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On the mechanism of radiationless deactivation of rhodamines

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Absorption and emission (fluorescence spectra and radiative decay curves) spectroscopies are used to determine the photophysical properties of rhodamines with non-alkylated amino groups (rhodamine 110 and 123) in water and in ethanol. The results are compared to those previously reported for rhodamines with alkylamino groups. Different mechanisms for internal conversion such as the amino group rotation hindered by solvent viscosity, amino N–H vibrations, the formation of a twisted intramolecular charge transfer state (TICT) and the open–close umbrella-like motion model (ULM) are considered. Both the TICT and the ULM models can explain the experimental results if an intramolecular xanthene–COOR interaction and specific rhodamine–solvent interactions are taken into account.

1. Introduction

The internal conversion of rhodamines has attracted considerable attention, since this process competes with the fluorescent emission of these dyes, affecting their laser characteristics.

The relation between the radiationless deactivation from the S_1 state of rhodamines and the rotation of amino groups of the dye (fig. 1) has received considerable support [1–3]. Rhodamines with rigid amino groups or in frozen solutions have a fluores-

cence efficiency near to 100% [1,4]. However, an intramolecular rotational diffusion process of the amino groups hindered by solvent viscosity is too simple a model to explain the internal conversion of rhodamines [5,6]. Thus, an increase in the rotational volume (amino groups alkylation) does not imply a decrease in the radiationless deactivation rate constant [6]. Moreover, the rate constant of internal conversion of RB does not correlate in a simple way with the solvent viscosity, since this rate constant for RB^\pm ($R_1=R_2=Et$ in fig. 1) in ethanol at $20^\circ C$ is similar to that in glycerol and three times smaller than that in water [7], whereas ethanol has a viscosity which is 15.8 times smaller than that of glycerol and 1.2 times higher than that of water.

In the eighties, an increasing number of researchers attributed the non-radiative deactivation of rhodamines to the population of the so-called “twisted intramolecular charge transfer” (TICT) state from the S_1 excited state [5,8–10]. The formation of the TICT state involves an electron transfer from the amino groups to the xanthene ring following a rotation of the bond linking both partners [11,12]. In the case of rhodamines the emission from this state has not yet been observed. This is thought to be due to a forbidden radiative transition and/or an ultrafast rate constant of internal conversion to the S_0 state [5,8–10]. The population probability of the TICT state

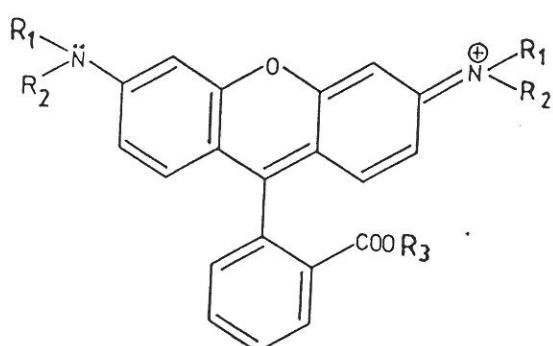


Fig. 1. General molecular structure of rhodamine dyes. Non-ethylaminated: ($R_1=R_2=H$), $R110^\pm$ ($R_3=-$), $R110H^+$ ($R_3=H$), $R123^\pm$ ($R_3=Met$). Mono-ethylaminated: ($R_1=H$, $R_2=Et$), $R19^\pm$ ($R_3=-$), $R19H^+$ ($R_3=H$), $R6G^+$ ($R_3=Et$). Diethylaminated: ($R_1=R_2=Et$), RB^\pm ($R_3=-$), RBH^+ ($R_3=H$), $R3B^+$ ($R_3=Et$).

from the S_1 state has to depend on the donor and acceptor capacities of the moieties and on the solvent polarity which would stabilize the highly polar structure of the TICT state with respect to the S_1 excited state.

This model explains the decrease in the internal conversion rate constant of the rhodamines with monoethylamino groups (R19 and R6G, fig. 1) with respect to that of diethylamined dyes (RB and R3B, fig. 1) by considering the electron donor–acceptor capacity of the moieties [5,8]. The decrease of the electron donor capacity of the amino groups due to the inductive effect $+I$ of the alkyl substituents generates a low-lying TICT state for the diethylamined derivatives. On the contrary, the TICT state of rhodamines with monoethylamino groups is thought not to be populated probably because of the energy of this state being higher than that of the S_1 state [5]. The activation energy of the internal conversion process of rhodamines with diethylamino groups ($20\text{--}30\text{ kJ mol}^{-1}$) is higher than that of the monoethylamined ones ($0\text{--}2\text{ kJ mol}^{-1}$) [5,6], supporting this interpretation. The higher internal conversion probability of rhodamines in aqueous solution than in ethanolic solution can be partially explained by the higher polarity and lower viscosity of the water, which stabilize and favour the formation of the TICT state [5].

However, some experimental aspects cannot be satisfactorily explained by the TICT model – mainly the influence of the orthocarboxyphenyl group and the large solvent effect:

(i) Rhodamines with the COO^- group have a much smaller internal conversion probability than the rhodamines with the COOH or the COOEt group. The inductive effect of COOR through the phenyl group cannot increase the acceptor capacity of the xanthene ring enough to produce such a large effect. A second TICT state with the carboxyphenyl group as the donor partner and the xanthene ring as the acceptor one has also been proposed for rhodamine dyes [13]. In this case, the COOR inductive effect could be more important, since this group is now directly attached to the electron donor fragment. Although the formation of this TICT state is uncertain it is expected to be less likely in rhodamines with the Ph-COOH group (RBH^+ , R19H^+ , R11OH^+) than in those with the Ph-COOEt group (R3B^+ , R6G^+ , R123^+), since the ionization potential of the benzoic acid (i.e. 9.73 eV

[14]) is higher than that of its corresponding methyl ester (i.e. 9.35 eV [14]). This contrasts with the higher internal conversion rate constant experimentally observed for the COOEt derivatives with respect to the related COOH ones [15–17]. An intramolecular interaction between the COOR group and the xanthene ring has also been proposed to explain the effect of the carboxyphenyl group [6,7,15–17].

(ii) The non-formation of the TICT state for rhodamines with monoethylamino groups should suggest a different radiationless mechanism for these dyes with respect to rhodamines with diethylamino groups, where the formation of the TICT state has been proposed. However, the influence of the solvent and of the carboxyphenyl group on the internal conversion rate constant is similar in rhodamines with mono- and diethylamino groups [16,17], suggesting a similar deactivation mechanism for both derivatives. The N-H vibrations were proposed as a possible radiationless deactivation pathway for rhodamines with non-alkyl amino groups [2], but results recently obtained in deuterated D_2O and EtOD solvents [18] indicate that this mechanism is not very important since the deuteration has a slight effect (<7%) on the photo-physics of rhodamines, and is independent of the alkylation of the amino groups.

(iii) The influence of the solvent has been considered until now by the TICT model as due to the polarity of the medium [5,8–10]. However, the effect of specific rhodamine–solvent interactions has been claimed from the solvent influence not only on the fluorescence quantum yield and lifetime but also on the maximum of the absorption and emission spectral bands and on the rotational relaxation time [6,7,15–19]. Particularly, water presents a peculiar behaviour with respect to hydroxylic organic solvents [7].

(iv) The observed correlation between the absorption and fluorescence maximum wavenumber and the internal conversion rate constant of RB [7] cannot be explained by the TICT model.

Recently, an alternative and, to a certain extent, complementary mechanism has been proposed to explain the internal conversion of rhodamines [15–17]. The radiationless deactivation is attributed to a structural change of the amino groups from a planar $\text{xanthene-N}^+<$ configuration (with an sp^2 hybridization for the nitrogen atom) to a pyramidal xan-

thene⁺-N< one (with a sp³ hybridization). This structural change involves a disruption of the xanthene=amine double bond to xanthene-amine single bond (now the amino group can rotate) and a displacement of the rhodamine positive charge from the amino N-atom to the xanthene ring. The radiationless deactivation can be visualized as the change between the symmetrically and energetically equivalent structures (a) and (c) of fig. 2, which could be stabilized by solvent and/or intramolecular interactions as it is discussed below. Although this open-close umbrella like motion (ULM model) mechanism could be related with the above ones, some conceptual differences can be distinguished.

(i) Not all the amino group rotations cause a radiationless deactivation process, but only those involved in a disruption of the electron π-system in the xanthene-amine bond; an increase of the xanthene-N double bond character implies more feasibility for the sp²-to-sp³ structural change and, therefore, a higher internal conversion rate constant.

(ii) There is a change in the electron density of the π-system in the xanthene-amine bond, but not a charge transfer state formation; consequently, all interactions that stabilize the rhodamine positive charge, and therefore the electron flow of the π-system, would decrease the non-radiative deactivation probability of rhodamines [16,17].

This ULM model has taken into account both the intramolecular COOR-xanthene and specific solute-solvent interactions to explain the photophysics of different mono- and diethylaminated rhodamines (R6G, R19, RB and R3B) [6,7,16,17].

In this work, the spectroscopic characteristics of non-alkylaminated rhodamines ($R_1=R_2=H$ in fig. 1) are determined (i.e., R123 and the molecular forms of R110) which permits to study the influence of the COO^- , COOH and COOMe groups on the photophysics of rhodamines. In order to discuss the amino

group alkylation effect, the present results are compared to those previously obtained for rhodamines with mono- and diethylamino groups. The influence of the specific dye-solvent interactions are studied using water and ethanol as solvents. The alcohol can solvate the alkylamino groups better than water because of hydrophobic reasons. On the contrary, the Ph-COO⁻ group is better solvated in aqueous than in ethanolic solutions. Therefore, water and ethanol are ideal media to study the specific solute-solvent interactions. The internal conversion rate constant is discussed on the basis of the TICT and ULM models, incorporating in both theories the effect of the intramolecular COOR-xanthene interaction and of the specific solute-solvent interactions.

2. Experimental

Rhodamine 110 and 123 were supplied by Kodak (Laser Grade) and used without further purification. The acid and zwitterion molecular forms of R110 were obtained at pH≈2 and pH≈8, respectively, in water and at pH≈4 and pH≈8, respectively, in ethanol [20] by adding appropriate amounts of NaOH and HCl to the solutions. Water was doubly distilled and absolute ethanol (Merck, pro-analysis) was supradried by distillation [21] in order to take off traces of water. The dye concentration was always $< 1.5 \times 10^{-6} \text{ M}$ in order to avoid dye aggregation [20] and to minimize the reabsorption and reemission effects [22].

Absorption and emission spectra were recorded on a Shimadzu (model UV-240) spectrophotometer and a Shimadzu (model RF-540) spectrofluorimeter, respectively, immediately after sample preparation. Samples were not degassed, as recommended [23], since oxygen does not appreciably quench the S₁ excited state of rhodamines. The RB[±]/EtOH system

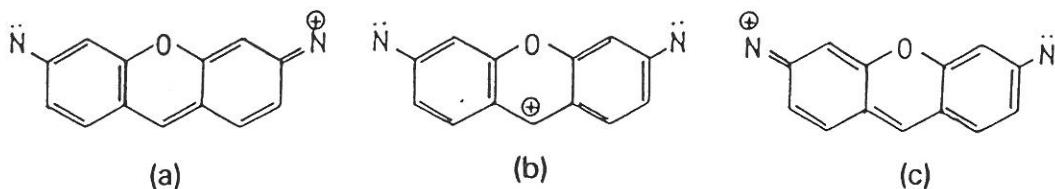


Fig. 2. Resonance structure of the rhodamine chromophore [1] (structures that involved an energetically less favoured oxonium configuration have not been included).

($\phi=0.70$ at 20°C [24]) was used as a reference to determine the fluorescence quantum yield of the samples. Radiative decay curves were measured in a nanosecond fluorescence spectrometer, described elsewhere [25], by the timing-correlated single-photon counting technique, using an Edinburgh flash-lamp for excitation. The quality of fit was controlled by the reduced χ^2 and the D.W. statistical parameters.

In order to minimize the important reabsorption and reemission effects in these dyes [23], the emission beam in both fluorescence techniques was detected in the front face mode (reflexion) with a 1 mm optical path cell. The absence of these effects was controlled by dilution.

3. Results and discussion

The radiative decay curve of the zwitterion ($R110^\pm$) and the cationic ($R110H^+$) molecular forms of R110 and that of $R123^+$ in water and in ethanol solutions can be analyzed as a single-exponential curve ($\chi^2 < 1.2$), as fig. 3 shows for the specific case of $R110H^+$ in water at 20°C. The obtained fluorescence lifetimes (τ°) are listed in table 1, together with other photophysical properties such as the maximum of the absorption (λ_{ab}) and emission (λ_{em}) spectral band, the fluorescence quantum yield (ϕ°) and the rate constant of non-radiative deactivation (k_{nr}) determined by the equation $k_{nr} = (1 - \phi^\circ)/\tau^\circ$. The results previously reported for rhodamines with mono- (R19, R6G) [16] and diethylamino groups (RB, R3B) [17] are also included in table 1 for comparison. Since the intersystem crossing probability of rhodamines is very low [26], the internal conversion process is the main non-radiative deactivation from the S_1 state of these dyes.

Table 1 shows that the internal conversion of rhodamines depends on the alkylation of the amino groups, on the protonation/esterification of the carboxyphenyl group and on the nature of the solvent. In spite of the inherent error in the ϕ° determination, the change in the k_{nr} value produced by such factors follows clear tendencies. These trends are now separately discussed by means of both the TICT and the ULM models. The discussion by this last model is carried through the resonance structures of the rho-

damine chromophore which are shown in fig. 2 [1].

3.1. Effect of the amino group alkylation.

The amino group alkylation produces a loss of the fluorescence capacity of the dye (mainly for the second alkylation), which is due to an increase of the internal conversion probability (table 1). The ethyl substituents imply a higher electron donor capacity of the amino groups, decreasing the TICT state energy. Consequently, this non-fluorescent state becomes more populated in alkylaminated rhodamines [5,8–13].

Otherwise, the ULM model takes into account that the inductive effect $+I$ of the ethyl substituents generates a higher electronic density in the xanthene–amine bond (the identical statistical weight of the (a) and (c) resonant forms of fig. 2 gets a more appreciable value) and, therefore, increases the radiationless deactivation rate constant since the sp^2-sp^3 structural change is more feasible. This interpretation is in agreement with the experimental results obtained for the activation energy of internal conversion: the ≈ 22 kJ mol $^{-1}$ [8,17] value obtained for rhodamines with diethylamino groups contrasts with the ≈ 1 kJ mol $^{-1}$ [5,16] value reported for the monoethylaminated dyes. The higher xanthene–N double bond character for the diethylaminated derivatives increases the probability of the structural change of the iminium group but the process would be energetically more difficult. The same arguments have been used to explain the absorption and fluorescence spectral shifts to smaller energies produced by the amino group alkylation [6,7,16,17] (table 1).

3.2. Effect of the protonation/esterification of the carboxy-phenyl group.

The protonation or esterification of the carboxylate group of rhodamine involves an increase of the intermolecular quenching process rate constant following the series $R110^\pm \ll R110H^+ < R123^+$, $R19^\pm \ll R19H^+ < R6G^+$ and $RB^\pm \ll RBH^+ < R3B^+$ (table 1). A shift to smaller energies of the absorption and emission spectra is also observed following the same series, table 1. This behaviour occurs in water and in ethanol, though the changes are more pronounced in the alcoholic medium (table 1). These

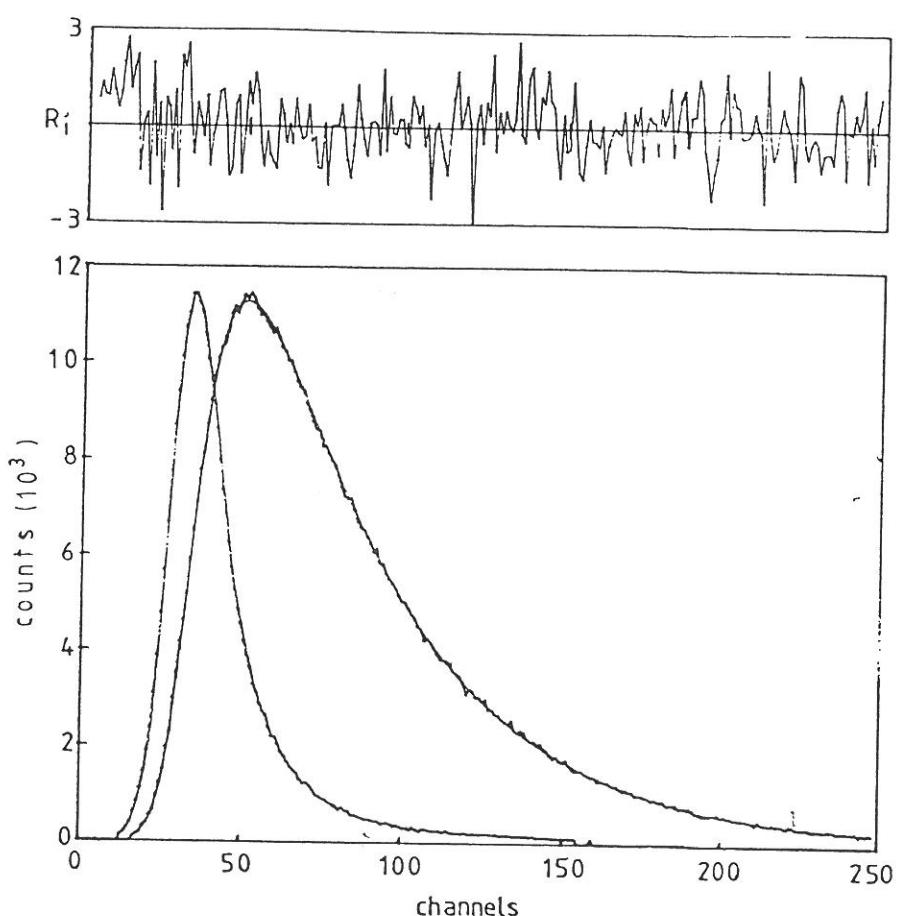


Fig. 3. Radiative decay curve of the zwitterion form of rhodamine 110 in water at 20°C. Channel scale: 0.105 ns/ch. $\chi^2 = 1.05$ and $\tau^\circ = 4.01$ ns.

spectral effects have been attributed to an intramolecular electrostatic interaction between the COOR group and the π -system of the xanthene [6,7,15–17]. Molecular models show the viability of this interaction since the carboxyphenyl group is sterically constrained to be roughly perpendicular to the planar xanthene skeleton [15]. This intramolecular xanthene–COOR interaction reduces the electronic density at the central 9-carbon of the chromophore (i.e., increasing the statistical weight of the mesomeric structure (b) of fig. 2), shifting the spectra to higher energies. Obviously, this interaction decreases in the series $\text{COO}^- \gg \text{COOH} > \text{COOMe}$.

If the intramolecular COOR–xanthene interaction is considered, the increase of the non-radiative deactivation in the series $\text{COO}^- \ll \text{COOH} < \text{COOEt}$ (table 1) can be explained by both the TICT and the ULM models. The intramolecular interaction stabilizes the positive charge on the central carbon of the

π -xanthene system, reducing the electron acceptor capacity of the chromophore. So, the TICT state energy is raised for rhodamines with the COO^- group ($\text{R}110^\pm$, $\text{R}19^\pm$ and RB^\pm) decreasing the tendency to populate the TICT state. Besides, the higher statistical weight of the (b) structure (fig. 2) in the zwitterion form of rhodamines implies a diminution of the xanthene–amine double bond character. So, the sp^2 – sp^3 structural change of the amino groups (ULM model) is less feasible, decreasing the internal conversion rate constant in these zwitterionic derivatives. This COOR effect is more pronounced in rhodamines with less degree of amino alkylation (table 1) because the (b) mesomeric structure acquires a higher participation. Since the COO^- group is better solvated by water molecules than ethanol ones, the COO^- effect is smaller in the aqueous than in the alcoholic solution (table 1).

Table 1

Photophysical properties (wavelength of the absorption and emission maxima, λ_{ab} and λ_{em} , fluorescence quantum yield and lifetime, ϕ and τ , and rate constant of non-radiative deactivation k_{nr}) of rhodamines with unsubstituted amino groups (R110 and R123), with monoethylamino groups (R19 and R6G) [16] and with diethylamino groups (RB and R3B) [17] in water and ethanol at 20°C

Non-ethylaminated	Water			Ethanol		
	R110 $^\pm$	R110H $^+$	R123 $^+$	R110 $^\pm$	R110H $^+$	R123 $^+$
λ_{ab} (nm)	496.4	499.6	500.4	501.0	509.6	511.4
λ_{em} (nm)	519.4	522.4	523.0	521.5	527.0	529.0
ϕ	0.93	0.78	0.74	0.99	0.85	0.81
τ (ns)	4.01	3.99	3.98	3.78	3.84	3.94
k_{nr} (10^8 s $^{-1}$)	0.17	0.55	0.65	0.03	0.39	0.48
Monoethylaminated	R19 $^\pm$	R19H $^+$	R6G $^+$	R19 $^\pm$	R19H $^+$	R6G $^+$
λ_{ab} (nm)	521.5	525.2	526.0	517.4	527.4	529.8
λ_{em} (nm)	546.4	550.4	551.3	542.1	549.6	551.8
ϕ	0.71	0.63	0.59	0.95	0.82	0.77
τ (ns)	3.93	3.94	3.95	3.73	3.80	3.85
k_{nr} (10^8 s $^{-1}$)	0.73	0.94	1.04	0.13	0.47	0.60
Diethylaminated	RB $^\pm$	RBH $^+$	R3B $^+$	RB $^\pm$	RBH $^+$	R3B $^+$
λ_{ab} (nm)	554.1	557.8	559.0	543.0	553.2	556.0
λ_{em} (nm)	572.9	577.1	578.1	563.3	572.4	574.2
ϕ	0.31	0.24	0.19	0.70	0.53	0.41
τ (ns)	1.75	1.58	1.53	2.88	2.42	2.27
k_{nr} (10^8 s $^{-1}$)	3.96	4.81	5.29	1.01	1.94	2.60

3.3. Effect of the solvent.

Finally, the important effect of the solvent on the photophysical characteristics of rhodamines (table 1) is discussed. The spectral shifts produced by the solvent depend on the alkylation of the rhodamine. Thus, the absorption and emission spectra of non-ethylaminated/diethylaminated rhodamines in ethanol appear at lower/higher energies than those obtained in water. Rhodamines with monoethylamino groups show an intermediate behaviour. Obviously, these spectral shifts cannot be attributed to the universal solvent effect but to specific rhodamine–solvent interactions which would depend on the alkylation of the amino groups of the dye. Moreover, an important reduction of the internal conversion rate constant (mainly for the zwitterion structure) is observed in the ethanolic solution with respect to the aqueous solution in all rhodamines.

Until now, the TICT model has considered that the influence of the solvent is due to the polarity of the

medium [5,8–10]. Thus, a near-linear relationship between the natural logarithm of k_{nr} and the solvent polarity parameter $E_T(30)$ [27–29] has been recently reported for RB $^\pm$ in water/ethanol mixtures [10]. However, in rich water mixtures a deviation from the linearity can be pointed out from this ref. [10]. A similar plot for the results previously obtained from our laboratory in the same system [17] is shown in fig. 4. From this figure, $\ln k_{nr}$ does not linearly correlate with $E_T(30)$ and exhibits, as in ref. [10], a sharp variation in the $0 < X_{\text{EtOH}} < 0.1$ range. The variation not only of the k_{nr} value (fig. 4) but also of the absorption and emission wavenumber upon increasing the X_{EtOH} value has been previously discussed [16,17] on the basis of specific solute–solvent interactions and the solvent framework of water/ethanol mixtures. The differences between Chang and Cheung [10] and our [17] results could be due to reabsorption [22]. Thus, though the reported absorption maximum of RB $^\pm$ in ethanol is the same in both cases, the fluorescence maximum obtained by

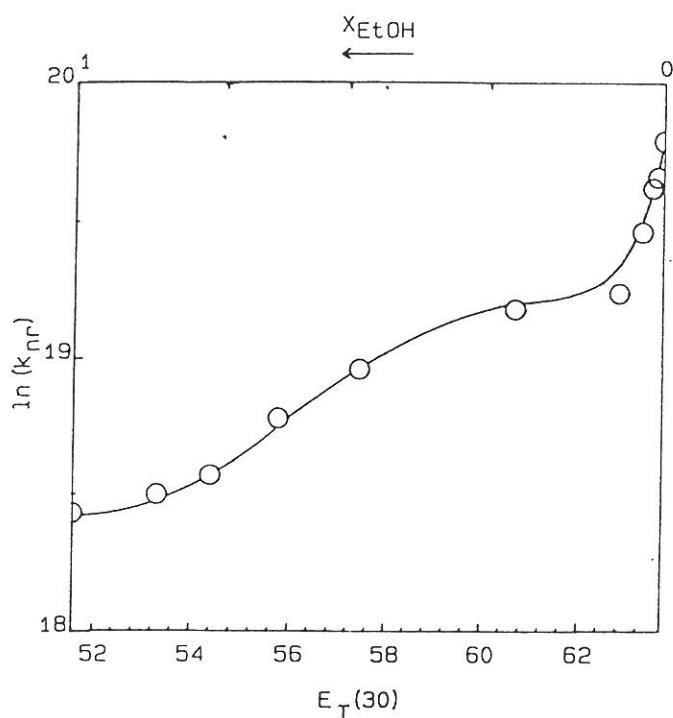


Fig. 4. Natural logarithm of the internal conversion rate constant of RB^+ in water/ethanol mixtures at 20°C [17] versus the solvent polarity parameter $E_T(30)$ [27–29].

Chang and Borst [9] is shifted 5 nm to lower energies with respect to that in table 1.

In any case, the effect of specific rhodamine–solvent interactions has been claimed not only from fluorescence quantum yield and lifetime results but also from the shift of the absorption and emission bands and from the rotational relaxation time [6,7,15–19]. Particularly, water exhibits a special behaviour with respect to hydroxylic organic solvents [7], as is also shown in fig. 4.

Three specific interactions between rhodamine dyes and hydroxylic solvents have been proposed [7,15] (fig. 5): (i) a hydrogen bond between the OH hydrogen-atom of the solvent and the electron lone-pair of the nitrogen-atom of the dye (interaction A); (ii) an electrostatic interaction between the electron lone pair of the OH oxygen atom of the solvent and the positive charge of the iminium group of the dye (interaction B); (iii) the above-mentioned COOR solvation (interaction C). Interactions A/B produce a shift of the absorption and emission spectra to higher/lower energies respectively [30], whereas interaction C implies the disruption of the intramolecular xanthene–COOR interaction [6].

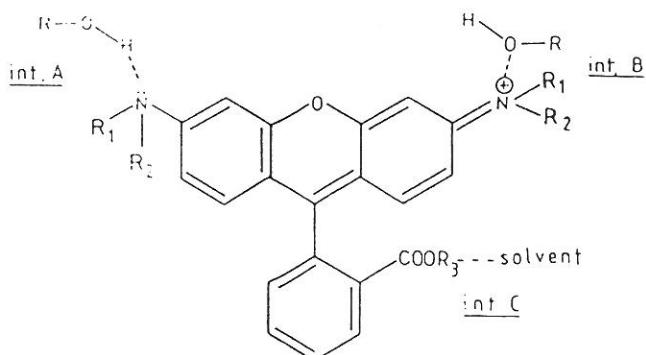


Fig. 5. Specific interactions between rhodamines and hydroxylic solvents [7,15].

In rhodamines with diethylamino groups (RB and R3B), both interactions A and B are favored in ethanol by hydrophobic forces; whereas water molecules are avoided at the diethylamino fragments of the dye. Interaction B should be more important than interaction A in diethylaminated rhodamines/ethanol systems because of the basic character of the alcohol and because the rhodamine positive charge is more localized on the amino nitrogen atoms (small statistical weight of (b), fig. 2). Interaction A (increasing the ionization potential of the NR_2 group) and interaction B (decreasing the electron affinity of the acceptor) tend to destabilize the TICT state. Besides, both interactions restrict the flow of the rhodamine positive charge through the xanthene ring, decreasing the change between the (a) and (c) resonant structures (ULM model). Consequently, the shift to higher energies of the spectra [5,16,17] and a decrease of the radiationless deactivation tendency are observed for rhodamines with diethylamino groups in ethanol with respect to those in aqueous solution (table 1).

In rhodamines with unsubstituted amino groups (R110 and R123), water molecules are not avoided at the amino groups. Now, a higher participation of interaction A can be expected in aqueous than in ethanolic solutions due to the large acidity of the former solvent. Interaction B is favored in ethanol because of its basic character. These interactions contribute to the observed blue spectral shifts for R123 and the R110 molecular forms in aqueous with respect to ethanolic solution (table 1). Moreover interaction B decreases the probability to form the TICT state and the mobility of the rhodamine positive charge (ULM model) as has been discussed, explain-

ing the diminution of the radiationless deactivation probability in ethanol (table 1).

Rhodamines with monoethylamino groups (R19 and R6G) have an intermediate behaviour between the rhodamines with non-ethylenediamine and diethylenediamine groups, table 1.

The variation of k_{nr} between the aqueous and ethanolic solution is larger in the zwitterionic than in the cationic or esterified rhodamines (table 1). The rigidity of the zwitterion forms generated by the intramolecular xanthene-COO⁻ interaction (in ethanol) is partially lost in aqueous solution due to the larger solvation of the carboxylate group by water molecules (interaction C).

4. Conclusions

Both the TICT and the ULM model can adequately explain the photophysics of rhodamines if the intramolecular xanthene-COOR and specific dye-solvent interactions are taken into account. The results shown in this work do not allow us to discern which of the two models is the appropriate to explain the radiationless pathway.

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References

- [1] K.H. Drexhage, in: *Dye Laser*, ed. F.P. Schäfer (Springer, Berlin, 1977).
- [2] K.H. Drexhage, *J. Res. Natl. Bur. Stand. A* 80 (1976) 421; *Laser Focus* 9 (1973) 35.
- [3] C.J. Tredwell and A.D. Osborne, *J. Chem. Soc. Faraday Trans. II* 76 (1980) 1627.
- [4] R.F. Kubin and A.N. Fletcher, *J. Luminescence* 27 (1982) 455.
- [5] M. Vogel, W. Rettig, R. Sens and K.H. Drexhage, *Chem. Phys. Letters* 147 (1988) 452, 461.
- [6] F. López Arbeloa, I. Urrecha Aguirresacona and I. López Arbeloa, *Chem. Phys.* 130 (1989) 371.
- [7] I. López Arbeloa and K.K. Rohatgi-Mukherjee, *Chem. Phys. Letters* 129 (1986) 607.
- [8] K.G. Casey and E.L. Quitevis, *J. Phys. Chem.* 92 (1988) 6590; *Fluor Detect.* 910 (1988) 144.
- [9] T.L. Chang and W. Borst, *J. Chem. Phys.* 93 (1990) 4724.
- [10] T.L. Chang and H.C. Cheung, *Chem. Phys. Letters* 173 (1990) 343.
- [11] Z.R. Grabowski, *Acta Phys. Polon. A* 71 (1987) 743.
- [12] W. Rettig, *Angew. Chem. Intern. Ed.* 25 (1986) 971; *Appl. Phys. B* 45 (1988) 461.
- [13] M. Vogel and W. Rettig, *Ber. Bunsenges. Phys. Chem.* 89 (1985) 962.
- [14] R.C. Weast, in: *Handbook of Chemistry and Physics*, 5th Ed., (CRC Press, Boca Raton, FL, 1975) p. E-76.
- [15] I. López Arbeloa K.K. Rohatgi-Mukherjee, *Chem. Phys. Letters* 128 (1986) 474.
- [16] F. López Arbeloa, T. López Arbeloa, E. Gil Lage, I. López Arbeloa and F.C. De Schryver, *J. Photochem. Photobiol. A* 56 (1991) 313.
- [17] F. López Arbeloa, T. López Arbeloa, M.J. Tapia Estévez and I. López Arbeloa, *J. Phys. Chem.* 95 (1991) 2203.
- [18] F. López Arbeloa, T. López Arbeloa, E. Gil Lage and I. López Arbeloa, *Appl. Fluor. Technol.* 2 (1990) 8.
- [19] A. von Jena and H.E. Lessig, *Chem. Phys.* 40 (1979) 245.
- [20] F. López Arbeloa, unpublished results.
- [21] A.I. Vogel, in: *Practical Organic Chemistry*, 4th Ed. (Longman, London, 1978).
- [22] I. López Arbeloa, *J. Photochem.* 14 (1980) 97.
- [23] M.J. Snare, F.E. Treolar, K.P. Ghiggino and P.I. Thistlethwaite, *J. Photochem.* 18 (1982) 335.
- [24] J. Ferguson and A.W.H. Mau, *Australian J. Chem.* 26 (1973) 1617.
- [25] A.U. Acuña, F. Amat, J. Catalán, A. Douhal and M.P. Lillo to be published.
- [26] V.E. Korobov, W.V. Shubin and A.K. Chibisov, *Chem. Phys. Letters* 45 (1977) 498.
- [27] K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, *Liebigs Ann. Chem.* 661 (1963) 1.
- [28] E.M. Kosower, in: *Introduction to Physics Organic Chemistry* (Wiley, New York, 1968) pp. 293-316.
- [29] C. Reichardt and E. Harbush-Goemart, *Liebigs Ann. Chem.* 721 (1983).
- [30] G. Köhler, *J. Photochem.* 38 (1987) 217.