the monomer-aggregate “effective critical radii” are increased with respect to the values obtained spectroscopically by the Förster equation. This confirms previous conclusions [10,16]. The efficiency of this multistep process is expected to be smaller in water than in ethanol since the mean separation distance between monomers at  $C_0^{\text{app}}$  (dye) is longer in the former solvent (table 3). This would contribute to the higher rate constants of quenching obtained in ethanol than in water (table 2).

The size and shape of the aggregates can also affect the efficiency of the last multi-step process. The molecular radius of the RB monomer is about  $6 \text{ \AA}$  [27,29], which means a length of about  $12 \text{ \AA}$ . The dimer of molecular forms of RB acquires a sandwich structure in water [8,9,11], whereas in ethanol the monomeric units are disposed linearly in the aggregate, i.e., end to end [12]. Therefore, the ethanol aggregates should fill a larger space, mainly the trimer, leading to a higher energy trap capacity for these aggregates. This is another factor that could produce an increase in the rate constant  $k_{\text{qd}}$  in ethanol which respect to that in water as well as a higher fluorescence quenching capacity of the trimer with respect to that of the dimer (table 2).

Another process to be considered is the molecular diffusion of the species. A diffusion length of  $37 \text{ \AA}$  for the monomer of Rhodamine 6G during its fluorescence lifetime in ethanol has been reported by Mataga et al. [30], whereas Porter and Tredwell [29] obtained a value of  $22 \text{ \AA}$  and Bojarski et al. [31] claims a smaller value. In any case,

the short separation distance between molecular species at  $C_0^{\text{app}}$  (dye) in ethanol (table 3) suggests that the molecular diffusion could be important in the ethanolic systems. The increase of the quenching rate constants with temperature, mainly in ethanol (table 2), seems to confirm this suggestion. Moreover, the activation energy of the quenching process in ethanol is very similar to that of the solvent viscosity ( $E_\eta = 13.9 \text{ kJ/mol}$  from International Critical Tables), whereas the value of  $E_a \approx 10 \text{ kJ/mol}$  of  $k_{\text{qd}}$  for aqueous systems is smaller than the activation energy of water viscosity ( $E_\eta = 16 \text{ kJ/mol}$ ). Therefore, the efficiency of the long-range energy transfer from monomer to aggregates and that of the multistep energy migration between monomers should be increased by the motion of the species. This should be important in ethanolic systems, cooperating to the higher quenching capacity of aggregates in ethanol.

In addition to these quenching processes, the  $22\text{--}37 \text{ \AA}$  [29,30] diffusion displacement during the fluorescence lifetime of the monomer excited state in ethanolic systems would decrease the  $\approx 60 \text{ \AA}$  intermolecular distance between the species in this solvent (table 3) to a separation distance at which the collision between species can be performed. Therefore, the M–M, M–D and M–T electron exchange energy transfer processes could also contribute to the fluorescence quenching of RB by its aggregates and to the energy migration between monomers in ethanol. Moreover, the extended disposition of the ethanolic aggregates could favour this collisional process. On the other hand, the long separation distance between species at  $C_0^{\text{app}}$  (dye) in water, about  $110 \text{ \AA}$  (table 3), does not allow the necessary approach between the molecules to produce collisional electron exchange. Moreover, the diffusion length of the species during the fluorescence lifetime is shorter in water than in ethanol since the lifetime of the RB excited state is shorter in the former solvent; see table 1.

Finally, excimer formation could also be a fluorescence quenching process [21]. It requires the approach of an excited and an unexcited monomer during the fluorescence lifetime of the dye. The short lifetime of RB in aqueous solution and the long intermolecular separation distance among

species at the  $C_0^{\text{app}}$  (dye) in this solvent should prevent the formation of the complex. In ethanolic systems, close approach between excited and unexcited monomers would lead to a collisional energy migration and/or excimer formation. The good solvation of the  $S_0$  and  $S_1$  states of RB by ethanol molecules [12,23] could indicate a small tendency to form the excimer state of the dye.

Summarizing, we have reported a large fluorescence quenching of the molecular forms of RB, by the dimer and trimer, which is higher in ethanolic than in aqueous solutions. The fluorescence quenching is not only due to the long-range dipole-dipole energy transfer from monomer to aggregates [10,16], but also to the electron exchange process mainly in ethanol. The excitation energy migration between monomers would also play an important role in the quenching mechanism, as has been previously reported [10,16]. The diffusion of the molecular species also seems to enhance the efficiency of the quenching in the ethanolic systems. The higher rate constant for the quenching produced by the trimer than that produced by the dimer is attributed to the longer size of the former aggregate.

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