

SHORT COMMUNICATIONS

SOLVENT DEPENDENCE OF THE ABSORPTION AND FLUORESCENCE SPECTRA OF 4-METHYL-5, 7-DIETHOXY COUMARIN

R. GIRI, S. S. RATHI, V. V. S. MURTI and M. K. MACHWE

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

THE present communication which is a continuation of our earlier work on polysubstituted coumarins^{1,2} discusses the effect of solvents on absorption and fluorescence spectra, quantum yield, natural lifetime and polarization of 4-methyl-5, 7-diethoxy coumarin.

The coumarin derivative under investigation was synthesized adopting standard methods³. The fluorescence and absorption spectra in different solvents were recorded at room temperature ($20 \pm 2^\circ\text{C}$) using spectrofluorometer (Aminco-Bowman) and UV-visible recording spectrometer (Shimadzu-260) respectively. The concentration of the compound in solution was kept low $\sim 1.4 \times 10^{-5}$ M to minimize the effect of self-absorption. Fluorescence polarization was obtained adopting the method described earlier⁴. The relative quantum yield was calculated in terms of the area under the fluorescence curve and the optical density of the solution for the excitation wavelength. When the intensity of fluorescence emission is moderately good, the polarization values are correct to $\pm 10\%$, but during weak emission the errors are larger ($\pm 10-15\%$). The natural lifetime has been calculated using the formula⁵:

$$\frac{1}{\tau_0} = 5.11 \times 10^{-9} n^2 \bar{\nu}_a^2 \sigma \epsilon_m \quad (1)$$

where n is the refractive index of the medium surrounding the solute, $\bar{\nu}_a$ is the absorption maxima in cm^{-1} , σ the half-band width in cm^{-1} and ϵ_m the extinction coefficient in $\text{M}^{-1} \text{cm}^{-1}$ at the absorption maxima.

The results compiled in table 1 summarize the experimental values of absorption and fluorescence maxima, percentage polarization, extinction coefficient, relative quantum yield and natural lifetime for 4-methyl-5, 7-diethoxy coumarin.

It is clear from table 1 that this coumarin deriva-

tive is highly fluorescent in polar solvents. In non-polar solvents like cyclohexane, benzene, toluene, dioxane, etc there is weak fluorescence. The polarity-induced interaction of the solvent with the solute molecule perturbs the energy levels of the solute molecule. The lack of fluorescence in solvents of low polarity can be explained in terms of the El-Sayed selection rule⁶. In solvents of low polarity the lowest excited $\pi \rightarrow \pi^*$ triplet state lies close to the first excited $n \rightarrow \pi^*$ singlet state, thus allowing extensive inter-system crossing at the expense of fluorescence. But in polar solvents, the S_1 state appears to be $\pi \rightarrow \pi^*$ and its inter-system crossing efficiency to $\pi \rightarrow \pi^*$ triplet state being low, causes increased fluorescence intensity. The lowest-lying $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ levels are affected to different extents by the solvent polarity. The present observations indicate that the relative positions of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ levels are reversed by the effect of solvent polarity so that the long absorption wavelength becomes $\pi \rightarrow \pi^*$ instead of $n \rightarrow \pi^*$ in polar solvents. In polar solvents where the molecule fluoresces, it is observed that the fluorescence yield (q_f) depends on the nature of the solvent. It is maximum in water where it is almost five times the minimum value in iso-propanol. This could be due to inter-molecular hydrogen bonding although the extent of this effect is unpredictable. The fluorescence band maxima is at 408 nm in *n*-butanol/*n*-propanol but shifts to 437 nm in water.

Table 1 Absorbance and fluorescence emission maxima, extinction coefficient, natural lifetime (τ_0), relative quantum yield (q_f) and polarization (p) of 4-methyl-5, 7-diethoxy coumarin, in various solvents

Solvent	λ_a (nm)	$\epsilon_m \times 10^{-2}$ ($\text{M}^{-1} \text{cm}^{-1}$)	τ_0 (ns)	λ_f (nm)	q_f	% p
Cyclohexane	309	115	2.2	}	Weak fluorescence	
Carbon-tetrachloride	318	116	2.0			
Benzene	319	107	2.4			
Toluene	317	109	2.3			
Dioxane	313	107	2.4			
Methanol	222, 320	104	2.7	417	0.68	3.9
<i>n</i> -butanol	228, 321	106	2.5	408	0.35	6.8
<i>n</i> -propanol	213, 322	99	2.8	408	0.29	6.0
Ethanol	223, 320	99	2.7	410	0.44	5.1
Iso-propanol	320	109	2.6	404	0.17	5.8
Water 205,	323	92	2.7	437	0.83	4.5
Formamide	322	111	2.1	418	0.82	4.8

This large shift in λ_f , also indicates the occurrence of hydrogen bonding in the excited state of the molecule.

There are two prominent absorption bands: Band I at (309–323 nm) and the other one, band II at a shorter wavelength (205–228 nm). The absorption band II at (205–228 nm) is absent in non-polar solvents while it is quite intense in polar solvents. The presence of band II in polar solvents can be attributed to solvent-solute interaction in the ground state.

The natural lifetimes (τ_0) in different solvents, calculated using relation (1), are given in table 1. The value of τ_0 lies between 2 and 2.8 ns. The τ_0 value is slightly higher in polar solvents, viz. water and alcohols as compared to non-polar solvents like cyclohexane, toluene, etc. Further the fluorescence lifetime can be calculated using the relation⁷:

$$\tau_f = q_f \tau_0 \quad (2)$$

where q_f is the quantum yield of fluorescence.

The fluorescence polarization measurements give information about the changes in structure brought about by external factors, viz. solvent, substituents, pH, changes in temperature, etc. As discussed above τ_0 and q_f change with solvent and it can be seen that these changes agree with changes in polarization. This becomes evident from the fact that τ_f in conjunction with the Perrin's formula can explain satisfactorily the observed variation in polarization in different solvents. According to Perrin's relation⁷:

$$\left(\frac{1}{p} - \frac{1}{3}\right) = \left[\left(\frac{1}{p_0} - \frac{1}{3}\right)\right] \left[\frac{1 + RT\tau_0 q_f / \eta V_0}{1 + RT\tau_0 q_f / \eta V_0}\right] \quad (3)$$

Figure 1 shows the graph between $1/p$ vs $(\tau_0 q_f / \eta)$ where η is the viscosity of the solvent. This graph is

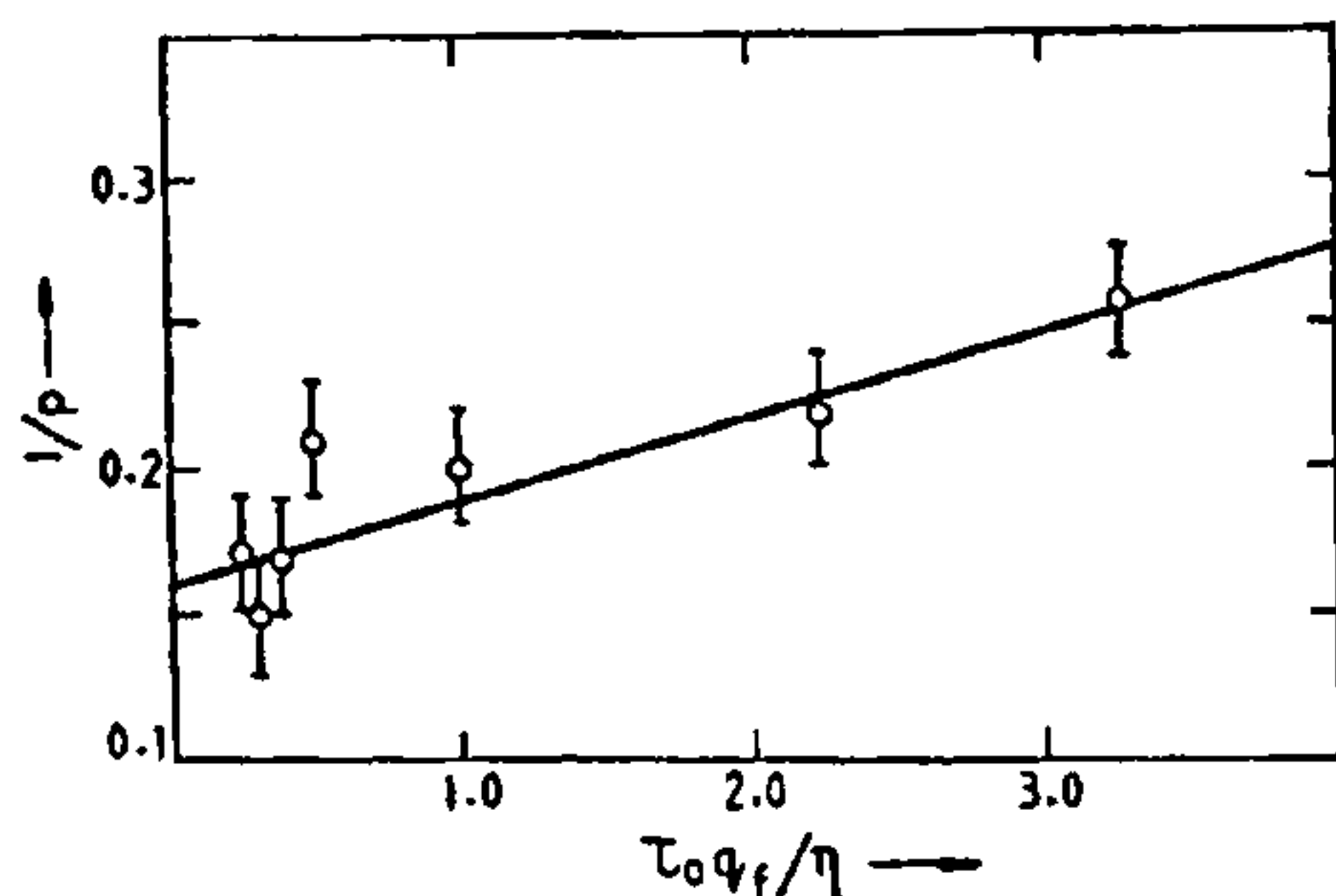


Figure 1. Plot of $1/p$ versus $\tau_0 q_f / \eta$.

linear and shows that fluorescence depolarization is essentially due to rotational relaxation of the molecule according to relation (3).

In the present study it has been shown that: (i) Absorption and fluorescence spectra of 4-methyl-5, 7-diethoxy coumarin depend on the polarity of the solvent. The fluorescence in non-polar solvents is weak; (ii) Fluorescence efficiency changes with solvent polarity; (iii) τ_0 is higher in polar solvents as compared to non-polar solvents; (iv) Fluorescence depolarization is due to rotational relaxation of the fluorescent molecule.

Financial support from CSIR, New Delhi, is gratefully acknowledged.

25 April 1988; Revised 5 September 1988

- Giri, R., Rathi, S. S., Machwe, M. K. and Murti, V. V. S., *Curr. Sci.*, 1987, 56, 1056.
- Giri, R., Rathi, S. S., Machwe, M. K. and Murti, V. V. S., *Spectrochim Acta*, 1988, A42, 805.
- Sethna, S. and Phadke, R., *Organic reactions*, (ed.) R. Adams, John Wiley, New York 1963, Vol. 7, p. 1.
- Pandya, M. L. and Machwe, M. K., *J. Chem. Phys.*, 1978, 68, 341.
- Weber, G. and Young, L. B., *J. Biol. Chem.*, 1964, 240, 1415.
- El-Sayed, M. A., *J. Chem. Phys.*, 1963, 38, 2834.
- Pasce, A. J., Rosen, C. G. and Pasby, T. L., *Fluorescence spectroscopy*, Marcel Dekker, New York, 1971.

OCCURRENCE OF LUPEOL IN *CALOTROPIS PROCERA* LATEX

RADHA PANT and KSHAMA CHATURVEDI
Chemistry Department, Allahabad Agricultural Institute,
Allahabad 211 007, India.

CALOTROPIS PROCERA latex has been extensively used in Indian medicine¹. On account of its irritant action on skin and the mucous membrane and due to the presence of cardioactive poisons, the latex has been employed as an arrow poison by the natives of Africa and Columbia². Several investigators³⁻⁸ have chemically analysed the latex and isolated a number of cardioactive glycosides.

The present communication describes the hitherto