

INVESTIGATION OF RATE PARAMETERS IN CHEMICAL REACTIONS OF EXCITED HYDROXYCOUMARINS IN DIFFERENT SOLVENTS

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Summary

The reaction kinetics in the excited state is determined by investigating the absorption and emission spectra and the time-dependence of the fluorescence intensity of 7-hydroxycoumarin and 4-methyl-7-hydroxycoumarin in different solvents. The results are interpreted using a model of the reaction which takes into account the dependence of diffusion-controlled rate parameters on the dielectric constant of the solution. By fitting the theoretical expressions for the rate parameters to the experimental values reaction parameters are obtained.

Introduction

We have investigated the chemical reactions (proton transfer reactions) in the excited state of 7-hydroxycoumarin (7-H) and 4-methyl-7-hydroxycoumarin (4-M) in the nanosecond region. These dyes are suited as fluorescent indicators and laser dyes [1 - 3]. In a restricted solvent range tunability of the laser output of 1700 Å was obtained [2, 4]. This wide range is explained by the fact that in the excited state different molecular forms are produced in the time range of the fluorescence decay, which are fluorescing at different wavelengths at the same time. Several molecular forms are associated with the same emission bands in the literature [1, 4 - 6].

In the fluorescence spectrum of 7-H and 4-M four molecular forms [5] appear in different solvents: an emission at 415 nm shows up in highly acidic solutions. In the ethanol-water mixtures used in this study, fluorescence maxima at 385, 450 and 480 nm appear at a constant absorption spectrum which corresponds to the neutral molecule (the absorption spectra corresponding to the other molecular forms can be obtained in acidic and basic solutions). The reaction constants in the excited state are therefore in the same range as the fluorescence decay constants.

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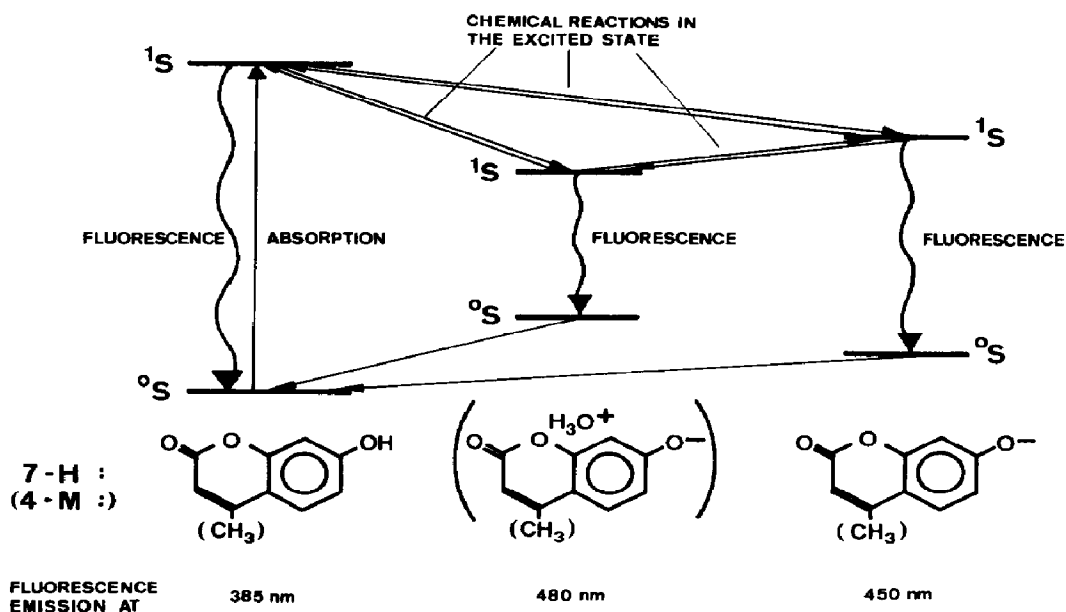


Fig. 1. Schematical representation of the reaction kinetics considered of 7-hydroxycoumarin (resp. 4-methyl-7-hydroxycoumarin) in ethanol-water solutions (see text).

The object of our investigation was the determination and physical interpretation of the rate constants in a model of the reaction kinetics. The following model (schematically shown in Fig. 1) allows a consistent interpretation of the results: the light-absorbing molecules in the singlet 1S can form a bound excited state with a proton acceptor (*e. g.* a water molecule) or else they can lose a proton, depending on the dielectric constant of the solution.

Theory

Model kinetics

The 3 fluorescing molecular forms of 4-M and 7-H are abbreviated by A (fluorescence peak at 385 nm), B (fluorescence peak at 450 nm) and C (fluorescence peak at 480 nm). We consider the model:



where the chemical reactions are initiated by molecules D (concentration of D, $[D]$, $\gg [A^*]$, $[B^*]$, $[C^*]$). Additional quenching processes are not supposed to be influenced by the composition of the solution.

If, in equilibrium, only A exists in the ground state, the quantum yield (QY) is defined by:

$$\Phi_A = \frac{I_A}{\alpha I_0} = \frac{k_{FA}[A^*]}{\alpha I_0}$$

where α is the absorbed fraction of the incident intensity I_0 . Accordingly we set

$$\Phi_B = \frac{k_{FB}[B^*]}{\alpha I_0} ; \Phi_C = \frac{k_{FC}[C^*]}{\alpha I_0}$$

We so obtain the relative QY from the stationary rate equations:

$$\frac{\Phi_B}{\Phi_A} = \frac{k_{FB}}{k_{FA}} \left(\frac{k_A k_{BC} + k_{BA} k_{AC}}{k_B k_{AC} + k_{AB} k_{BC}} \right) ; \quad \begin{aligned} k_A &= k_{MA} + k_{BA} + k_{CA} \\ k_B &= k_{MB} + k_{AB} + k_{CB} \\ k_C &= k_{MC} + k_{AC} + k_{BC} \end{aligned} \quad (2)$$

$$\frac{\Phi_C}{\Phi_A} = \frac{k_{FC}}{k_{FA}} \left(\frac{k_A k_{CB} + k_{CA} k_{AB}}{k_C k_{AB} + k_{AC} k_{CB}} \right)$$

$$\frac{\Phi_C}{\Phi_A} = \frac{k_{FB}}{k_{FC}} \left(\frac{k_{BA} k_C + k_{CA} k_{BC}}{k_{CA} k_B + k_{BA} k_{CB}} \right)$$

The general time-dependent solution of the rate equations for the fluorescence of the different molecular forms is a sum of three exponentials for each component [7]:

$$[X^*] = \sum_{j=1}^3 a_{Xj} e^{\lambda_j t}, \quad X = A, B, C \quad (3)$$

For explicit solutions see *e. g.* ref. 8.

Rate parameters

The rate parameters used for the bimolecular reactions $A^* + D \rightleftharpoons C^*$ (or B^*) involved are calculated by Schurr [10]. For Coulomb interaction between A and D they are given by

$$k_{CA} = [D] \frac{k_D e^2}{4\pi\epsilon\epsilon_0 k T a} [\exp(e^2/4\pi\epsilon\epsilon_0 k T a) - 1]^{-1} \quad (4a)$$

$$k_{AC} = [D] \frac{k_2 k_D e^2}{k_1 4\pi\epsilon\epsilon_0 k T a} [1 - \exp(-e^2/4\pi\epsilon\epsilon_0 k T a)]^{-1} \quad (4b)$$

where $k_D = 4\pi D_{AD} a$, $D_{AD} = D_A + D_D =$ sum of diffusion constants, $a =$ reaction radius, k_1 and $k_2 =$ intrinsic rate constants of the molecular reaction.

Experimental

Reagents

Chemically pure dyes 7-H and 4-M from Bender and Hobein AG, Zürich and quinine bisulphate from Schuchardt G.m.b.H., München, were used

without further purification. The solvents from E. Merck, Darmstadt, were if obtainable "spectroscopic grade", otherwise p. a.

Absorption and emission spectra

Absorption spectra were obtained using a Unicam SP800 u.v. spectrophotometer, fluorescence spectra using an Aminco-Bowman spectrofluorimeter. The samples were $\sim 10^{-4}$ M solutions in quartz vials at 20 °C.

By comparing the measured fluorescence spectrum of 10^{-4} M quinine bisulphate in 0.1 N H₂SO₄ with a normal spectrum [11] a correction function $K(\lambda)$ was determined and used in the quantum yield measurements.

It was checked in 10^{-5} M solutions that self-absorption effects can be neglected because of the small overlap of absorption and emission spectra.

The relative quantum yields were obtained by comparing superpositions of spectra of pure molecular forms (the superpositions were calculated on a digital computer Nuclear Data 812 and displayed on an oscilloscope) with the experimental spectra in different solvents.

Time dependence of the fluorescence intensity

The fluorescence decay at the emission wavelengths of the three molecular forms were measured with the single photon method [12, 13]. The excitation flashlamp (a free-running discharge lamp in air with 1.3 ns FWHM) is described in refs. 14 and 15). An afterpulse at 20 ns (see Fig. 9) was attributed to secondary effects in the stop-photomultiplier and was considered in the evaluation of the rate parameters.

The measured function $J_1(t)$ is given for linear fluorescence kinetics by the convolution:

$$J_1(t) \propto \int_0^t g(t-s) F(s) ds$$

where $g(t)$ is the resolution of the set-up, given essentially by the finite width of the excitation flash and the transit time fluctuations of the stop-photomultiplier and $F(t)$ is the fluorescence decay function of the dye. The resolution $g(t)$ is determined experimentally with a straying solution (Ludox).

Evaluation of the rate parameters

The decay function of the theory must be convoluted with $g(t)$ because the decay times of 7-H and 4-M are in the same order as the resolution of the set-up. This evaluation procedure showed several disadvantages, especially a complicated relation between the rate parameters and the measured decay constants, and a long computing time to obtain a catalogue of trialfunctions, including effects such as the excitation of several molecular ground-state forms, superposition of spectra, stray light and noise. Moreover, in an automatic, non-linear regression, oscillations of the solutions may appear [13]. Theoretical expressions (3) (see above and ref. 8) were therefore used for qualitative deductions, whereas the quantitative rate parameters were obtained by simulating the differential equations of the model kinetics and comparing the

resulting functions with the measured curves [13]. Afterwards the statistical accuracy of the fit can be determined on a digital computer and the rate parameters can be improved further by regression.

The measurements were evaluated by simulation on an analogue computer and the results of the simplified model obtained were checked by digital simulation on a ND 812 computer. The calculated function $J'_1(t)$ was displayed together with measured curve $J_1(t)$ on a (storage-) oscilloscope and was fitted by adjusting the rate parameters.

Results

Spectra of 4-M in different solvent mixtures are shown in Figs. 2 to 5 (similar spectra are obtained for 7-H).

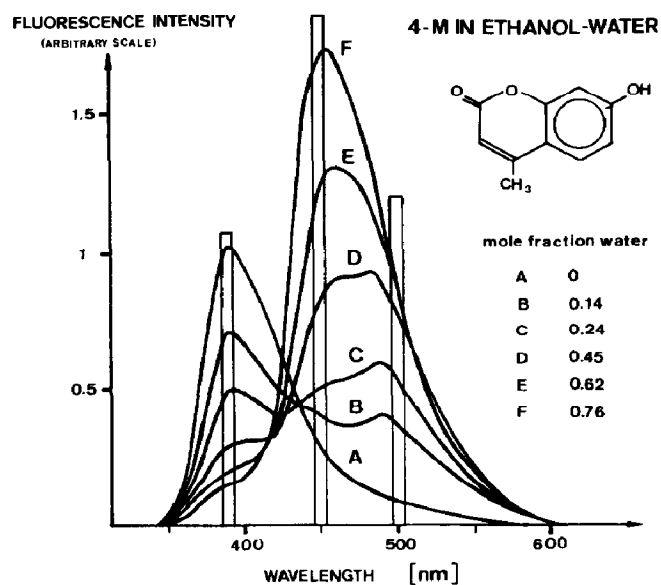


Fig. 2. Emission spectra of $10^{-4} M$ 4-methyl-7-hydroxycoumarin in ethanol ($\epsilon \cong 29$)-water ($\epsilon \cong 80$) mixtures. The form of the absorption spectrum is constant whereas the peak of the emission spectrum shifts from 385 to 483 nm and to 450 nm with increasing water concentration. The vertical bars mark the settings of the emission monochromator in the decay time measurements (see Fig. 8, curves b, c and d).

Figures 6 and 7 show examples of the fluorescence decay of 4-M at three emission wavelengths and in four solvents.

The absorption spectra of the reaction products are known [5]. However, all samples used in this investigation showed the same shape of the absorption spectrum, so that ground state reactions were neglected in the model kinetics.

The emission spectra in ethanol-water solutions were used to obtain relative quantum yields (Figs. 8 and 9). Absolute quantum yields (QY), determined by comparison with normal spectra of quinine bisulphate ($QY = 0.54$ [16])

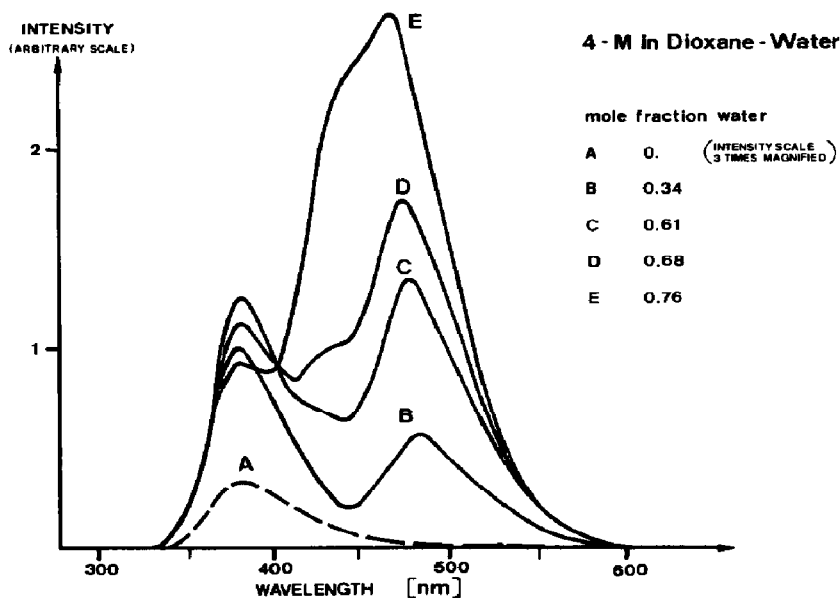


Fig. 3. Emission spectra of 4-M in dioxane ($\epsilon = 2.21$)-water ($\epsilon = 80.2$) mixtures. Relative to Fig. 4 the peak at 480 nm is pronounced and the emission at 450 nm appears at higher water concentrations.

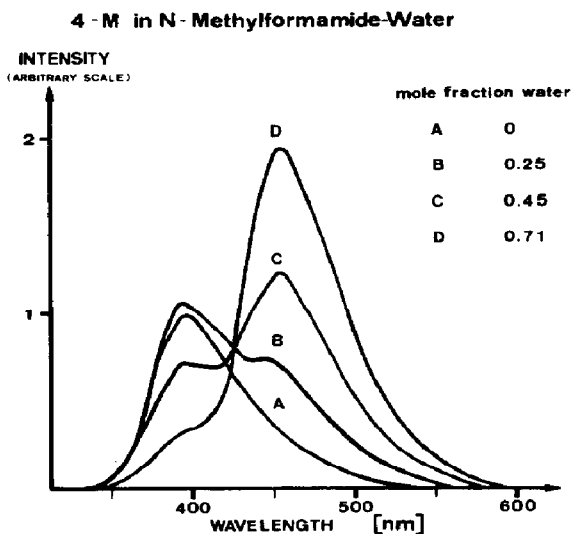


Fig. 4. Emission spectra of 4-M in *N*-methylformamide ($\epsilon = 182.4$)-water mixtures. No peak appears at 480 nm corresponding to a "bound ion pair".

are listed in Table 1. (In these measurements the solvent was chosen to produce pure molecular forms without quenching, *e. g.* k_{CA} (or k_{BA}) \gg other reaction rate parameters.) An error of 10 - 30% must be attributed to inaccuracies of these spectra and the evaluation difficulties because of superpositions of spectra.

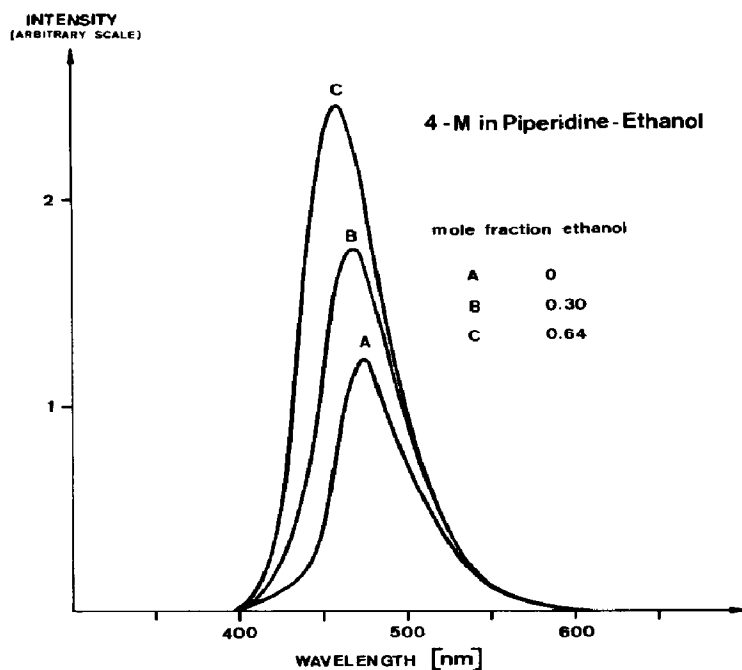


Fig. 5. Emission spectra of 4-M in piperidine ($\epsilon = 5.8$)–ethanol ($\epsilon = 29$) mixtures. The peak at 470 nm corresponds to a bound state 4-M + piperidine.

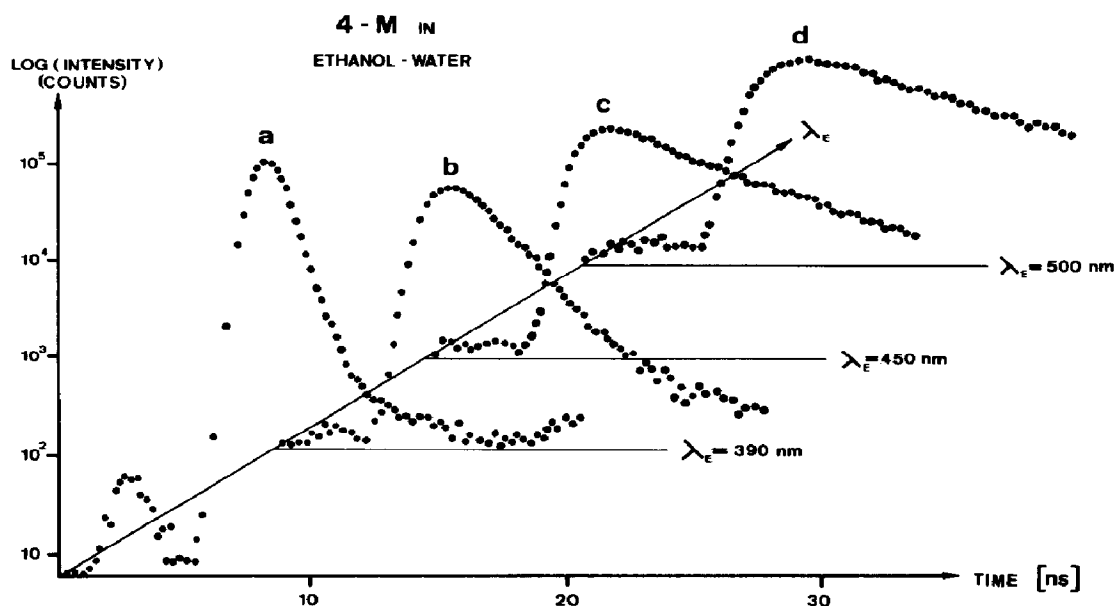


Fig. 6. The decay of the fluorescence intensity of 4-M at the emission wavelengths of 390 nm (b), 450 nm (c) and 500 nm (d) after excitation with the light flash (a) in an ethanol–water mixture (mole fraction water = 0.25). Rise time and decay are slower at longer wavelengths.

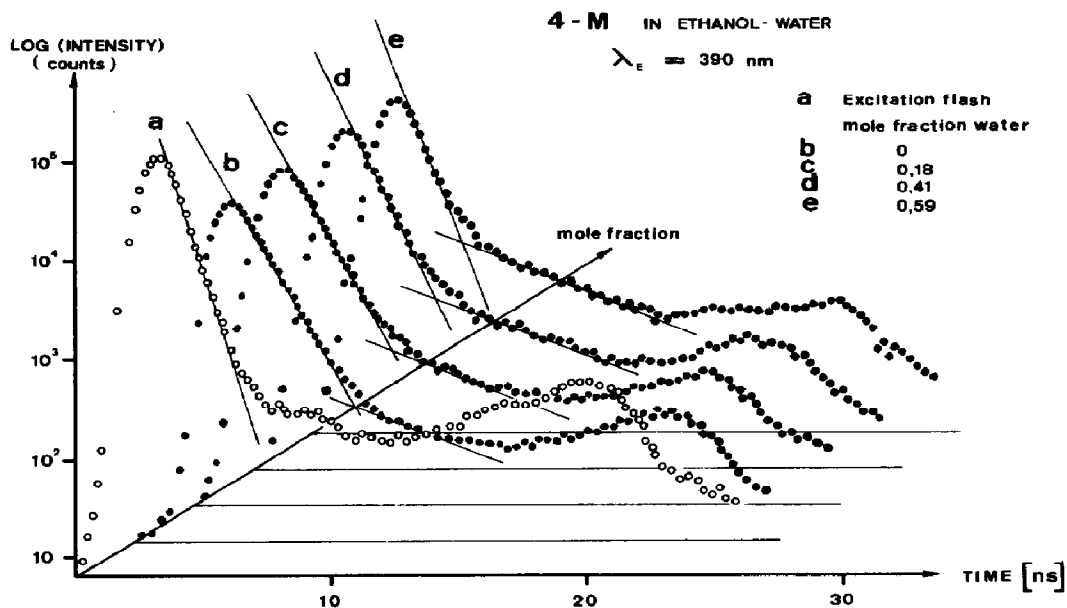


Fig. 7. Fluorescence decay of 4-M in different ethanol-water mixtures at emission wavelength $\lambda_E = 390 \text{ nm}$ excited by the light flash (a). Two decay components can be distinguished in (b) to (e): a prompt component decays faster with increasing water concentration and a delayed component with constant decay but increasing intensity.

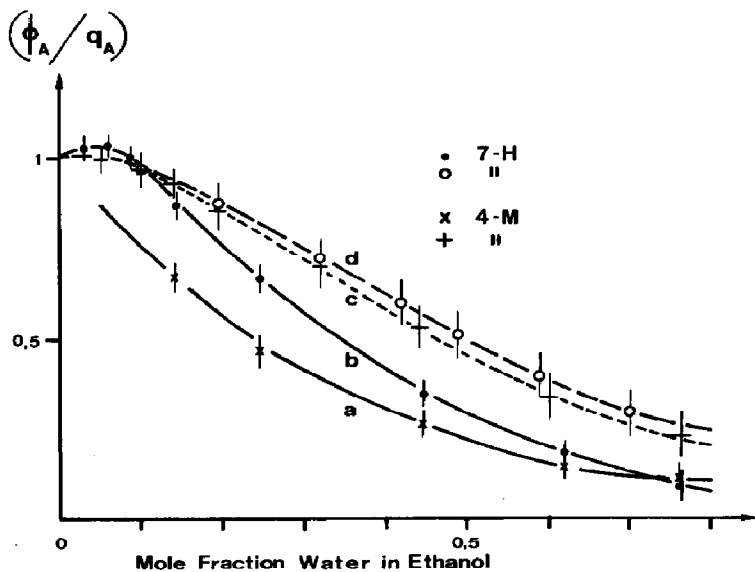


Fig. 8. Relative quantum yields of 7-H and 4-M in ethanol-water mixtures. (a), (b): Values gained from superpositions of pure spectra of A with corrected measured spectra in ethanol-water solutions; (c), (d): values gained from rate parameters k_A , k_{MA} out of decay time measurements.

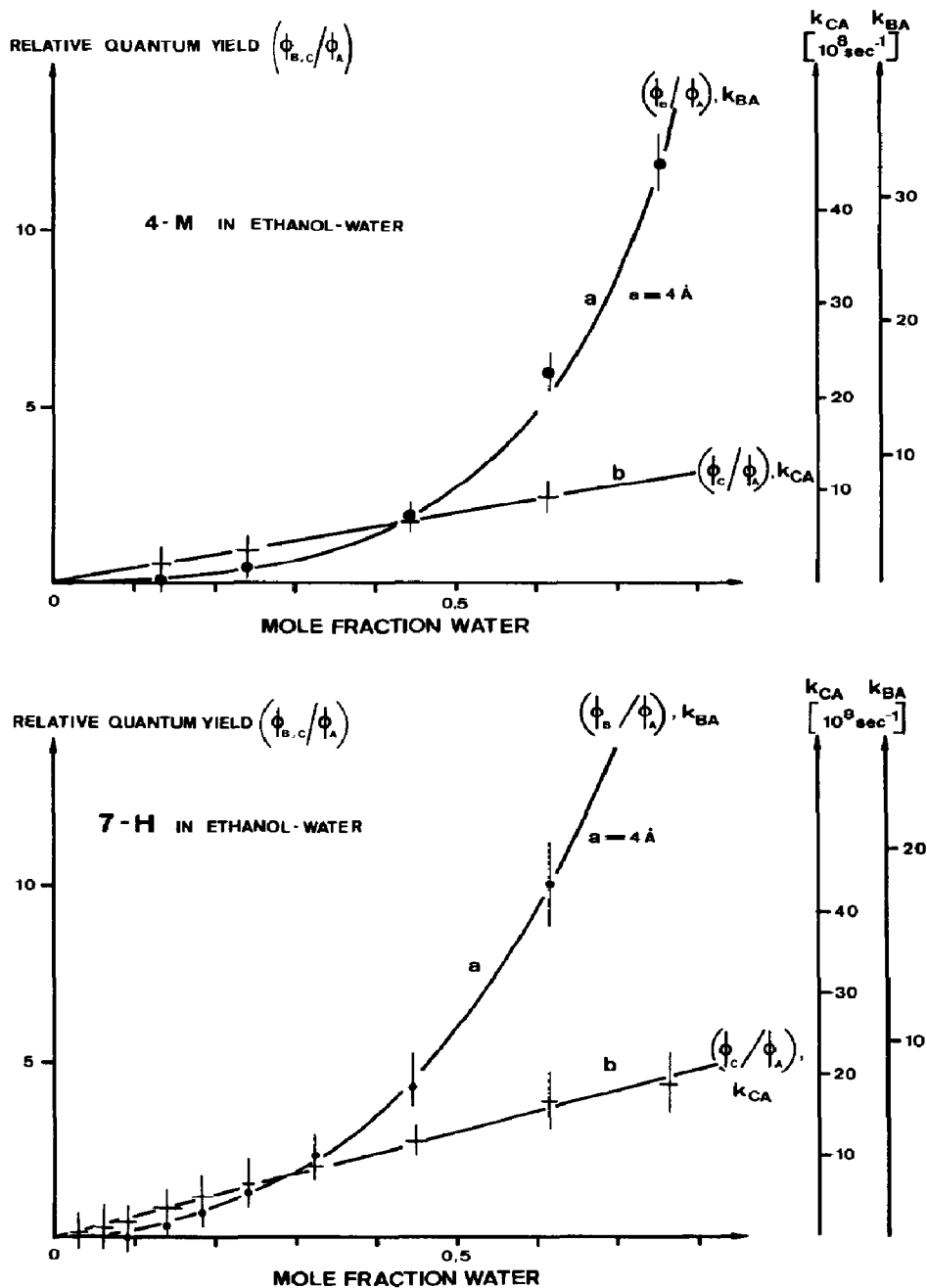


Fig. 9. Relative quantum yields Φ_B/Φ_A , Φ_C/Φ_A and rate parameters k_{CA} , k_{BA} for (a) 4-M and (b) 7-M in ethanol-water mixtures: corrected experimental values. As shown in eqn. (6) the rate parameters are proportional to the relative quantum yields. The measured values are fitted with a linear function for k_{CA} and with eqn. (5b) for k_{BA} .

TABLE 1

Absolute quantum yields

Molecule	Quantum yield, q_X	Solvent
Quinine bisulphate	$0.54 [16] \pm 0.03$	0.1 N H ₂ SO ₄
4-M: A	0.19 ± 0.03	ethanol
B	0.50 ± 0.05	water
C	0.36 ± 0.07	0.5 N HClO ₄ in ethanol-water (mole fraction water = 0.1)
7-H: A	0.11 ± 0.02	ethanol
B	0.66 ± 0.07	water
C	0.23 ± 0.05	0.5 N HClO ₄ in ethanol-water (mole fraction water = 0.1)

By comparison with expression (2) the reaction kinetics is deducible. If all reaction rate parameters are of lower than second order, we obtain for Φ_B/Φ_C the formula:

$$\frac{\Phi_B}{\Phi_C} = \frac{m + n[D]}{o + p[D]}$$

with $m, n, o, p \geq 0$. With increasing concentration $[D]$ this function increases or decreases with monotonously decreasing slope, contrary to the effective behaviour in Fig. 9. We therefore also have to consider rate parameters of higher than first order. The number of parameters together with the inaccuracies of the measurements does not allow an unequivocal deduction of the kinetics through the quantum yields, so that the decay time measurements have to be taken into consideration.

In the evaluation of decay time curves an agreement of the parameters at the three emission wavelengths of one solvent mixture was searched in three steps: (i) the prompt decay times $\tau = 1/k$ (Fig. 10) were determined. (The same values were found for solutions bubbled with N₂.) The accuracy is limited by the resolution function $g(t)$ and the subjectivity of the evaluation process: the error is 0.05 - 0.1 ns below decay times of 2 ns and 5% above 2 ns. The lower limit of measurable decay times was 0.3 ns; (ii) measurements at 390 nm were simulated with the model (1) considering the calculated superposition of emission spectra; (iii) it was checked if the deduced parameters would reproduce correctly the curves at 450 and 500 nm.

Resulting model

A model for the reaction of the dyes in ethanol-water solutions was deduced and tested in the other solvents.

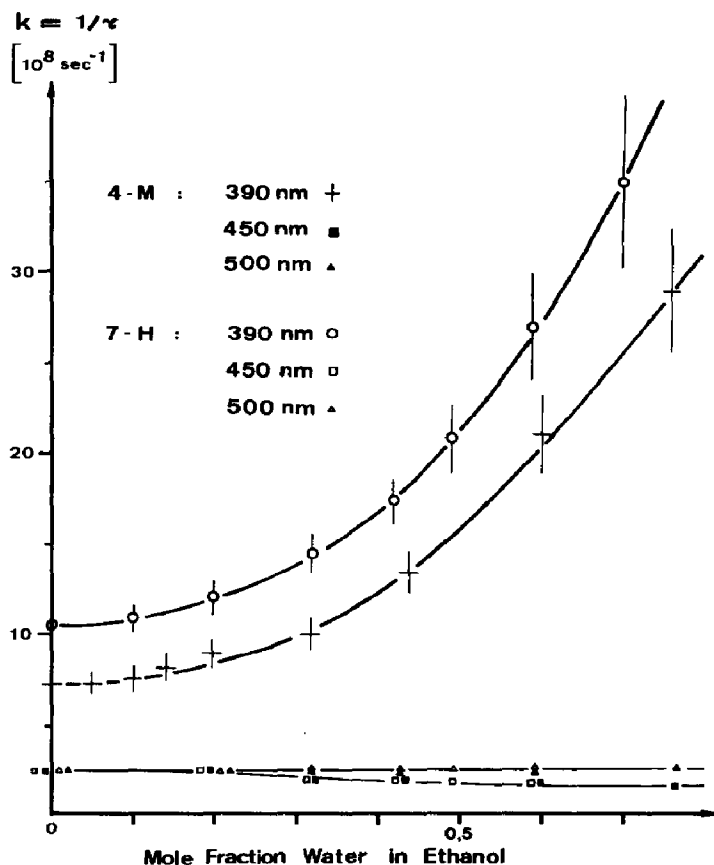
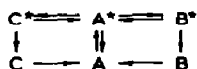


Fig. 10. Rate parameters $k = 1/\tau$ deduced from the prompt fluorescence decay (see Fig. 9).

(1). Only a model



can reproduce correctly the results. In a model $A^* \rightarrow C^* \rightleftharpoons B^*$, the fluorescence intensity of B should rise approximately following the decay of C^* , *e. g.* much slower than the measurements indicate (Fig. 6).

(2). Upper bounds for back reaction constants $k_{AB} = k_{AB}'[H_2O]$, $k_{AC} = k_{AC}'[H_2O]$, deduced in the simulations, are given in Table 2.

TABLE 2

Reaction rate constants

	4-M/mole fraction ⁻¹ s ⁻¹	7-H/mole fraction ⁻¹ s ⁻¹
k_{AB}'	$\lesssim 3 \times 10^8$	$\lesssim 1.5 \times 10^8$
k_{AC}'	$\leq 0.6 \times 10^8$	$\leq 0.8 \times 10^8$

The decrease of k at 450 nm and the constancy of k at 500 nm in Fig. 10 is explained by the superposition of emission spectra: at low water concentration the decay at 450 nm is dominated by C ($k_{MC} = (2.2 \pm 0.1) \times 10^8 \text{ s}^{-1}$), at high water concentrations by B ($k_{MB} = (1.85 \pm 0.1) \times 10^8 \text{ s}^{-1}$). Efficient back reactions would cause an increase of the decay parameters. Therefore the valid model is approximately:



(3). The rate parameters k_{BA} and k_{CA} can now be separated by the use of relative quantum yields, using the relations (eqn. 2, with $k_{AC} \cong k_{AB} \cong k_{BC} \cong k_{CB} \cong 0$):

$$\frac{\Phi_B}{\Phi_A} = \frac{k_{FB}}{k_{FA}} \cdot \frac{k_{BA}}{k_{MB}} = \left(\frac{q_B}{q_A k_{MA}} \right) k_{BA} ;$$

$$\frac{\Phi_C}{\Phi_A} = \frac{k_{FC}}{k_{FA}} \cdot \frac{k_{CA}}{k_{MB}} = \frac{q_C}{q_A k_{MA}} k_{CA} \quad (6)$$

Differences in Φ_A/q_A (Fig. 8), and in the sum $k_{BA} + k_{CA}$ gained in eqn. (6) and in decay times ($1/\tau = k_{MA} + k_{BA} + k_{CA}$) are attributed to (i) static quenching of the fluorescence of A^* or non-stationary rate parameters (a correction curve for this effect is deduced from Fig. 8; Figs. 9a and 9b show corrected relative quantum yields), and (ii) changing quantum yield q_A (the dependence of the rate constant for radiationless relaxation on $[\text{H}_2\text{O}]$ was calculated from the differences in $k_{BA} + k_{CA}$).

Summarizing, the consistent reaction rate parameters are given in Fig. 9 and Table 2: k_{BA} shows an exponential increase with the mole fraction of water, k_{CA} is proportional to the mole fraction and can be written as:

$$4\text{-M: } k_{CA} = (15.7 \pm 2.5) \times 10^8 (\text{mole fraction H}_2\text{O})^{-1} \text{ s}^{-1}$$

$$7\text{-H: } k_{CA} = (28.6 \pm 4.5) \times 10^8 (\text{mole fraction H}_2\text{O})^{-1} \text{ s}^{-1}$$

Discussion

The results may now be interpreted considering two separate bimolecular processes (i) and (ii). The underlying model of the excited state reaction is shown in Fig. 11. A collision between a neutral, excited dye molecule and a water molecule produces an encounter complex, in which the proton of the hydroxy group may be transferred over a distance of $\sim 4 \text{ \AA}$ (see Table 3).

Subsequently the H_3O^+ may be bound to the anion with smaller distance between the ions (1) (a charge transfer complex or an associated ion pair is formed) or the ions separate by diffusion (2).

(i) *Reaction* $A^* \rightleftharpoons C^*$: A is the neutral dye and C is a bound state of the dye ion (proton donor) and water (proton acceptor). The rate constant k_{CA} is proportional to the mole fraction of H_2O and independent of ϵ , giving

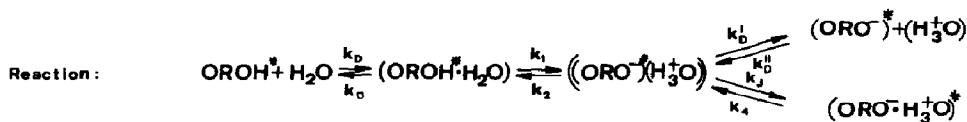


Fig. 11. Model of the reaction 7-H (4-M) + H₂O in ethanol in the excited state (k_D = diffusion-controlled rate parameter $\cong 6 \times 10^9$ l/mol s).

TABLE 3

Parameters of the rate constants in eqns. (4)

4-M		7-H	
a/A	$k_1 k_D / k_2 / \text{mole fraction}^{-1} \text{ s}^{-1}$	a/A	$k_1 k_D / k_2 / \text{mole fraction}^{-1} \text{ s}^{-1}$
3.5 ± 0.5	$(2 \pm 1) \times 10^{10}$	4 ± 0.5	$(2.1 \pm 0.6) \times 10^{10}$

for the mole fraction $\ll 1$: $k_{CA} \cong 0.9 \times 10^8$ mol/l s⁻¹ (4-M) and $k_{CA} \cong 1.7 \times 10^8$ mol/l s⁻¹ (7-H). This rate is activation energy controlled. The backreaction rate parameters k_{AC} are smaller than k_{CA} by more than a factor of 30 (Table 2).

(ii) Reaction $A^* \rightleftharpoons B^*$: B is the dye anion. The exponential increase of k_{BA} with the mole fraction of H₂O is explained by the weaker interionic forces at high dielectric constant ϵ which favour the separation of the ions formed in the reaction. The parameters of eqns. (4) following from a fit of the experimental values (see Fig. 9) are listed in Table 3. Back reactions follow from collisions of the anion with water molecules (activation energy controlled) or with H₃O⁺ ions. An upper limit of the ion reaction parameter is given by:

$$k_{AB}'[\text{H}_3\text{O}^+] \leq k_D[\text{H}_3\text{O}^+] \leq 6 \times 10^9 \times 10^{-4} \text{ s}^{-1} = 6 \times 10^5 \text{ s}^{-1}$$

because $k_D \geq k_{AB}'$ and $[\text{H}_3\text{O}^+] < 10^{-4} \text{ M}$ (= dye concentration). The model described was tested in three different solvent mixtures (Figs. 3 - 5).

Dioxane-water

Dioxane ($\epsilon = 2.21$, an aprotic solvent) does not take part in a proton transfer reaction, but it is quenching the fluorescence of 7-H and 4-M. Figure 3 shows an initial increase of the fluorescence at 385 nm, supporting the remark made earlier. A dioxane-water mixture reaches the ϵ value allowing a separation of the ions at higher water concentrations than an ethanol ($\epsilon = 29$)-water mixture: taking over the values for k_1 , a and k_{CA} from ethanol-water mixtures of 4-M and varying only the dependence of the dielectric constant on the solvent mixture, the model gives a fluorescence change $\Phi_B / \Phi_C = 1$ at mole fraction of H₂O = 0.79 compared to the value of 0.77 obtained from the decomposition of the spectra in Fig. 3.

N-methylformamide-water

N-methylformamide ($\epsilon = 183.4$ at 25 °C) is a proton-donor ($\text{p}K_a =$

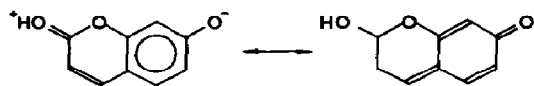
— 0.04 at 20 °C in H₂O). With increasing water concentration only a fluorescence peak at 450 nm appears (anion) but no bound state emitting at 480 nm because of the high ϵ value (see Fig. 4).

Piperidine-ethanol

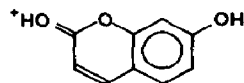
Piperidine (a proton acceptor, $pK_{BH^+} = 11.12$ at 25 °C in H₂O, $\epsilon = 5.8$) – ethanol mixtures show the fluorescence emission in Fig. 5. Besides, absorption spectra show that also in the ground state a proton is transferred from the dye to the piperidine. A bound state, emitting a 470 nm is formed. The distance a in this complex is larger than in a water complex, so that a separation of the ions is possible also in ethanol.

Comparison with results in the literature

By spectroscopic investigations of similar molecules (*e. g.* hydroxycoumarin esters), Nakashima [5] and Yakatan [1] associate the emission at 480 nm to a zwitterion (⁺HORO⁻):



whereas Fink [6] attributes the same emission to the cation (⁺HOROH):



The same result was obtained by Shank and Dienes [2, 4] by investigating the time difference between pumping pulse and laser pulse in a dye laser.

The measurements presented, in mixtures of inert and reacting solvents, which allow a decomposition of the reaction steps impossible in aqueous solutions, show that even the experimentally better supported zwitterion cannot explain the results; the model kinetics does not allow a two proton transfer at small water concentrations (addition of a proton at the carbonyl group, dissociation of a proton at the hydroxy group) and a one proton transfer at high water concentrations. Therefore, apart from pure molecular forms, bound states of the reacting particles (charge transfer complex (A⁻D⁺)^{*} or bound ion pair (A⁻)^{*} (D⁺)) are to be considered.

Conclusions

(1). This paper reports investigations on the reaction kinetics of 7-hydroxycoumarin and 4-methyl-7-hydroxycoumarin in the excited state using absorption and fluorescence emission spectra and the time dependence of the fluorescence intensity in several solutions.

(2). Decay times were measured with the single photon method. Because of the short decay times (5 ns and below 1 ns) a fast excitation flash lamp had

to be used and the evaluation of the rate parameters was performed by simulating the model kinetics taking into consideration the time resolution of the set-up.

(3). The rate parameters obtained are interpreted in the following model. The excited dye molecules can transfer a proton during an encounter in the solution (*e. g.* to a water molecule). Depending on the value of the dielectric constant, ϵ , of the solution a bound state of the dye anion and the proton acceptor (with a rate constant proportional to the concentration of the water) or a solvated dye anion (with a rate constant exponentially dependent upon ϵ) is formed. Both reaction products and the neutral dye molecule show fluorescence emission at different wavelengths.

(4). By fitting theoretical expressions for the dependence of the rate constants on parameter of the solvent, reaction parameters are obtained.

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