

INFLUENCE OF SOLVENTS AND TEMPERATURE ON THE EXCITED STATE CHARACTERISTICS OF COUMARIN LASER DYES

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(Received in revised form 1 March 1990)

The present work deals with the effect of solvents and temperature on the photophysical properties of 4-methyl-7-aminocoumarin (I), and 4-methyl-7-dimethylaminocoumarin (II). Change of solvent gives rise to Stokes' shift but due to specific interactions, the excited state dipole moments cannot be calculated. Experimental values of percentage polarization in different polar solvents indicate the formation of 1:1 solute-solvent exciplexes/intermolecular hydrogen bonding. Further, it is observed that the fluorescence intensity decreases with increase in temperature for the compound II, but remains constant for compound I. This difference in behaviour is examined in terms of intramolecular charge transfer (ICT) and twisted intramolecular charge transfer (TICT) states of the coumarin molecule.

1. Introduction

A large number of coumarin derivatives are used as laser dyes [1-3]. The lasing wavelengths (usually broad bands) for the coumarins lie in the spectral region from ~ 440 nm to 540 nm. The choice of the solvent depends on the nature of the coumarin and in many cases it is found that ethanol serves the purpose well, though other solvents are also used. The selection of proper solvent depends on the knowledge of the effect of solvents on the spectral properties of the lasing dye. It is known that the fluorescence emission depends critically both on the pattern of substitution and the nature of the solvent used [4]. To some extent it is possible to understand the effect of a single substituent, but when two or more substituents are present, the task becomes quite difficult. The magnitude of spectral changes due to substituents/solvents is linked to the structure of the molecule and serves as a useful tool for its study. In this paper we examine the behaviour of the excited states of two commonly used coumarins in lasers, viz: 4-methyl-7-aminocoumarin (Compound I) and 4-methyl-7-dimethylaminocoumarin (Compound II).

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2. Experimental

The coumarin compounds investigated were obtained from Sigma Chemical Co. The absorption spectra were obtained with a Shimadzu-260, UV-VIS recording spectrophotometer and the fluorescence spectra using an Aminco-Bowman spectrophotofluorometer. The concentration of the solute was always kept low $\sim 10^{-6}$ M to avoid aggregation and to minimize inner filter effect. The temperature dependence of fluorescence intensity was measured from 20°C to 80°C with temperature variations maintained within $\pm 2^\circ$ C. The values of the degree of fluorescence polarization and radiative lifetime were obtained using methods described in our earlier papers [5,6].

For each compound the relative values of quantum yields in different solvents were estimated using the absorption and emission curves. These values have not been normalized against any standard value.

The recorded fluorescence emission wavelengths are accurate within ± 2 nm and the absorption wavelengths within ± 1 nm. The polarization values, when the intensity of fluorescence is moderately good are correct to 10% but in case of weak fluorescence the errors are larger 15% to 20%. The values of relative quantum yields and radiative lifetimes are correct to 10%.

3. Results and discussion

The observed values of absorption maximum $\bar{\nu}_a$ (corresponding to the absorption band at the longest wavelengths), fluorescence maximum $\bar{\nu}_f$, half band width of the absorption band σ , and the calculated values of absorptivity coefficient ϵ_m , radiative lifetime τ_0 , relative quantum yield q and percentage polarization of fluorescence p , for 4-methyl-7-aminocoumarin (I), 4-methyl-7-dimethylaminocoumarin (II) are listed in Tables I and II.

i. Absorption and emission maxima

The longest absorption and the fluorescence emission wavelengths maxima shift to the longer wavelength side on increasing the solvent polarity. The bathochromic shift is observed for both the compounds investigated. These changes are in conformity with the fact that the transitions involved are $\pi \rightarrow \pi^*$.

ii. Radiative lifetimes

The values of τ_0 are calculated using methods described earlier [5,6]. These values correspond to the ideal situation of quantum yield equal to unity, i.e. the probabilities of emission and absorption being exactly the same. It can be seen from Tables I and II that τ_0 is slightly higher in polar solvents as compared to the nonpolar solvents.

Table I
 Calculated values of bandwidth (σ), extinction coefficient (ϵ_m), radiative lifetime (τ_0), relative quantum yield (q) and percentage polarization (p) along with the values of absorption ($\bar{\nu}_a$) and fluorescence ($\bar{\nu}_f$) wavelenghts maxima for 4-methyl-7-aminocoumarin

Solvent	Absorption max. $\bar{\nu}_a$ ($\times 10^{-2} \text{ cm}^{-1}$)	Half band width σ ($\times 10^{-2} \text{ cm}^{-1}$)	Absorptivity coeff. ϵ_m ($\times 10^{-2} \text{ M}^{-1} \text{ cm}^{-1}$)	Fluorescence max. $\bar{\nu}_f$ ($\times 10^{-2} \text{ cm}^{-1}$)	Relative quantum yield q	Radiative lifetime τ_0 (ns)	Percentage polarization p
Cyclohexane	299	28	129	248	0.57	3.0	2.0
Hexane	301	31	133	247	0.44	2.7	4.6
Heptane	300	28	148	249	0.38	2.7	2.6
Benzene	298	26	159	251	0.36	2.4	1.9
Toluene	299	25	141	250	0.76	2.8	2.7
Dioxane	294	25	156	246	0.53	2.9	4.7
Chloroform	296	24	137	243	0.59	3.2	4.6
Dichloromethane	297	25	155	239	0.36	2.8	4.5
Methanol	285	27	159	229	0.52	3.2	2.8
Ethanol	282	26	149	230	0.56	3.4	3.5
n-propanol	284	26	141	231	0.57	3.4	4.5
n-butanol	282	26	127	233	0.85	3.8	5.3
Water	292	28	129	224	0.66	3.6	2.1
Formamide	285	27	128	227	0.48	3.3	3.7

Table II
 Calculated values of bandwidth (σ), extinction coefficient (ϵ_m), radiative lifetime (τ_0), relative quantum yield (q) and percentage polarization (p) along with the values of absorption (ν_a) and fluorescence ($\bar{\nu}_f$) wavelengths maxima for 4-methyl-7-dimethylaminocoumarin

Solvent	Absorption max. ν_a ($\times 10^{-2} \text{cm}^{-1}$)	Half band width σ ($\times 10^{-2} \text{cm}^{-1}$)	Absorptivity coeff. ϵ_m ($\times 10^{-2} \text{M}^{-1} \text{cm}^{-1}$)	Fluorescence max. $\bar{\nu}_f$ ($\times 10^{-2} \text{cm}^{-1}$)	Relative quantum yield q	Radiative lifetime τ_0 (ns)	Percentage polarization p
Cyclohexane	288	19	331	251	0.65	1.9	4.0
Benzene	282	22	325	240	0.83	1.9	2.4
Dioxane	280	23	283	233	0.62	1.9	4.7
Chloroform	275	26	267	235	0.41	1.7	4.2
Dichloromethane	275	23	319	235	0.54	1.7	4.4
Methanol	271	24	280	217	0.40	2.2	3.6
Ethanol	271	26	240	220	0.51	2.3	4.6
n-propanol	271	24	308	220	0.72	1.8	5.7
n-butanol	271	25	245	220	0.56	2.2	6.9
Water	269	27	216	207	0.82	2.6	2.8

iii. Excited state dipole moment

Solvetochromic analysis is generally used for estimating the excited state dipole moment of the fluorescing molecules [7-9]. According to Lippert's theory [10], a plot of $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_1(D, n)$ is linear, where $F_1(D, n)$ is:

$$F_1(D, n) = \left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right] \frac{2n^2+1}{n^2+2}. \quad (1)$$

The slope of this graph gives the excited state dipole moment of the molecule. These plots, for the compounds investigated are shown in Fig. 1 and it can be noted that they are not quite as expected from the Lippert's theory. As the points corresponding to alcoholic solvents show larger deviations it can be inferred that these deviations are caused by intermolecular hydrogen bonding.

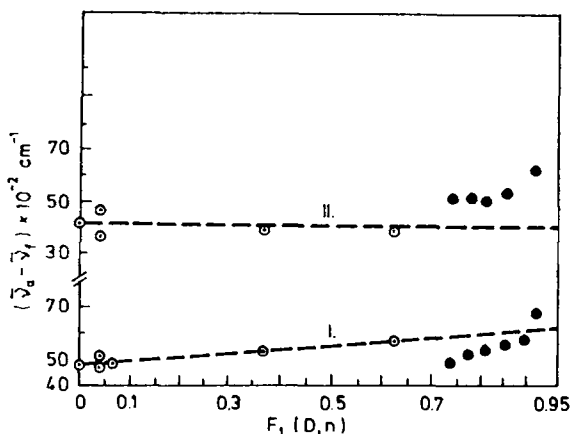


Fig. 1. Plot of Stokes' shift versus $F_1(D, n)$

A further amino/dimethylamino group at position 7 provides an additional nonradiative decay path due to the twisting/rotation of these groups. This takes place through possible transition from an intramolecular charge transfer (ICT) excited state to a nonfluorescent twisted intramolecular charge transfer state (TICT). Due to these perturbations, the excited state dipole moments cannot be obtained using the Stokes' shift data.

iv. Temperature dependence of fluorescence yield

Fig. 2 shows the variation of fluorescence intensity F/F_0 with temperature for the aqueous solutions of the compounds I and II. As there was no noticeable change

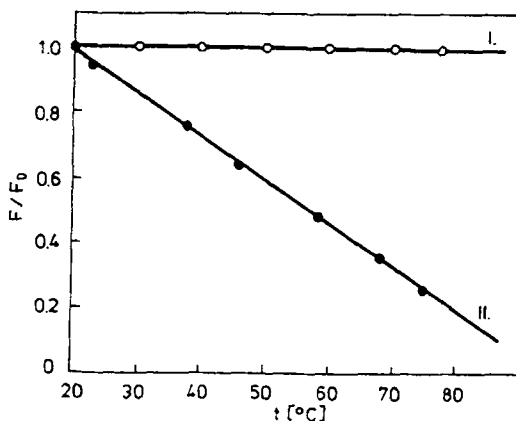
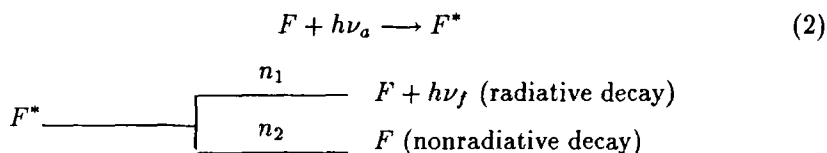


Fig. 2. The effect of temperature on fluorescence intensity of Compounds I and II

in the shape of the emission band with temperature, the fluorescence emission at different temperatures is compared by measurement of the heights of band maxima. It can be seen from Fig. 2 that with increase in temperature the fluorescence intensity decreases in case of compound II but remains almost constant in case of compound I. The kinetic scheme for the fluorescence quenching in the absence of an external quencher can be written as:



where F and F^* represent the fluorophore in the ground and excited states and n_1 and n_2 are the radiative and nonradiative transition probabilities. The lifetime τ_f of the excited molecule at t °C is given by:

$$\tau_f(t) = \frac{1}{\eta_1 + \eta_2(t)}, \quad (3)$$

where it is assumed that over a small range of temperature (20 °C–80 °C), n_1 is independent of temperature. τ_f can be estimated using the following relation:

$$\tau_f(t) = \tau_f(20) \frac{q_0(t)}{q_0(20)}, \quad (4)$$

where $\tau_f(20)$, $\tau_f(t)$, $q_0(t)$ and $q_0(20)$ are the lifetimes and the quantum yields at 20 °C and t °C. As there is no change in optical density corresponding to the longest absorption wavelengths with temperature, the values of fluorescence intensities are used in Eq. (4) instead of quantum yield. The variation of lifetime of the excited molecule with temperature is calculated using relation (4). The values of $\tau_f(t)$ decrease linearly with temperature for compounds II but there is no change in case of compound I. As there is no shift in the fluorescence wavelength upon raising the temperature, it can be assumed that the fluorescing state is not altered on heating.

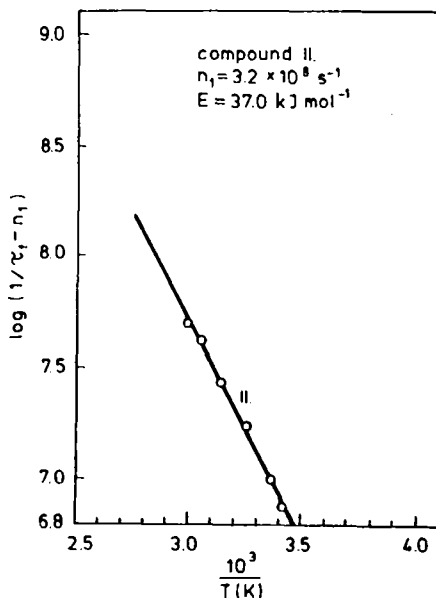


Fig. 3. $\text{Log}(\frac{1}{\tau_f} - n_1)$ versus $\frac{1}{T}$ for the aqueous solutions of compound II

If there is one dominant radiationless deactivation process, the temperature dependence of lifetime can be expressed as:

$$\frac{1}{\tau_f(t)} - n_1 = n_2(t) = n^0 \exp(-E/RT), \quad (5)$$

where E is the activation energy for the deactivation process. By numerical fitting a value of n_1 is determined which gives a linear plot between $\text{log}[\frac{1}{\tau_f(t)} - n_1]$ vs $\frac{1}{T}$. Such a plot for compound II is shown in Fig. 3. The slope of this line gives the value of E . As there is no change in fluorescence intensity with temperature for compound I, the value of E is zero for it. The value of E obtained for compound II is 37.0 kJmol⁻¹. This value is comparable to the value of E obtained for other 4 methyl coumarin

derivatives earlier viz. 4-methyl-7-methoxy coumarin; $E = 34.3 \text{ kJmol}^{-1}$ [11] and 4-methyl-7-ethoxy coumarin $E = 32.5 \text{ kJmol}^{-1}$ [12].

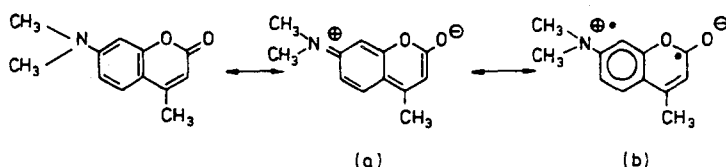


Fig. 4. Possible resonance structures of 4-methyl-7-dimethylaminocoumarin (a) intramolecular charge transfer (ICT) (b) twisted intramolecular charge transfer (TICT)

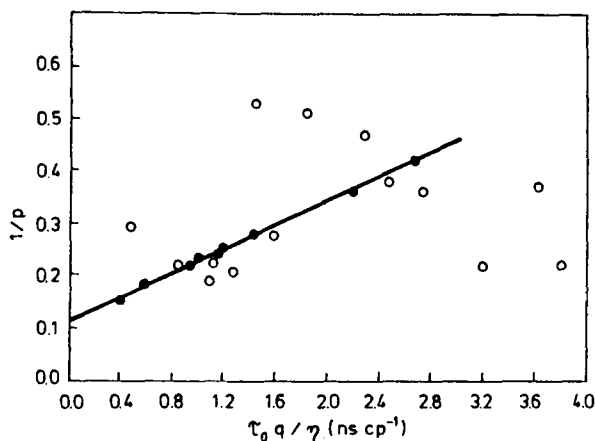


Fig. 5. Plot of $\tau_0 q / \eta$ versus $1/p$ for 4-methyl-7-aminocoumarin (○) and for 4-methyl-7-dimethylaminocoumarin (●)

It is thus clear that with increase in temperature, the radiationless deactivation of the excited state increases. This could be explained in terms of the ICT-TICT model of substituted coumarins [13-14]. According to this model fluorescence emission takes place from either a planar excited molecule or from an intramolecular charge transfer state in which the molecule could be planar (ICT) or twisted (TICT). In the present case the substituent group at position 7 is capable of rotatory motion and provides an additional non-radiative decay mode. The rotary decay mode is sensitive to structural and solvent influences. An excited coumarin molecule in solution can exist in two states with different conformations (Fig. 4): a planar excited molecule or a planar intramolecular charge transfer (ICT) excited state and possibly a nonfluorescent twisted charge transfer (TICT) state arising due to the rotation of the attached functional group at position 7. The steep temperature dependence (Fig. 2) of intensity on temperature of compounds II can be

accounted for in terms of a transition from ICT to TICT state. In some cases the molecule in the TICT state may be still fluorescent with little or no reduction in fluorescence intensity. In such cases fluorescence will be observed even after a substantial rise in temperature. Probably the fluorescence observed in case of compound I, which in fact is highly fluorescent in polar as well as nonpolar solvent, belongs to this category.

v. Fluorescence polarization

The Perrin relation [15] gives a correlation between polarization, rotational relaxation and the excited state lifetime of a molecule. It is obvious from Table I and Table II that the observed variations in polarization cannot be accounted for as merely viscosity effect. In fact polarization shows an anomalous effect in a sense that the value of p increases with lowering solvent viscosity and a graph between $1/p$ and $1/\eta$ is not linear as expected from Perrin's relation. It is clear that the fluorescence lifetime τ_f in Perrin's relation cannot be taken as constant and it is necessary to take into consideration its variations due to viscosity and/or polarity of the solvent by way of K_{nr} — nonradiative transitions. To account for these variations we have replaced τ_f by the observed values τ_{0q} and plotted graphs between $1/p$ and τ_{0q}/η . These graphs are shown in Fig. 5. It is seen that while for compound II the plot is fairly linear, the points corresponding to compound I show a large scatter. It is therefore necessary that other processes which influence polarization should be examined. One such process which seems important is the formation of solvent-solute exciplexes through hydrogen bonding particularly in polar solvents. The exciplexes so formed will have their own characteristic values of p_0 (intrinsic polarization), $\tau_f = \tau_{0q}$ (fluorescence lifetime) and V_0 (molecular volume). The extent and strength of hydrogen bonding would, of course, be different for different solvents. But in every case, whenever hydrogen bonding takes place, the effective molecular volume of the bonded complex molecule will be larger. It is not possible to calculate exactly the molecular volume of the hydrogen bonded molecule but a good approximation would be to assume that with higher molecular weight of the solvent the effective size would be larger. These changes in volume may not be linearly dependent on the molecular weight. Fig. 6 shows plots p versus molecular weight M of the solvents for both the compounds I and II. It can be noticed that while the points corresponding to polar solvents lie on a straight line, other points corresponding nonpolar solvents show large deviations from it. This correlation of p with molecular weight seems quite interesting and, if it is not completely accidental, reflects an important aspect of the solute-solvent interaction. This points to an obvious conclusion that the compounds I and II form 1:1 solute-solvent exciplexes in polar solvents. Earlier a similar behaviour of 4-methyl-7-hydroxycoumarin in polar solvents was reported [16]. These exciplexes are certainly due to intermolecular hydrogen bonding and are formed due to the OH/NH₂ group at position 7.

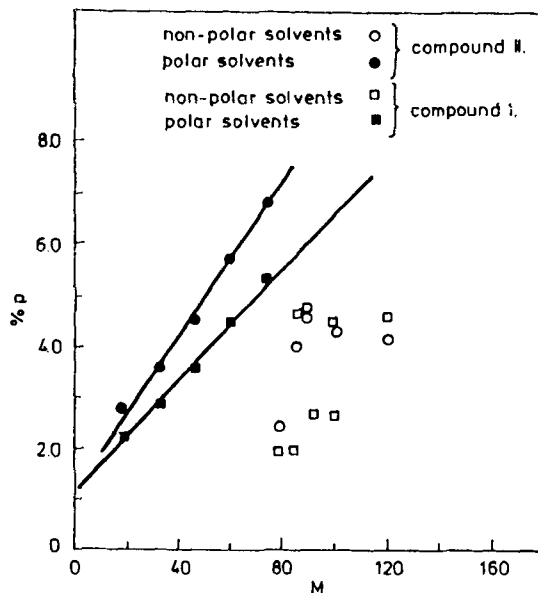


Fig. 6. Plots of $p\%$ versus molecular weight (M) of the solvents for 4-methyl coumarins

4. Conclusions

The present investigation thus shows that:

1. The increase in solvent polarity causes a bathochromic shift for the longest absorption band maximum as well as for the fluorescence peak for both compounds.
2. The Stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) versus $F_1(D, n)$ is not linear. The deviation is large for polar solvents indicating the possibility of hydrogen bonding. Excited state dipole moments cannot be determined using the solvatochromic theories.
3. Effect of temperature indicates that the fluorescence of these coumarin solutions arises from two states in which the conformation is not the same. The decrease in fluorescence intensity with rise in temperature for compounds II arises due to a transition ICT \rightarrow TICT.
4. The variation of percentage polarization in different solvents also indicates hydrogen bonding or formation of solute-solvent exciplexes.

Acknowledgements

We are grateful to the Council of Scientific and Industrial Research, New Delhi, for financial assistance and Senior Research Fellowship to RG. We are also thankful to Prof. V. V. S. Murti for helpful discussions.

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