Fluorescence-properties and excited state interactions of 7-hydroxy-4-methylcoumarin laser dye

FLUORESCENCE PROPERTIES AND EXCITED STATE INTERACTIONS OF 7-HYDROXY-4-METHYLCOUMARIN LASER DYE

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Summary

The effect of solvent on some photophysical properties of 7-hydroxy-4-methylcoumarin (4-methylumbelliferone) is examined. Light absorption results in the population of a locally excited (LE) first singlet state (S_1, $\pi\pi^*$) mixed with $n\pi^*$. This is characterized by extensive non-radiative energy dissipation on the subnanosecond time scale, which shows a sensitivity to environmental factors (solvent polarity and hydrogen-bonding ability) that may be exploited profitably in various systems of industrial and biological importance. Moreover, excellent linear correlations are established between some photophysical properties of 7-hydroxy-4-methylcoumarin and some solvent properties. The results are discussed on the basis of quantum chemical data obtained by application of the CNDO method.

The fluorescence spectra in alcoholic solvents and water show complex formation via hydrogen-bonding interactions. The equilibrium constants K for complex formation (dye–water followed by ultrafast proton transfer) are determined at various temperatures. Small K values in the range 13 - 19 l mol^{-1} are obtained. Some thermodynamic parameters are also determined. The results indicate an associative excited state complex with a dissociative ground state. The weak excited state complex formed with water is characterized by an extended strong blue–green fluorescence which can be attributed to tautomer formation via intramolecular proton transfer.

1. Introduction

Coumarin dyes are widely used in dye lasers to achieve tunable blue-green light, and are also employed in other important applications of

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industrial and biological interest, *e.g.* in enzyme determination, photo-biological energy transfer processes, fluorescent probe techniques and fluorescence whiteners in detergent products [1 - 4].

Of the vast number of coumarins studied, hydroxycoumarin dyes have received most attention because of their interesting anomalous pH-dependent fluorescence spectra [1 - 5]. The variety of emission wavelengths available from the various prototropic species derived from 7-hydroxy-4-methylcoumarin has been suggested as the basis for the construction of acidity-tunable dye lasers [2 - 4]. Evidence for exciplex laser action in the acidified solutions of some hydroxycoumarin laser dyes has been obtained by measurement of stimulated fluorescence [3].

Despite the various contributions made to the subject [1 - 7], no detailed study has been carried out on the effect of solute—solvent interactions, particularly specific interactions, on the photophysical properties (fluorescence energy, quantum yield ϕ_f and non-radiative rate constant k_{nr}) and fluorescence quenching of 7-hydroxy-4-methylcoumarin due to excited state complex formation. This information is highly desirable for the characterization of the dye—solvent laser systems and could be useful in providing a fluorescent probe with unique features for possible analytical applications.

In this paper the effects of solute—solvent interactions on the photophysics of 7-hydroxy-4-methylcoumarin are studied. An examination is made of the influence of solvent on the following parameters: the fluorescence quantum yield, the non-radiative rate constant, fluorescence quenching due to solvent interactions and the equilibrium constants of such interactions at various temperatures.

2. Experimental details

7-Hydroxy-4-methylcoumarin was obtained by the condensation of resorcinol with ethyl acetoacetate in the presence of concentrated H_2SO_4 according to the Beckmann reaction (*Chem. Abstr. 98* (1983) 107 121). Its purity was checked by thin layer chromatography (TLC). Optically pure solvents (BDH Spectrosol grade or Merck) were used.

UV and visible absorption spectra were recorded on SP 1800 Pye—Unicam and Perkin—Elmer Lambda 3B spectrophotometers.

Fluorescence and excitation spectra were recorded using a Schimadzu RF 510 spectrofluorometer equipped with a Rhodamine B quantum counter. Fluorescence quantum yields were determined by comparing with a quinine fluorescence standard ($\phi_f = 0.55$ in 1 N H_2SO_4). Fluorescence quenching by dissolved oxygen was found to be inefficient. The concentrations of the final dye solutions measured were of the order of 10^{-5} mol dm^{-3}. In all measurements, the absorbance at the excitation wavelength was less than 0.10.

Molecular orbital (MO) calculations within the framework of the well-known all-valence electrons CNDO/2 approximation [8] were carried

out using microcomputer programs suppled by the Quantum Chemistry Program Exchange (QCPE), Indiana University [8]. Bond lengths and angles were taken from the literature.

The least-squares regression analysis and the fitting of the spectral data to linear and multilinear equations were performed using the Simfit program supplied by QCPE; error minimization was achieved using the sequential simplex statistical procedure [9]. All computations were performed using an AT & T PC6300-XT computer.

3. Results and discussion

3.1. Photophysics of 7-hydroxy-4-methylcoumarin

Absorption and fluorescence spectral data of 7-hydroxy-4-methylcoumarin in different solvents are compiled in Table 1 and some results are depicted in Fig. 1. Changing the solvent polarity has a negligible influence on the wavelength of maximum absorption or fluorescence (the maximum solvent-induced spectral shift is about 4 nm). The solution of 7-hydroxy-4-methylcoumarin in water represents an exceptional case where a broad, strong fluorescence band appears at 450 nm (Fig. 1). This band is attributed to tautomer formation via specific dye–water complex interactions leading to ultra-fast excited state intramolecular proton transfer. Such a spectral shift is not observed in the absorption spectrum of aqueous solutions of 7-hydroxy-4-methylcoumarin suggesting that the dye–water excited state complex [10] dissociates in the ground state. Such a proton transfer process should be facilitated by increasing the acidity of the

TABLE 1

Spectral and photophysical data of 7-hydroxy-4-methylcoumarin

Solvent	λ_a (nm)	λ_f (nm)	ϕ_f	$\epsilon \times 10^{-4}$ (l mol^{-1} cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	k_r (10^9 s^{-1})	k_{nr} (10^9 s^{-1})
1 Water	320	450	0.356	1.49	4808	0.4185	0.75
2 MeOH	320	387	0.266	1.26	3971	0.4737	1.30
3 EtOH	320	385	0.208	1.38	4171	0.6635	2.52
4 Iso-PrOH	323	386	0.169	1.26	4321	0.7456	3.66
5 Iso-BuOH	323	385	0.202	2.96	4402	1.465	5.78
6 DMSO	320	386	0.132	1.61	5567	1.220	8.02
7 DMF	320	386	0.081	1.46	6302	1.802	20.45
8 CH$_2$Cl$_2$	320	385	0.026	3.11	5625	11.96	448.1
9 CHCl$_3$	320	382	0.099	1.21	4231	1.222	11.12
10 Ethyl acetate	320	383	0.015	1.09	3173	7.267	477.2
11 n-Hexane	324	385	0.063	2.30	4714	3.651	54.30
12 n-Heptane	325	386	0.105	1.͜͡ͅ	͜`͢18	1.867	15.91

$k_r = 1/\tau_r$; $\tau_r = \tau_0\phi_f$; $\tau_0 = 10^{-4}/\epsilon$; $k_{nr} = k_r\{(1/\phi_f) - 1\}$.
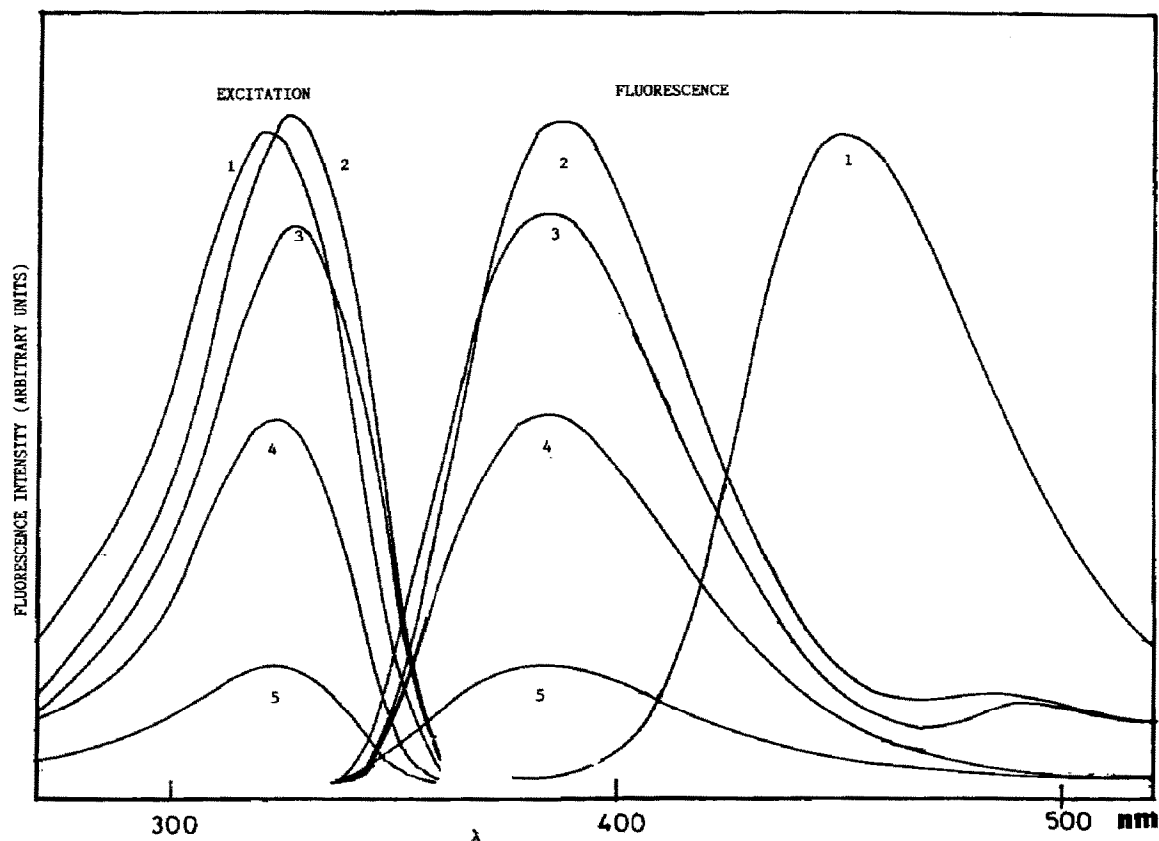
Fig. 1. Excitation and fluorescence spectra of 7-hydroxy-4-methylcoumarin in different solvents: 1, H_2O; 2, iso-BuOH; 3, n-hexane; 4, CH_2Cl_2; 5, ethyl acetate.

hydroxyl group by optical pumping. Our CNDO results for 7-hydroxy-4-methylcoumarin (discussed below) are consistent with this prediction.

Moreover, attempted correlations between some photophysical parameters of 7-hydroxy-4-methylcoumarin and some solvent properties (*e.g.* E_T^N [11], π and α values [12]) result in excellent linear relationships (Table 2). Again, water represents an exceptional case; in all these correlations water was excluded because of the strong deviation from linearity. It is also worth noting that the inclusion of a viscosity term does not result in a better correlation, and an attempt to fit the data to a multiparameter equation was unsuccessful. The established correlations show a linear response of the Stokes shift, the fluorescence quantum yield ϕ_f and the calculated non-radiative energy dissipation rate constant k_{nr} to the polarity (E_T^N and π values) and hydrogen-bonding donor ability α of the solvent.

These results can be rationalized on the basis of the following discussion.

Molecular orbital calculations within the CNDO approximation permit us to establish the nature of the lowest excited singlet state. It is interesting to examine the charge densities and bond orders predicted by the CNDO

TABLE 2

The established linear correlations between some photophysical parameters (Y) and some solvent properties (X) according to the relation $Y = a + bX$

Y	a	b	X	r^2	NOBS[a]
$\bar{\nu}_a - \bar{\nu}_f$	4932 ± 92	565 ± 208	E_T^{N} [b]	0.992	11(1)
	4929 ± 84	384 ± 126	π [c]	0.993	11(1)
$\ln \phi_f$	-2.97 ± 0.18	2.15 ± 0.36	E_T^{N}	0.955	9(1, 8, 10)
$\ln k_{nr}$	24.50 ± 0.37	-4.18 ± 0.78	E_T^{N}	0.996	9(1, 8, 10)
	23.90 ± 0.40	-1.28 ± 0.60	π	0.998	7(1 - 3, 8, 10)
	23.60 ± 0.28	-2.25 ± 0.51	α [c]	0.99	9(1, 8, 10)

[a]NOBS, number of active observations included in the correlation (numbers in parentheses are omitted solvents, see Table 1).
[b]Normalized E_T solvent parameter [11].
[c]Polarity π and hydrogen-bonding donor ability α of the solvent [12].

TABLE 3

π charge density and bond orders in the S_0 and S_1 states of 7-hydroxy-4-methylcoumarin

| Atom number	Charge density		Bond order	
	$q(S_0)$	$q(S_1)$	$C-OH$	$C=O$
1	1.764	1.707	S_0 0.302	0.821
2	0.806	0.885	S_1 0.332	0.731
3	1.115	1.112		
4	0.880	1.081		
5	0.947	1.078		
6	1.103	0.986		
7	0.908	0.950		
8	1.147	1.192		
9	0.913	0.868		
10	1.114	0.978		
11	0.955	0.957		
12	1.915	1.862		
13	1.408	1.288		
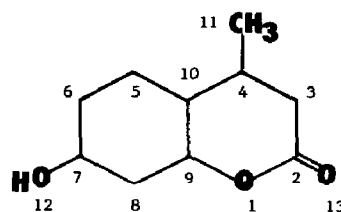
method for the ground (S_0) and excited (S_1) states of 7-hydroxy-4-methylcoumarin, and these are shown in Table 3. It can be seen that light absorption results mainly in a locally excited (LE) $S_1(\pi\pi^*)$ state. Although the entire electron system is involved in the excitation, no major charge transfer between different molecular subunits is observed as would be the case in electron donor–acceptor molecules [13]. This accounts for the absence of spectral shifts on changing the solvent polarity. Based on molecular structure, it is expected that light absorption should result in an $S_1(\pi\pi^*)$ state with some long-lived $n\pi^*$ character which facilitates energy dissipation by non-radiative transitions, particularly in an aprotic solvent where a low ϕ_f

value and a fast rate constant k_{nr} are obtained (Table 1). Moreover, decreasing the $n\pi^*$ contribution of the S_1 state by specific hydrogen-bonding interactions (including the possibility of hydrogen-bonding complex formation) exerted by an alcohol should result in an enhanced ϕ_f value and a slowing down of the rate of non-radiative energy dissipation. Our results (Table 1) are consistent with this idea; the ϕ_f value increases markedly with increasing hydrogen-bond donor ability of the solvents. Furthermore, no noticeable increase in the fluorescence quantum yield of an ethanol solution of 7-hydroxy-4-methylcoumarin is observed on lowering the temperature to 77 K, a situation where all dynamic motions (including proton transfer) are expected to be frozen and thereby the ϕ_f value should approach unity. This result eliminates the possibility of energy dissipation via a free rotor mechanism [14].

From the discussion above it seems reasonable to conclude that optical pumping should result in the population of an LE S_1 state with a long-lived $n\pi^*$ nature which plays a key role in the characterization of the photophysical properties of 7-hydroxy-4-methylcoumarin in aprotic solvents and alcohols. Moreover, the viscosity-independent behaviour of the ϕ_f value indicates the insignificant role of torsional motions of 7-hydroxy-4-methylcoumarin in the deactivation process.

3.2. Excited state interactions

Excited state complex formation involving intermolecular hydrogen bonding may be the cause of the observed enhancement of the fluorescence quantum yield in alcoholic solvents. A steady growth of the fluorescence intensity of 7-hydroxy-4-methylcoumarin in ethyl acetate solution is observed (Fig. 2) on addition of increasing amounts of methanol which diminish the $n\pi^*$ character of the S_1 state by specific interactions with the available n electrons; thus the rate of non-radiative energy dissipation is significantly slowed down and the ϕ_f value is enhanced. This provides evidence for an excited state complex equilibrium

$$m \ \text{Dye}^* + n \ \text{CH}_3\text{OH} \rightleftharpoons (m \ \text{Dye}{:}n \ \text{HOCH}_3)^*$$
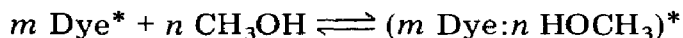
Similar suggestions have been reported in the literature [2, 3, 5, 6, 15]. It has also been assumed that in alcoholic solutions of some hydroxy dyes of related structure, the proton transfer barrier is very large, leading to emission from the neutral (normal) form of the dye molecules [6, 15].

A much more pronounced spectral shift is observed in the case of water–methanol mixed solvents. In methanol, simultaneous with the quenching of the fluorescence of 7-hydroxy-4-methylcoumarin (I) by added water, a new broad multiple peak emission band emerges in the long wavelength region (Fig. 3). A sharp isoemissive point appears at 420 nm, indicating a very fast equilibrium established between different polar prototropic complex species in the S_1 state. The most widely accepted mechanism for explaining such an observation is the existence of an ultrafast intramolecular proton transfer process via pre-existing water–dye
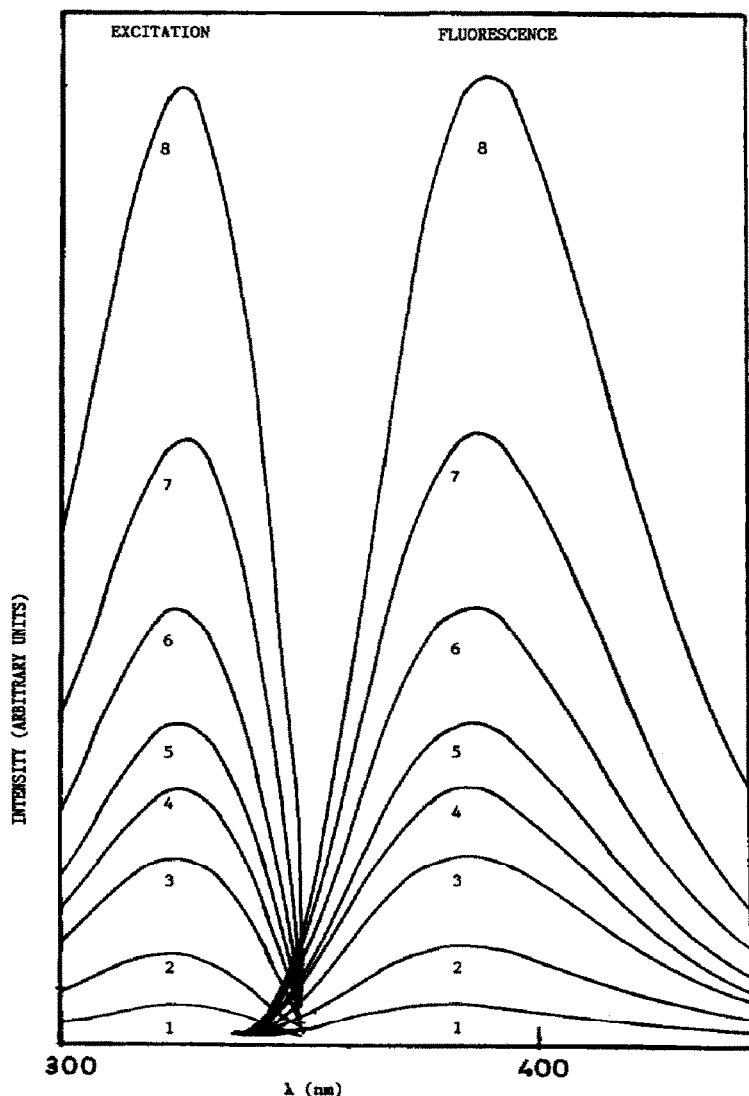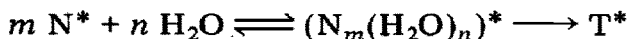
Fig. 2. Growth of fluorescence intensity on addition of methanol (spectra 2 - 8) to the ethyl acetate solution of 7-hydroxy-4-methylcoumarin (spectrum 1).

complex in the S_1 state leading to tautomer formation. The overall excited state proton transfer process can be represented as

$$m \, N^* + n \, H_2O \rightleftharpoons (N_m(H_2O)_n)^* \longrightarrow T^*$$

where N is the normal isomer ($\lambda_f = 380$ nm) and T is the tautomer (having a multiple fluorescence band at a longer wavelength) which can be represented as
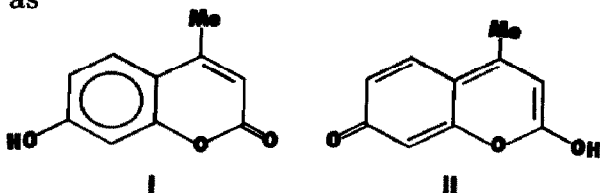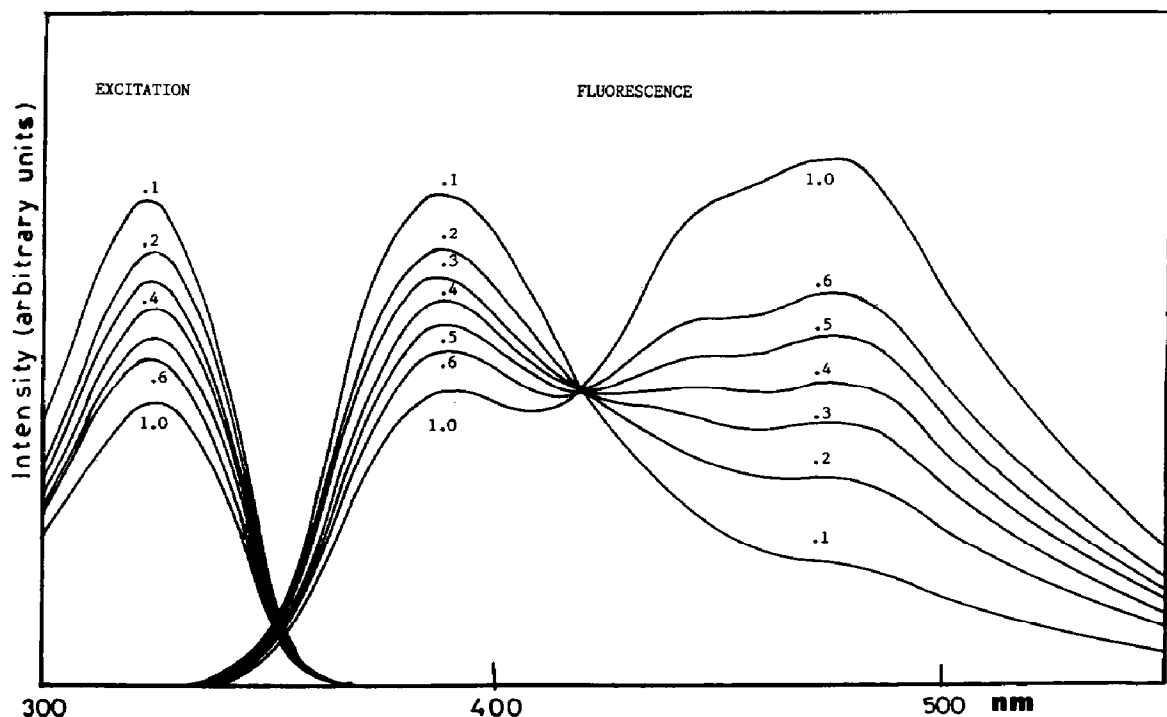
Fig. 3. Fluorescence spectrum of a solution of 7-hydroxy-4-methylcoumarin in methanol–water mixed solvent (water content in millilitre per ten millilitres of solution). Dye concentration = 3×10^{-5} M; temperature = 25 °C.
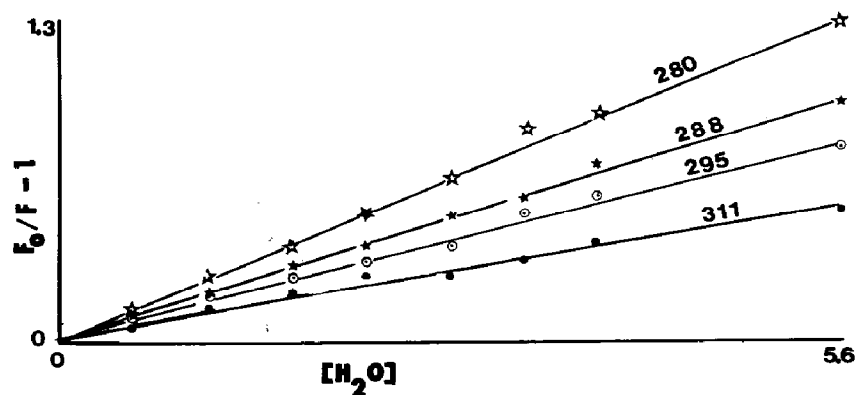

Fig. 4. Least-squares Stern–Volmer plots for the quenching of 7-hydroxy-4-methylcoumarin fluorescence F_0 by added water (molar concentration) at various temperatures (K).

The determination of the fluorescence quenching rate constant (the observed Stern–Volmer quenching constant) as a function of temperature (Fig. 4) yields a value for the enthalpy ΔH_f of dye–water complex formation involving very fast proton transfer according to the equation [10]

$$\ln K_{SV} = -\Delta H_f / RT + \text{constant}$$

Fig. 5. Least-squares plot of ln K_{SV} vs. $1/T$ for 7-hydroxy-4-methylcoumarin–water complex system.

Thus a plot of ln K_{SV} vs. $1/T$ should yield a straight line (Fig. 5) with a slope from which ΔH_f can be obtained. The least-squares treatment of our data yields a value of about -5.6 kcal mol^{-1} for ΔH_f, indicating an attractive (associative) S_1 state.

From the ΔH_f value and using the fluorescence maxima of the free and the complex species we estimated the enthalpy of formation $\Delta H_f(FC)$ of the Frank–Condon ground state species formed by radiative or non-radiative decay of the dye–water complex according to the frequently used equation [10]

$$h\nu(\text{free}) = h\nu(\text{complex}) + \Delta H_f(\text{complex}) + \Delta H_f(FC)$$

(All values are in kilocalories per mole). We obtained a positive value of about 10 kcal mol^{-1} for $\Delta H_f(FC)$, indicating a dissociative (repulsive) ground state. These results immediately suggest that such dye–water solutions can be exploited profitably as a successful dye laser system in the blue–green region [2, 3].

More quantitative data of the presumed excited state equilibrium need to be obtained. We recorded the fluorescence spectrum of 7-hydroxy-4-methylcoumarin as a function of water concentration (Fig. 3) at several temperatures. We calculated the equilibrium constant K of complex formation by analysing the experimental data at 480 nm using a simplified equilibrium relation

$$K[\text{H}_2\text{O}]^n = I_f$$

where n is the number of water molecules involved in the complex and I_f is the fluorescence intensity due to complex formation. Excellent linear least-squares plots of log I_f vs. log[H$_2$O] were obtained (with a correlation coefficient of 0.997). An example is shown in Fig. 6. From the intercept and the slope of such linear plots the values of K and n can be calculated. The data are collected in Table 4. The thermodynamic parameters of complex
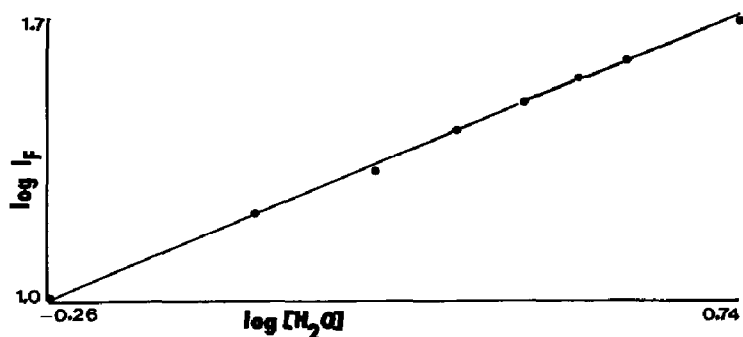
Fig. 6. Least-squares log–log plot of the fluorescence intensity of the excited state 7-hydroxy-4-methylcoumarin–water complex *vs.* water concentration (M).

TABLE 4

Thermodynamic data for the excited state reaction $m \ \mathrm{Dye}^* + n \ \mathrm{H_2O} \rightleftharpoons (m \ \mathrm{Dye} \cdots n \ \mathrm{H_2O})^* \rightarrow \mathrm{T}^*$

Temperature (°C)	K (l mol^{-1})	n	ΔH (kcal mol^{-1})	ΔS (kcal mol^{-1})
38	13	0.66		
32	14	0.66		
27	15	0.66		
22	16	0.63	≈ -2.1	≈ -0.02
15	18	0.57		
7	19	0.57		

Dye, 7-hydroxy-4-methylcoumarin.
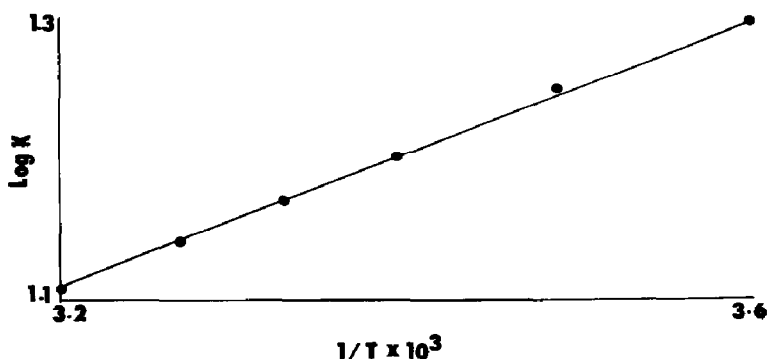T* is the tautomer formed by excited state intramolecular proton transfer via dye–water complex.

Fig. 7. Least-squares Arrhenius plot for the excited state equilibrium $m \ \mathrm{Dye}^* + n \ \mathrm{H_2O} \rightleftharpoons (\mathrm{Dye}^*)_m (\mathrm{H_2O})_n \rightarrow \mathrm{T}^*$ (see text).

formation (the enthalpy and entropy) were obtained (Table 4) by least-squares analysis of the $\log K$ vs. $1/T$ plot (Fig. 7) according to the linear relation

$$\log K = - \frac{\Delta H_f}{2.303RT} + \frac{\Delta S_f}{2.303R}$$

The n value obtained is about 0.66, giving rise to a stoichiometry of two molecules of water for three molecules of 7-hydroxy-4-methylcoumarin. The results of Table 4 indicate that the complexes formed are weak. The numerical values of the thermodynamic parameters are comparable with those values reported in the literature for other excited state complexes involving the formation of hydrogen bonds [12].

We also calculated the K and n values for methanol interaction with 7-hydroxy-4-methylcoumarin in ethyl acetate at 27 °C following the same treatment as above. In this case $n = 1.2$, giving rise to an approximate stoichiometry of five molecules of 7-hydroxy-4-methylcoumarin for six molecules of methanol. Moreover, a weaker complex is formed; $K = 2.0\ M^{-1}$.

Finally, it is worth mentioning that the dynamics of the excited state intramolecular proton transfer process $(N^* \rightarrow T^*)$ are a subtle function of the nature of the solvent. However, it can reasonably be concluded that the barrier height of such a dynamic process depends on the relative strength of the pre-formed dye–solvent excited state complex; the stronger the interactions, the smaller the proton transfer barrier height.

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