

Experimentally Measured Rotational Reorientation Time of Coumarin 6 Laser Dye in Ethanol and Acetonitrile Solvents

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The photophysical properties of coumarin 6 laser dye have been studied in two solvents; ethanol and acetonitrile using steady-state fluorescence depolarization technique. The experimentally measured reorientation time of coumarin 6 is more or less the same in given solvents at particular temperature. It is found that coumarin 6 rotates slower in acetonitrile than in ethanol especially at higher values of viscosity over temperature. We also measure the ground and excited state dipole moments of coumarin 6 by solvent perturbation method. The results found that excited state dipole moment is greater than ground state dipole moment, which indicates that excited state is more polar than the ground state.

key words: Coumarin 6 laser dye, fluorescence polarization, rotational reorientation, anisotropy, dipole moment

INTRODUCTION

Solute-solvent interactions play a major role in determining the physicochemical properties of solution, yet our understanding of this subject is far from complete. Rotational diffusion studies of medium-sized molecules provide a useful means to probe these interactions [1]. Because of continuous interactions with their neighbors, molecules rotating in liquids experience friction. By modeling this friction using various continuum based theories one can get better insight into the nature of the solute-solvent interactions. The general approach is to measure the reorientation times of solute molecule in a liquid experimentally and model its rotation using the diffusion-based theories of Stokes-Einstein-Debye (SED) [2].

The first direct measurement of orientation relaxation of a large dye molecule in solution was made by Eisenthal and Drexhage in 1969 [3]. They used a picoseconds laser to excite the Rodhamine 590 laser dye (Rh6G) in ethylene glycol and probed the polarization of the absorbance as a function of time. In a subsequent paper Chuang and Eisenthal [4] studied Rh6G in various protic, polar solvents, notably linear alcohols and tested for the first time the validity of the hydrodynamic Stokes-Einstein-Debye (SED) theory on the reorientation dynamics of a dye molecule immersed in a continuous fluid [3].

The SED-theory treats the molecular rotation as a diffusive process and expresses the solute orientation relaxation time as a function of the macroscopic solvent properties, viscosity and temperature. In its original form, SED theory is expressed

by equation (1)

$$\tau_R^{SED} = \frac{\eta V}{k_B T} \quad (1)$$

Equation (1) is valid only for a spherical molecule, but it has been extended to axiosymmetrical ellipsoidal solutes [4] and also to account for different types of solute-solvent interactions.

Strong absorption cross-section and high fluorescence quantum yield of coumarin dyes make them excellent laser dyes for blue-green region [5,6]. Chemically, these dyes are the derivatives of 1,2-benzopyrone and display a number of unique properties like, very strong solvent properties, substantial changes in the dipole moments on photo excitation etc. These interesting properties have made the coumarin dyes are very useful probes in investigating a variety of physicochemical processes under different conditions. A few to mention are: studies on solvatochromic behaviors Jones et al [7], characterizations of microenvironments and their polarities [8], investigations of photo induced electron transfer processes [9] and estimations of the solvent relaxation times (τ_s) [10] etc. Biomedical applications of some of the coumarin derivatives have also been reported in literature. Studies on the interaction of 7-aminocoumarin dyes with human serum albumin using fluorescence techniques have been interesting research topics, as these dyes act as anti-blood-coagulant agent and the protein albumin blinds almost 90% of different drugs, including the anti-coagulants [11]. Some coumarin derivatives are also being their cholesterol and triglyceride lowering activity [12]. Coumarin doped 4,4'-di(N-carbazole) biphenyl (CBP) films have been used as organic semiconductor. Use of these films as a laser medium has shown to lower the laser threshold and thus extends the operational life of the lasers [13].

The present work deals with temperature-dependent

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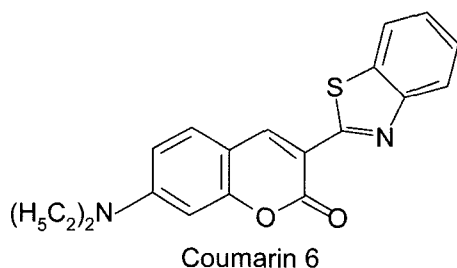


Figure 1. Molecular structure of coumarin 6

rotational diffusion studies of coumarin 6 in ethanol and acetonitrile solvents of different dielectric properties. The molecular structure of coumarin 6 is given in Figure 1. We also report the ground and excited state dipole moments of coumarin 6.

MATERIAL AND METHODS

Reorientation times of coumarin 6 are measured using steady-state depolarization method. The steady-state anisotropy $\langle r \rangle$ is related to experimentally measured intensities by the following equation

$$\langle r \rangle = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2GI_{\perp}} \quad (2)$$

where I_{\parallel} and I_{\perp} are the polarized fluorescence intensities parallel and perpendicular with respect to the excitation radiation respectively. G is an instrumental factor which corrects for the polarization bias in the detection system and is obtained by measuring the fluorescence intensity by keeping the excitation polarizer horizontal, the emission polarizer vertical I_{HV} and keeping the fluorescence intensity both the polarizer horizontal I_{HH} and taking the ratio

$$G = \frac{I_{HV}}{I_{HH}} \quad (3)$$

Reorientation times can be obtained from the measured steady-state anisotropies by the following Perrin relation if the decay of fluorescence and the decay of anisotropy are single exponential [14].

$$\tau_r = \frac{\tau_f}{\left[\left(\frac{r_0}{\langle r \rangle} \right) - 1 \right]} \quad (4)$$

where r_0 , τ_f and τ_r are limiting anisotropy, fluorescence lifetime and reorientation time respectively. The limiting anisotropy $r_0=0.366$ value was determined by measuring the steady-state anisotropies of the probe in glycerol at low temperature. As glycerol has high viscosity in this condition, all the rotational motions are frozen.

Hitachi F2000 Spectrofluorimeter was used to measure the steady-state fluorescence anisotropies and Hitachi U-3200 UV-Vis spectrophotometer was used to measure the absorp-

tion spectra. The sample was excited at 442 nm and emission was monitored from 450 to 540 nm. The measurement of $\langle r \rangle$ involves recording four spectra one each for I_{\parallel} and I_{\perp} , two for the G-factor. Each anisotropy measurement was repeated 5-6 times and for every trial the G-factor was determined. The fluctuations in the measured values of $\langle r \rangle$ in the required wavelength range are within the limits of experimental error for a given probe/solvent combination. The experiments were performed in the range 298-343°K.

Time resolved fluorescence measurements were carried out using an IBH (Scotland, UK) fluorescence spectrometer based on Time-Related-Single-Photon-Counting technique [15]. The sample was excited by laser pulse of 420 nm, 1 MHz repetition rate, from a diode laser of pulse width of ~100 ps. The fluorescence was detected by a PMT based detection module (model TBX4, IBH, Scotland, UK) placed at right angles to the excitation path. The instrument response function is estimated to be ~230 ps. The temperature of the sample was controlled with a cold finger arrangement, using a temperature controller (model 2216e, IBH, Scotland, UK). The probe coumarin 6 from Aldrich Chemical Co, the solvents ethanol and acetonitrile of the highest available purity from Spectrochem India Ltd., were used as such.

We have determined the ground state (μ_g) and excited state (μ_e) dipole moments of coumarin 6 laser dye by solvent perturbation method [17] based on absorption and fluorescence shifts in various solvents. The solvents used on these studies are cyclohexane, hexane, dioxane, ethyl ether, ethyl acetate, toluene and acetonitrile, which are of spectroscopic grade. The absorption and fluorescence spectra were recorded at room temperature for measurement of dipole moments.

RESULTS AND DISCUSSION

Figure 2 shows the absorption and fluorescence emission spectrum of coumarin 6. The reorientation times of coumarin 6 in ethanol and acetonitrile as a function of temperature, which are calculating using equation (4), are given in Tables 1 and 2 respectively. Fluorescence decay curves of coumarin 6 in ethanol and acetonitrile are single exponential throughout

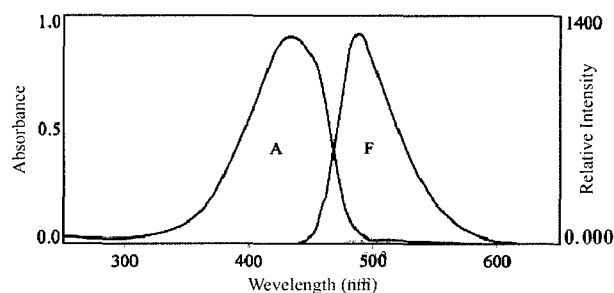


Figure 2. Absorption and fluorescence spectrum of coumarin 6 in acetonitrile.

Table 1. Steady-state anisotropy $\langle r \rangle$, fluorescence lifetime (τ_f) and reorientation times (τ_r) of coumarin 6 in ethanol as function of temperature together with the solvent viscosities^a.

Temperature/ ^o K	η /mPas	$\langle r \rangle$	τ_f /ns	τ_r /ps
298	1.074	0.0194	2.487	139.5
303	0.989	0.0165	2.493	117.8
308	0.926	0.0150	2.496	106.9
313	0.868	0.0149	2.499	106.2
318	0.808	0.0124	2.501	87.9
323	0.694	0.0109	2.505	77.0
328	0.683	0.0108	2.507	76.5
333	0.627	0.0101	2.510	71.4
338	0.567	0.008	2.513	58.6
343	0.509	0.0081	2.515	57.5

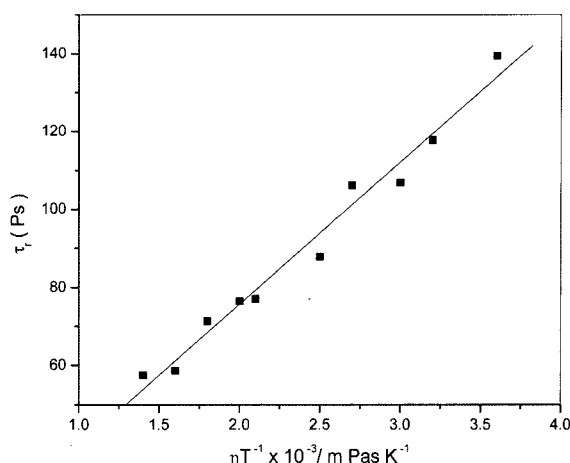
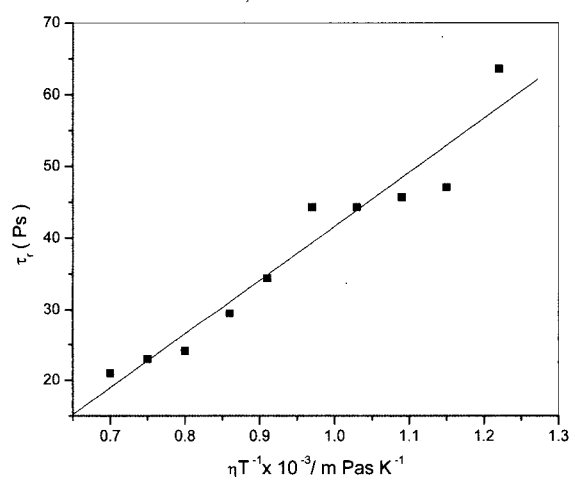
^aViscosity data from ref [18].**Table 2.** Steady-state anisotropy $\langle r \rangle$, fluorescence lifetime (τ_f) and reorientation times (τ_r) of coumarin 6 in acetonitrile as function of temperature together with the solvent viscosities^a.

Temperature/ ^o K	η /mPas	$\langle r \rangle$	τ_f /ns	τ_r /ps
298	0.365	0.0091	2.478	63.6
303	0.351	0.0068	2.489	47.2
308	0.338	0.0065	2.500	45.7
313	0.323	0.0063	2.510	44.3
318	0.309	0.0063	2.520	44.3
323	0.294	0.0049	2.531	34.4
328	0.283	0.0042	2.540	29.5
333	0.268	0.0034	2.553	24.1
338	0.254	0.0032	2.561	23.1
343	0.241	0.0029	2.572	21.1

^aViscosity data from ref [18].

the temperature range used in the study. Dutt et al. [16] have reported that the anisotropy of the coumarin follows the single exponential behavior also in 1-decanol. The observed reorientation times are calculated from equation (4), by using the values of $\langle r \rangle$, r_0 and t_f justified. Probe rotates faster in lower viscosities, i.e. rotation of probe decreases with an increase in viscosity of solvent.

Figures 3 and 4 give plots of τ_r versus η / T for coumarin 6 in ethanol and acetonitrile. From the Tables 1 and 2, it can be seen that there is a linear relationship between τ_r (ps) and η / T (mPasK⁻¹). From the linear regression (Table 3) of coumarin 6 in ethanol i.e. slope is 36.4 ps / mPasK⁻¹, intercept 2.8 ps and correlation between the τ_r (ps) and η / T (mPasK⁻¹) r is 0.98, where as for acetonitrile solvent, slope is -33.8 ps / mPasK⁻¹, intercept is 7.8 ps and r is 0.96. This shows that the ethanol solvent having good correlation compared to acetonitrile solvent. However, coumarin 6 experiencing more friction in acetonitrile

**Figure 3.** Plot of τ_r vs η / T for coumarin 6 in ethanol.**Figure 4.** Plot of τ_r vs η / T for coumarin 6 in acetonitrile.

as compared to ethanol especially at higher values of viscosity over temperature. This can be explained by considering the interaction of alcohol molecules with probe molecule, which results from hydrogen bonding. The cavities formed in this network of solvent molecules become regions of reduced friction and hence the probe molecule can rotate faster in ethanol than acetonitrile.

The ground and excited state dipole moments of coumarin 6 have been measured by employing a solvent perturbation method utilizing the solvent polarity parameter of dielectric constant (ϵ) and refractive index (n) [17]. The result shows that excited state dipole moment of coumarin 6 (radius $a=4.2$ Å) is 7.69 D and the change in dipole moment is 1.87 D.

Table 3. Linear regression results of rotational reorientation times of coumarin 6 in ethanol and acetonitrile solvents.

Solute	Ethanol			Acetonitrile		
	Slope, ps/ m PasK ⁻¹	Intercept, ps	Correlation coefficient	Slope, ps/ mPas K ⁻¹	Intercept, ps	Correlation coefficient
coumarin 6	36.4	2.8	0.98	7.8	-33.8	0.96

CONCLUSION

Rotational relaxations of coumarin 6 have been measured in two solvents, ethanol and acetonitrile as a function of temperature. The experimental rotational correlation times for both solvents are well represented as linear function of h/T . Rotational relaxation studies of probe molecules serve as a means of understanding solute-solvent interactions. It has been observed that hydrogen bonding and other specific interactions between rotating probe molecule and surrounding solvent medium are responsible for faster rotation of coumarin 6 in ethanol than in acetonitrile.

We have also determined the ground and excited state dipole moments of coumarin 6; the excited state dipole moment (μ_e) is found to be greater than the ground state dipole moment (μ_g). These values are positive, which means that the excited state is more polar than ground state.

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