incidence than landslide size. The size of established landslides seems more closely related to the history and current condition of the landslide system than to external stimuli.

Slope aspect and the depth of regolith, rather than true soil, rank with a number of more obvious significant differences between rockfall-like and slump-like landslide types. 'Rockfalls' are found on higher, cooler, roadcuts with less obvious, apparent rock dip towards the road-bed. Slumps are found on warmer, wetter, sites with steeper apparent dips, lower roadcuts and greater depths of beneath-topsoil regolith.

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RESEARCH COMMUNICATIONS

Estimation of excited state dipole moment of substituted coumarins

R. Giri and M. M. Bajaj

Department of Physics and Astrophysics, University of Delhi, Delhi 110 007, India

Coumarins are important constituents of natural products. Many of them exhibit fluorescence. We report UV-absorption and fluorescence emission spectra of 4-methyl-5,7-diethoxycoumarin, 4-methyl-5-ethoxy-7-methoxycoumarin and 4-methyl-7,8-diethoxycoumarin in different polar and nonpolar organic solvents. We estimated the change in dipole moment upon excitation using solvatochromic data, and interpret the increase in excited state dipole moment in terms of the possible resonance structure. This method cannot be used when substituent groups are present at two consecutive positions because of the specific interaction and hindrance occurring in such cases.

THE widespread occurrence of coumarin derivatives in nature and their variety of applications, viz. as fluorescent indicators[1,2], fluorescent whiteners in detergent products[3], sunburn preventives[4], as laser dyes[5-7], for the estimation of enzymes[8], for studying biological systems[9] and also in other interesting areas[10], have given impetus to the study of their fluorescence characteristics.

Coumarin molecule as such in aqueous solution is non-fluorescent but it becomes moderately/highly fluorescent on substituting various groups at different positions in it. In general, fluorescence characteristics of a fluorophore depend upon the position and the nature of the substituent as well as the nature of the surrounding medium[11,12]. The magnitude of spectral changes due to substituents/solvents is linked to the structural aspects of the molecule and serve as useful tool for its detail investigations. Up to some extent it is easy to study the spectral characteristics of single substituted coumarin, however, when substituents are present at two or more positions, the study becomes quite complicated. In the present work we have investigated the effect of solvent and substituent on absorption and fluorescence spectra of the coumarin derivatives, and solvatochromic data so obtained is used in estimating their excited state dipole moments.

The coumarins used were prepared by standard

methods[13] and checked for purity by m.p. and TLC according to the literature values. The absorption spectra were recorded using a UV-vis recording spectrophotometer (Shimadzu-260) and the fluorescence spectra using a spectrophotofluorometer (Aminco-Bowman). In order to avoid aggregation and to minimize inner filter effect, the concentration of the solute was kept quite low $\sim 10^{-6}$ M. The recorded absorption wavelengths are accurate within ± 1 nm and fluorescence wavelengths within ± 2 nm.

Solvents are found useful to determine the values of quantum yield, polarization, radiative lifetime, excited state dipole moment and solute–solvent interactions[14,15]. In the present study we have estimated the change in dipole moment of 4-methyl-5,7-diethoxycoumarin (I), 4-methyl-5-ethoxy-7-methoxycoumarin (II) and 4-methyl-7,8-diethoxycoumarin (III) upon excitation, using solvatochromic data. To calculate the excited state dipole moment, the following mathematical equations were used[14].

$$(\bar{v}_a - \bar{v}_f) = S_1 F_1(D,n) + C_1 \tag{1}$$

according to Bakshiev, and

$$1/2(\bar{v}_a + \bar{v}_f) = S_2 F_2(D,n) + C_2 \tag{2}$$

according to Chamma and Viallet. The expression for $F_1(D,n)$ and $F_2(D,n)$ are given as

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

$$F_2(D,n) = \frac{2n^2+1}{2(n^2+2)}\left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right] \frac{3}{2}\frac{n^4-1}{(n^2+2)^2},$$

where $\bar{v}_a$ and $\bar{v}_f$ are absorption and fluorescence frequencies in per cm respectively, μ^* and μ are permanent dipole moments in excited and ground states, a the Onsager cavity radius, D the dielectric constant and n the refractive index of the solvent.

From the above equations it follows that $(\bar{v}_a - \bar{v}_f)$ versus $F_1(D,n)$ and $1/2(\bar{v}_a + \bar{v}_f)$ versus $F_2(D,n)$ should give linear graphs with slopes S_1 and S_2, where

$$S_1 = \frac{2(\mu^* - \mu)^2}{h\,Ca^3} \tag{3}$$

and

$$S_2 = \frac{-2(\mu^{*2} - \mu^2)}{h\,Ca^3} \tag{4}$$

Table 1. Solvatochromic shift data of 4-methyl-5,7-diethoxycoumarin (I), 4-methyl-5-ethoxy-7-methoxycoumarin (II) and of 4-methyl-7,8-diethoxycoumarin (III) along with the calculated values of $F_1(D,n)$ and $F_2(D,n)$

Solvent	$\bar{v}_a$ ($\times 10^{-2}$ cm^{-1})	$\bar{v}_f$ ($\times 10^{-2}$ cm^{-1})	$(\bar{v}_a - \bar{v}_f)$ ($\times 10^{-2}$ cm^{-1})	$1/2(\bar{v}_a + \bar{v}_f)$ ($\times 10^{-2}$ cm^{-1})	$F_1(D,n)$	$F_2(D,n)$
Benzene	313	256	57	285	0.005	0.34
	314	260	54	287		
	–	–	–	–		
Methanol	313	240	73	277	0.85	0.66
	314	244	70	279		
	–	–	–	–		
n-Butanol	312	245	67	279	0.74	0.65
	312	245	67	279		
	315	220	95	268		
n-Propanol	311	245	66	278	0.78	0.51
	–	–	–	–		
	313	220	93	267		
Ethanol	310	244	66	277	0.81	0.65
	313	244	69	279		
	314	215	99	265		
Water	310	229	81	270	0.91	0.68
	312	228	84	270		
	314	198	116	256		
Formamide	311	239	72	275	0.89	0.75
	–	–	–	–		
	–	–	–	–		
Dioxane	–			–	0.04	0.31
	315	251	64	283		
	312	–	–	–		
Chloroform	–	–	–	–	0.37	0.49
	314	256	58	285		
	313	229	84	271		

Data given in the first line are for 4-methyl-5,7-diethoxycoumarin, in the second line for 4-methyl-5-ethoxy-7-methoxycoumarin and in the third line for 4-methyl-7,8-diethoxycoumarin

From equations (3) and (4) it follows that the ratio of the excited state and ground state dipole moments is given by

$$\frac{\mu^*}{\mu} = \frac{|S_1 - S_2|}{|S_1 + S_2|} \qquad (5)$$

Table 1 summarizes the band shift data for I, II and III coumarins respectively, along with the calculated values of various solvents. For coumarins I and II graphs for $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_1(D,n)$ and $1/2(\bar{\nu}_a + \bar{\nu}_f)$ versus $F_2(D,n)$ give good linear plots within the limit of experimental errors (Figures 1 and 2). But for coumarin III graphs are not linear (Figure 3). Taking the slopes of the graphs given in Figures 1 and 2 along with the equation (5) it is obtained that: For 4-methyl-5, 7-diethoxycoumarin (I) $\mu^* = 4.3\,\mu$ and for 4-methyl-5-ethoxy-7-methoxycoumarin (II) $\mu^* = 5.0\,\mu$.

Small scattering in the points (Figures 1 and 2) occurs due to approximations made in the present solvatochromic theories. The increase in the values of dipole moment for I and II coumarins upon excitation may happen due to their possible resonance structures (Figures 4 and 5), which suggests higher polarity in the excited state. Further, replacing a ethoxy group at position 7 of 4-methyl-5, 7-diethoxycoumarin by a methoxy group, an increase in the μ^* value is obtained. It suggests that the excited state of 4-methyl-5-ethoxy-7-methoxycoumarin in more polar than 4-methyl-5,7-diethoxycoumarin. It is also seen that the calculated value of μ^* for 4-methyl-5-ethoxy-7-metho-
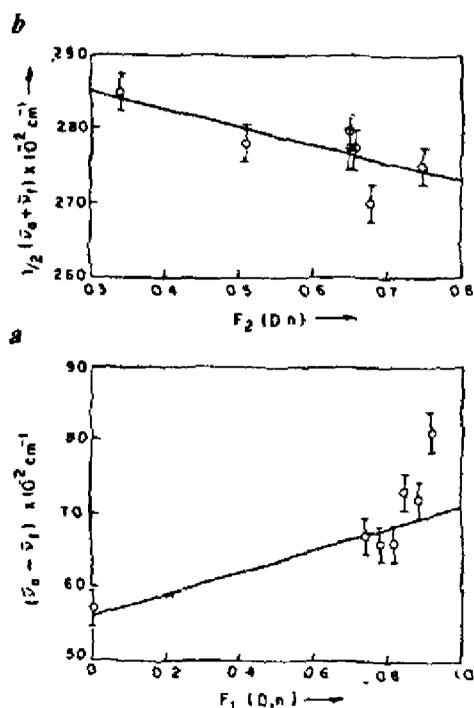

Figure 2. *a*, Stokes' shift $(\bar{\nu}_a - \bar{\nu}_f)$ versus F_1 (D,n) for 4-methyl-5-ethoxy-7-methoxycoumarin. *b*, $1/2(\bar{\nu}_a + \bar{\nu}_f)$ versus $F_2(D,n)$ for 4-methyl-5-ethoxy-7-methoxycoumarin.

Figure 1. *a*, Stokes' $(\bar{\nu}_a - \bar{\nu}_f)$ versus F_1 (D,n) for 4-methyl-5,7-diethoxycoumarin. *b*, $1/2(\bar{\nu}_a + \bar{\nu}_f)$ versus $F_2(D,n)$ for 4-methyl-5,7-diethoxycoumarin.
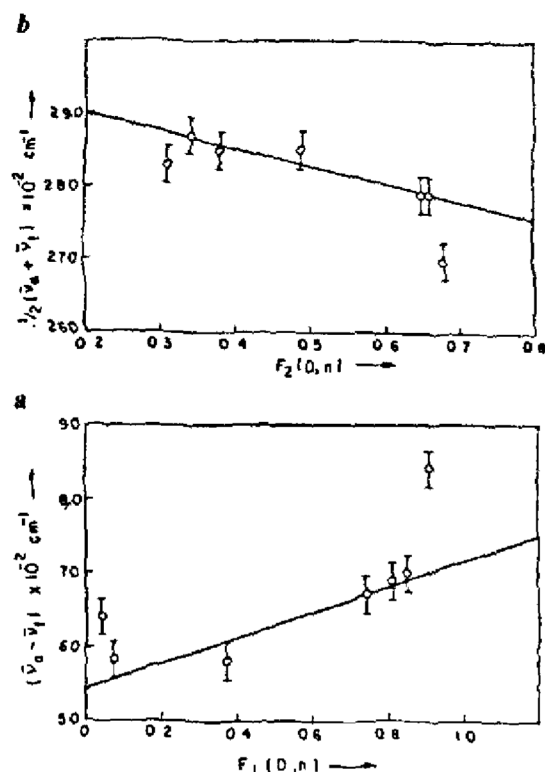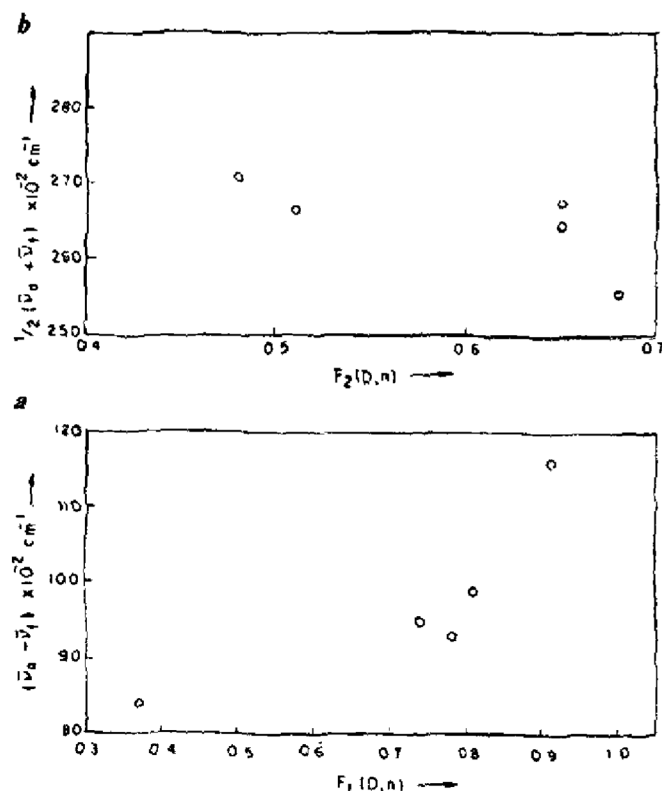
Figure 3. Stokes' shift $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_1(D,n)$ for 4-methyl-7,8-diethoxycoumarin. *b*, $1/2(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_2(D,n)$ for 4-methyl-7,8-diethoxycoumarin.
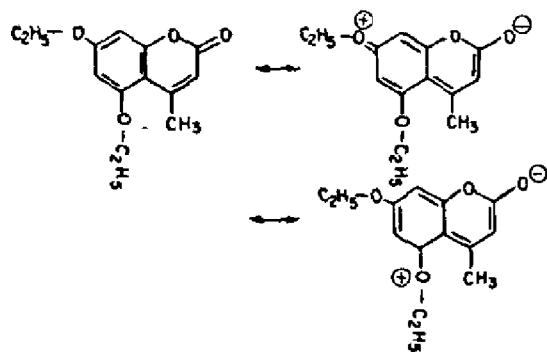
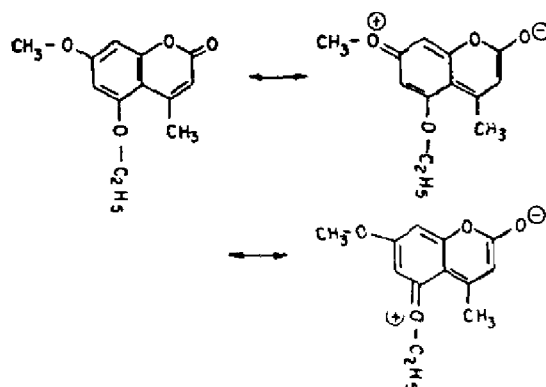**Figure 4.** Resonance spectra of 4-methyl-5,7-diethoxycoumarin (I).

Figure 5. Resonance spectra of 4-methyl-5-ethoxy-7-methoxy-coumarin (II)

xycoumarin is more than the value of 4-methyl-7-methoxycoumarin[15].

Let us consider the data and graphs of coumarin III, it is clear that the wavelength shift plots are not straight lines (Figure 3). Therefore we could not calculate the change in dipole moment of 4-methyl-7, 8-diethoxycoumarin with the help of present solvatochromic methods. It appears as solute–solvent interaction and steric hindrance effects take place due to the substituents present at two adjacent positions. We had also observed the same problem in determining the excited state dipole moment of 4-methyl-6, 7-dimethoxycoumarin in an earlier work[15].

Further, solvatochromic data can be used to identify the spectra, viz. $\pi \to \pi^*$, $n \to \pi^*$, etc. It is noticed from the Table 1 that, with increase in the polarity of the solvent, the fluorescence emission peak undergoes a bathochromic shift, confirming a $\pi \to \pi^*$ transition. The shift of the fluorescence wavelengths towards longer wavelengths could be caused if the excited state charge distribution in the solute is markedly different from the ground state charge distribution and is such as to give rise to a stronger interaction with polar solvents in the excited state.

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Monsoon effect on isotopic composition of atmospheric carbon dioxide

S. K. Bhattacharya and R. A. Jani

Physical Research Laboratory, Navrangpura, Ahmedabad 380 009, India

The Indian subcontinent and the adjoining seas (the Arabian Sea and the Bay of Bengal) experience seasonal reversal of wind systems and associated weather changes resulting from summer and winter monsoons. The monsoons are associated with significant changes in the oceanic and continental -biosphere and are therefore expected to have considerable effect on the content and isotopic composition of atmospheric carbon dioxide. We have attempted to measure this effect in ground-level carbon dioxide samples collected in the city of Ahmedabad during 1990. The CO_2 content is in general agreement with values obtained elsewhere. The $\delta^{13}C$ value of air CO_2 shows a minor effect due to the increase of productivity on land during the southwest monsoon season. The $\delta^{18}O$ value of CO_2 is slightly enriched compared to northern high-latitude values owing to the equilibration of CO_2 with enriched leaf water expected in a tropical country like India.

The southwest monsoon brings a dramatic change in the climatic regime operating on the Indian subcontinent