FLUORESCENCE CHARACTERISTICS OF 7,4-SUBSTITUTED COUMARINS

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ABSTRACT

The absorption and emission spectra of six coumarin compounds are reported in a few typical polar solvents. The effect of solvent on the positions and intensity of the absorption and emission maxima is explained. It is found that the 4-phenyl substituent increases the dissipation of the excitation energy through non-radiative process. In solvents like water and formamide, exciplexes are formed which give rise to fluorescence emission in the longer wavelength region. Effects of change of substituent, in either 7-position or 4-position, on fluorescence emission are compared.

INTRODUCTION

A LARGE number of coumarins occur as natural products and have also been synthesized. Many of them are intensely fluorescent and possess physiological activity. Because of their analytical and biological importance, the study of the fluorescence properties of coumarins has assumed importance[1-3]. Further, substituents in different positions in coumarins cause significant changes in fluorescence[4,5]. Recently, the fluorescence properties of coumarins with various substituents have been used to study the charge transfer and twisted intra-molecular charge transfer (TICT) processes[4]. Solvent-solute interaction also affects the fluorescence of the solute molecule. The study of fluorescence in different solvents, therefore, provides a method for getting information about the solute molecule in the excited state. With a view to studying the effect of substituents and solvents on the fluorescence of coumarins, compounds with three different substituents viz hydroxy, acetoxy and methoxy-group in 7-position and each of these substituents in combination with 4-methyl and 4-phenyl groups have been selected for the present investigation.

EXPERIMENTAL

The electronic absorption spectra were recorded with Shimadzu UV – visible recording spectrophotometer and the fluorescence emission spectra with an Aminco-Bowman spectrophotofluorometer, at room temperature (25° ± 2°C). The fluorescence spectra have been corrected for the nonlinear response of the detector photomultiplier tube (IP-21) and the non-uniform emission of the excitation source—the Xenon lamp. The recorded emission wavelengths were accurate within ±2 nm and the absorption maxima within ±1 nm.

The coumarins used for the present study were synthesized according to literature methods[6] and were checked for purity by m.p. and TLC. Double-distilled water and AR grade solvents were used for preparation of the solutions. The purity of the solvents was checked by absorption studies for any possible contamination. The effect of scattering by solvents was checked by performing blank experiments and necessary corrections were applied. The concentration of the compounds in solution was kept quite low (~ 10^{-6} to 10^{-5} g/cc) to minimize the effect of self-absorption. The relative quantum yields of fluorescence were estimated from the areas under the respective emission spectra and by noting the relative absorption at the excitation wavelengths. The structures of coumarins studied are shown in figure 1.

RESULTS AND DISCUSSION

Table 1 lists the absorption and fluorescence band maxima in different polar solvents (dipole moments increasing from left to right). It is obvious that the solvent-solute interaction perturbs both the ground

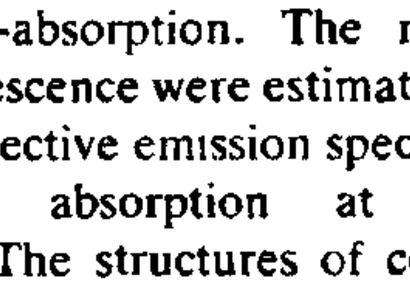

Figure 1. 7,4-Substituted coumarins. I. $R_1 = OH$ and $R_2 = CH_3$. II. $R_1 = OH$ and $R_2 = C_6H_5$. III. $R_1 = CH_3COO$ and $R_2 = CH_3$. IV. $R_1 = CH_3COO$ and $R_2 = C_6H_5$. V. $R_1 = OCH_3$ and $R_2 = CH_3$. VI. $R_1 = OCH_3$ and $R_2 = C_6H_5$.

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Table 1 *Absorbance and fluorescence emission maxima (nm) of the coumarins.*

Coumarin		Dioxane	Propanol	Butanol	Ethanol	Methanol	Acetone	Water	Formamide
I	λ_{ab}	321	324	325	324	323	327	322	325
	λ_{em}	380	388	388	387	389	388	451	452
II	λ_{ab}	326	332	333	330	329	330	331	334
	λ_{em}	ND	ND	391(W)	395(W) 508(W)	392(W)	ND	507	508
III	λ_{ab}	315	313	313	321	311	320	310	317
	λ_{em}	379	381	384	386	388	385	378(W) 450	454
IV	λ_{ab}	318	320	320	320	318	329	317	333
	λ_{em}	ND	ND	ND	ND	ND	ND	506	512
V	λ_{ab}	319	320	322	320	320	328	321	322
	λ_{em}	379	381	382	382	382	384	386	386
VI	λ_{ab}	324	328	327	327	326	329	329	331
	λ_{em}	ND	ND	390	388(W)	394(W)	ND	391	403

W – Relatively weak, ND – No detectable fluorescence.

as well as the excited state of the molecule. But the interaction seems to have a more pronounced effect on the excited state as the change in solvent causes a larger shift of the fluorescence peak (maximum shift ~ 120 nm) as compared to the shift of the absorption peak (~ 16 nm). Fluorescence bands reported in table 1, fall in two different regions: (i) in the wavelength region at ~ 390 nm (say normal fluorescence F_N) and (ii) in the longer wavelength region between 450 and 512 nm, (say anomalous fluorescence F_A). Normal fluorescence is emitted by coumarins I, II and III in all the solvents except water and formamide. While coumarins V and VI give only normal fluorescence, coumarin IV shows no emission in F_N region. Anomalous fluorescence is obtained from the solutions of coumarins I, II, III and IV in water and formamide. Coumarin II in ethanol and coumarin III in water exhibit dual fluorescence in the regions F_N and F_A.

The non-specific solute-solvent nteraction is usually treated by considering the solvent as a continuous dielectric media[7,8] and is evaluated in terms of the coupling between the dipole moment of the solute to the reaction field created by it in the solvent. This further gives a method for determining the excited state dipole moment of the solute molecule in terms of the solvent-induced spectral shifts. A perusal of the normal fluorescence, in the present case, shows that the solvent-induced spectral shifts are quite small and hence one can conclude that dipole moment of the solute molecule in the excited state S_1 is not much different from the S_0 state. A small difference in the dipole moments in the S_1 and S_0 states can arise due to intramolecular charge transfer in the excited state ($S_0 \rightarrow S_1 \rightarrow S_{ICT}$). The energy of the S_{ICT} state would depend on the polarity of the surrounding solvent and hence fluorescence emission $S_{ICT} \rightarrow S_0$ in different solvents would show the type of variation as observed.

As far as the anomalous fluorescence is concerned, it could be attributed to a variety of causes viz solute-solvent exciplexes-hydrogen bonding, twisted intramolecular charge transfer (TICT), excimers, isomerization, protonation etc[10-19]. In the present case, anomalous fluorescence is essentially obtained in water and formamide. It is known that these two solvents can give rise to strong hydrogen bonding and hence it is likely that the anomalous fluorescence is emitted by the hydrogen bonded species. This is also in agreement with the fact that coumarins V and VI do not give rise to anomalous fluorescence as the methoxy group is less amicable to form hydrogen bonds. Coumarin II in ethanol and coumarin III in water exist in two different forms, with and without hydrogen bonding, and hence give rise to two fluorescence peaks.

The normal fluorescence from coumarins II, IV and VI which have a phenyl group in position 4, is weak and even absent in some solvents. It appears that the 4-phenyl group facilitates the process of non-radiative transfer of excitation energy. The phenyl group is linked to the rest of the molecule with a comparatively weak bond which impairs its

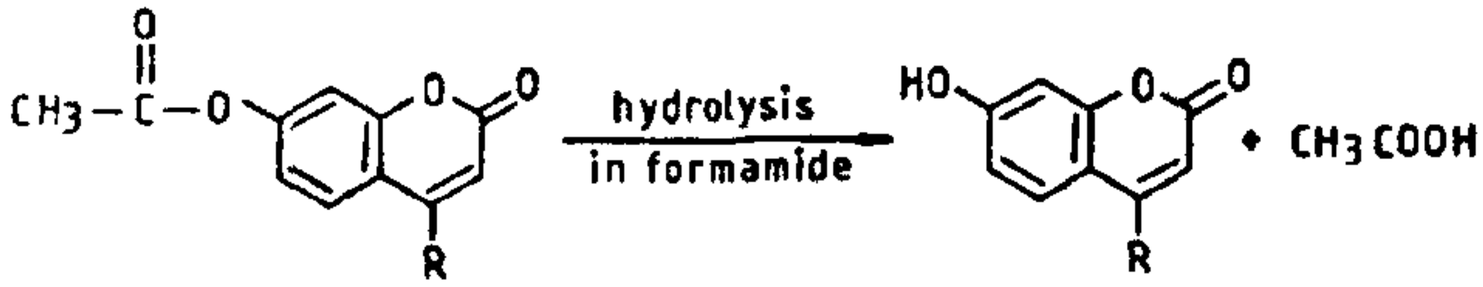

Figure 2. Hydrolysis of 7-acetoxy coumarins.

rigidity. Rigidity is an important criterion for fluorescence emission[20]. When the molecule is excited, a part of the excitation energy may find its way to the phenyl group and twist it out of plane rendering the molecule less fluorescent/non-fluorescent as observed. However, these coumarins with 4-phenyl group, possibly due to hydrogen bonding which has a stabilizing effect on the excited state, give rise to fluorescence in the longer wavelength region in water and formamide. But it is observed that the quantum yield of fluorescence of 4-phenyl derivative is less than that of the 4-methyl derivative. This too indicates the role of phenyl substituent in dissipating the excitation energy.

The long wavelength fluorescence of 7-acetoxy-4-methyl coumarin in formamide at ~ 454 nm shows many-fold increase in intensity with time which attains a stable maximum value after a lapse of about 20 hr or so. A similar but less pronounced increase in intensity of F_A is observed in the case of 7-acetoxy-4-phenyl coumarin in formamide. In both these cases the absorption also goes on increasing with time but the positions of absorption and emission maxima remain unchanged. A possible explanation for this could be a slow hydrolysis of 7-acetoxy coumarin to 7-hydroxy coumarin (figure 2) which emits at the same wavelength with a higher quantum yield.

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