

# Effect of Solvents and Substituents on the Fluorescence Behaviour of Coumarin Dye Lasers

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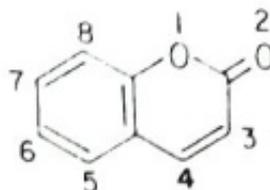
*In order to investigate the effect of solvents and substituents on the fluorescence behaviour of coumarin derivatives the absorption and fluorescence emission spectra of 4-phenyl substituted coumarins namely: 4-phenyl-7-hydroxy coumarin (1), 4-phenyl-7-methoxy coumarin (2), 4-phenyl-6-hydroxy-7-methoxy coumarin (3), 4-phenyl-6,7-dimethoxy coumarin (4) and 4-phenyl-6,7-dihydroxy coumarin (5) have been studied in various organic solvents of varying dipole moment. It was found that in a given solvent the position of the absorption and fluorescence maxima depends on the nature and position of the additional substituent group linked to the 4-phenyl coumarin and the wavelengths shifts obtained are interpreted in terms of the changes in the mobility of  $\pi$  electrons. From the fluorescence emission spectra of the present coumarins it was found that the 4-phenyl coumarins are less fluorescent and show a smaller change in polarity on excitation as compared to the corresponding 3-phenyl derivatives. These changes are interpreted in terms of the possible resonance structures of the coumarin derivatives.*

**Keywords:** Fluorescence, Dipole moment, Resonance structures.

## 1. INTRODUCTION

Coumarin derivatives occur in nature as plant products and most of them have been synthesized. Many of these coumarins have been used as dye lasers [1] owing to their remarkable characteristics in terms of tunability and conversion efficiency. These compounds also show a large Stokes shift and consequent small overlap between the absorption and emission spectra. The effects of the environment (solvent) on photophysical characteristics of coumarins have been investigated with steady state and time resolved spectroscopy [2,3]. The coumarin derivatives are an important structural unit for probes widely used in monitoring the polarity and micro-viscosity of the environment in various simple, mixed or ionic solvents. These studies are also useful in the characterization of materials prepared by sol-gel processes, and of nano-particles such as silica and silver. Coumarin derivatives are widely studied due to their importance as non linear optical chromophores and as excellent probe to studying solvation dynamics in the homogeneous solutions as well as organized media along with variety of numerous applications [4-9].

In the present work we investigated the change in the absorption and fluorescence spectra of 4-phenyl coumarins due to the substitution of methoxy or hydroxy group at 6 and/or 7 positions in various organic solvents. Further, in order to study the effect of position of phenyl group we have compared the spectral data of 4-phenyl-7-methoxy coumarin and 3-phenyl-7-methoxy coumarin in various solvents. The structures of coumarin derivatives studied are shown in Figure 1. The experimental procedure in the present studies is as given in our earlier paper [6].



**Fig. 1:** Coumarin 4=phenyl, 7=hydroxy; (2) 4= phenyl, 7=methoxy; (3) 4= phenyl, 6=hydroxy, 7= methoxy; (4) 4= phenyl, 6 and 7-methoxy; (5) 4=phenyl, 6 and 7= hydroxy.

## 2. RESULTS AND DISCUSSION

Table 1 summarizes the values of absorption and fluorescence band maxima in different solvents. It is evident from the wavelength data listed for various coumarin derivatives that solute–solvent interaction alters both the ground and excited states. The wavelength shift in fluorescence maxima is greater than the absorption maxima. It indicates that solute-solvent interaction is more pronounced in the excited state than the ground state.

**Table 1:** Absorption ( $\lambda_a$ ) and fluorescence emission ( $\lambda_f$ ) wavelength maxima in nano meter (nm) for 4-phenyl substituted coumarins in different organic solvents.

Solvent	Coumarin-1		Coumarin-2		Coumarin-3		Coumarin-4		Coumarin-5	
	$\lambda_a$ (nm)	$\lambda_f$ (nm)								
Dioxane	326	ND	324	ND	345	465	350	470	-----	-----
Ethanol	330	395(W) 508(W)	327	388	353	482	357	473	366	505
n-propanol	332	ND	328	ND	352	478	353	477	363	495
n-butanol	333	391(W)	327	390	351	475	345	470	362	501
Water	331	507	329	391	365	503	348	484	-----	-----

ND- fluorescence not detected.

Let us bifurcate our discussion in the following ways:

**(a) Substituent Effect:**

(i) Disubstituted Coumarin: On comparing the data of wavelength of absorption maxima and emission maxima as given in Table 1, it is observed that :

$\lambda_a$  and  $\lambda_f$  for 4-Ph-7-OH coumarin (1)  $>$   $\lambda_a$  and  $\lambda_f$  for 4-Ph-7-CH<sub>3</sub>O coumarin (2)

The above observed shifts in  $\lambda_a$  and  $\lambda_f$  apparently indicate the change in the mobility of the  $\pi$  electrons due to different variety of substituents. It is a well known fact that the substituent which enhance electron mobility, shift the wavelength maxima towards the longer side and vice-versa. Further, in case of 4-Ph-7-CH<sub>3</sub>O coumarin (2), the lone pairs of oxygen at 7-methoxy group is shielded due to electron positive tendency of hydrogen atom, which in turn contribute towards the decrease of the mobility of  $\pi$  electrons on the benzene ring. However, in case of 4-Ph-7-OH coumarin (1), in OH group at position 7, oxygen atom is attached only to the hydrogen atom, which in turn negate such kind of shielding. Thus in this case the mobility of  $\pi$  electron will be quite higher than 4-Ph-7-CH<sub>3</sub>O coumarin (2) with the result that the wavelength maxima values of 4-Ph-7-OH coumarin (1) will be greater than the corresponding spectral values of 4-Ph-7-CH<sub>3</sub>O coumarin (2).

(ii) Trisubstituted Coumarin: The effects of poly-substitution are really very complicated as the overall effect on the  $\pi$  electrons mobility produced by different substituents must be taken in to consideration.

From Table 1:  $\lambda_a$  and  $\lambda_f$  for 4-Ph-6-OH-7-CH<sub>3</sub>O coumarin (3)  $>$   $\lambda_a$  and  $\lambda_f$  for 4-Ph-6,7-(CH<sub>3</sub>O)<sub>2</sub> coumarin (4) except absorption wavelength maxima in dioxane and ethanol. And  $\lambda_a$  and  $\lambda_f$  for 4-Ph-6,7-(OH)<sub>2</sub> coumarin (5)  $>$   $\lambda_a$  and  $\lambda_f$  for 4-Ph-6,7-(CH<sub>3</sub>O)<sub>2</sub> coumarin (4).

The above mentioned results can also be explained exactly on the similar line as of the disubstituted coumarin derivatives. When a methoxy group in 4-Ph-6,7-(CH<sub>3</sub>O)<sub>2</sub> coumarin (4) present at position 6, is replaced by a -OH group i.e. 4-Ph-6-OH-7-CH<sub>3</sub>O coumarin (3),  $\pi$  electron mobility of the later has to be more which causes bathochromic shift. If both the methoxy group of 4-Ph-6,7-(CH<sub>3</sub>O)<sub>2</sub> coumarin (4) are replaced by two -OH groups i.e. 4-Ph-6,7-(OH)<sub>2</sub> coumarin (5), it further causes a shift in the wavelength data towards the longer side. Therefore it is inferred that methoxy group when present at position 6 or 7 or at both will reduce mobility of  $\pi$ -electrons in the benzene ring of coumarin molecule. On the other hand -OH group at the same position or positions that enhance the mobility of  $\pi$ -electrons leads to the bathochromic shift. It also appears that the small shifts in absorption and emission wavelengths are due to intramolecular charge transfer, however, large shifts in emission wavelengths maxima may be due to intermolecular hydrogen bonding or molecular complex formation.

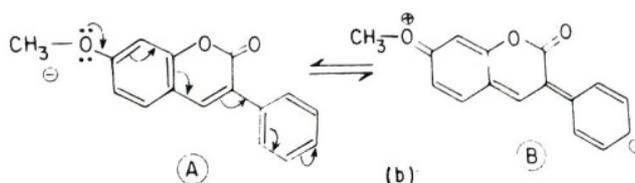
**(b) Solvent Effect:** In general, the non-specific solute-solvent interaction is described the solvent as the continuous dielectric media [10] and is evaluated in terms of the coupling between the dipole moment of the solute to the reaction field produced by it in

the solvent. This provides a method for calculating the change in the dipole moment of the solute molecule upon excitation using solvatochromic data [6].

In the present case we find that only in the case of compound (2) the graphs between  $(v_a - v_f)$  vs  $F_1(D, n)$  and  $\frac{1}{2}(v_a + v_f)$  vs  $F_2(D, n)$  are linear and hence the value of  $\mu^*/\mu$  can be calculated following the method described in our earlier paper [6]. In case of other coumarin derivatives 1,3,4 and 5 it was checked that no linear relation exists between  $(v_a - v_f)$  vs  $F_1(D, n)$  and  $\frac{1}{2}(v_a + v_f)$  vs  $F_2(D, n)$  and hence the values of excited state dipole moment of such coumarin derivatives could not be calculated. These studies indicate that if substituent groups are present at two consecutive positions, the present solvatochromic method fails to give any information about the quantitative value of the excited state dipole moment. In the present case, compound 3,4 and 5 have substituents at consecutive positions 6 and 7 and the present tool fails to give the value of dipole moment in the excited state. These findings are also in conformity with our earlier studies [11].

The ratio of the excited state dipole to the ground state dipole moment calculated for 4-phenyl-7-methoxy coumarin (2) is 3.0 and the corresponding value for 3-phenyl-7-methoxy coumarin is 3.4 [6]. The higher value of excited state dipole moment of 3-phenyl-7-methoxy coumarin than 4-phenyl-7-methoxy coumarin is quite possible from the structure of these coumarins. Unlike 4-phenyl-7-methoxy coumarin (2) phenyl ring in 3-phenyl-7-methoxy coumarin is in conjugation with the methoxy group present at position 7 which results in a large intramolecular charge transfer (ICT) in the excited state. It therefore renders 3-phenyl-7-methoxy coumarin more polar in the excited state in comparison to the ground state.

We have also observed that the fluorescence of 4-phenyl-7-methoxy coumarin (2) is very weak than the 3-phenyl-7-methoxy coumarin and even in some solvents it is non-fluorescent. It appears that phenyl substituent at position 4 facilitates the process of non-radiative transfer of excitation energy.



**Fig. 2:** Resonance structure of 3-Ph-7-methoxy coumarin.

From possible resonance structures of 4-Ph-7-methoxy coumarin and 3-Ph-7-methoxy coumarin (Figure 2) it appears that phenyl ring at position 4 is attached to the rest of the coumarin molecule with a relatively single weaker bond as compared to a double bond for phenyl group at position 3, and thus deduces its rigidity significantly. It is an established fact that the rigidity of the molecule plays an important role in its fluorescence behaviour [10]. On excitation of 4-Ph-7-methoxy coumarin a part of the excitation energy may get non-radiatively dissipated in twisting the phenyl ring out of

plane and making the molecule less fluorescent. On the other hand, as stated above, phenyl ring in 3-Ph-7-methoxy coumarin is more rigidly bonded, the probability of its getting out of plane is less and hence it is more fluorescent than 4-Ph-7-methoxy coumarin.

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