ISSN 2229-5518

Rotational Diffusion of Coumarin Dye Molecules in polar and non-polar solvents

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Absract: Rotational dynamics of two structurally similar coumarins; coumarin 7 and coumarin 30 has been studied using a steady state fluorescence depolarization technique and time correlated single photon counting method as a function of temperature in ethanol and n-decane solvents. Experimentally measured reorientation times of these coumarins are identical in a given solvents at a particular temperature. The present study has been undertaken to examine the role of friction experienced by the polar solutes in a polar solvents. Molecular shape and size are similar but the friction experienced by these probes in ethanol and n-decanol solvents were varies. However, it was observed that coumarin 30, coumarin 7 rotates faster in alcohol than alkane and the observed results are discussed in the last section.

Keywords: Coumarinlaserdyes, anisotropy, lifetime, rotational reorientation times.

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1 INTRODUCTION

Laser dyes have several applications such as anticoagulants, fluorescence indicator and possess anthelmintic and optical brightness properties [1]. The interest in fluorescent dyes for qualitative and quantitative assays has increased considerably during last two decades. Sensitivity, simplicity and selectivity of fluorescence based techniques make them particular attractive for vitro and in vitro cellular and molecular biology studies [2]. Dye-sensitized solar cells (DSSCs) have considerable promise for future commercialization due to their high-energy conversion efficiency and low production cost, making them viable alternatives to silicon solar cells [3].

The 1,2-benzopyronderivatives, commonly known as the coumarin dyes, have drawn much attention in recent years in the field of physical chemistry, owing to their interesting photophysical and photochemical properties [4-23]. The 7-aminocoumarinscompose a special class of compounds among the coumarin dyes. It has been observed that the Stokes shifts, fluorescence quantum yields, and fluorescence lifetimes of 7-aminocoumarins in nonpolar solvents are often significantly different from those in polar solvents [4-17]. The explanation for such unusual behavior of 7-aminocoumarins in the solvent polarity [4-7, 9-13], and hydrogen bonding etc., [14-17]. Three types of hydrogen bond [15-17] can be formed for the 7-aminocoumarins, which include participation of the amino nitrogen lone pair (type i), carbonyl oxygen (type ii), and amino hydrogen (type iii) with hydrogen-bonding solvents. Arbeloa et al. have assumed that type (i) is more probable in the ground state, whereas the types (ii) and (iii) are more important in the first excited state [15]. However, the validity of this assumption has not been tested. Gustavsson et al. recently examined the dynamic Stokesshifts of three amino-substituted coumarin dyes in methanol and dimethyl sulfoxide (DMSO) using time-resolved fluorescence spectra, concluding that, upon photoexcitation, hydrogen

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bonds type (i) and type (iii) are weakened or broken down, whereas hydrogen bond type (ii) is strengthened [16]. As all the coumarin dyes possess a carbonyl group, researchers have paid much more attention to hydrogen bond type (ii) than hydrogen bonds type (i) and type (iii).

Palit et al. studied [21] on hydrogen bond dynamics in the excited state of C102 in aniline revealed that the reformation of hydrogen bonds between carbonyl oxygens and solvents takes place within 30 ps after the breakage of the same, which was found to be completed within 250 fs. However, that conclusion seems to contradict the calculations [22] made in our laboratory for excited states of C102 in isolated (gas-phase) complexes.

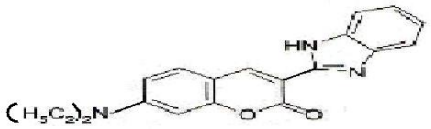
Wells et al. [23] studied the hydrogen bond dynamics of C102 in acetonitrile–water binary mixtures using ultrafast spectroscopic techniques combined with Monte Carlo simulations. They suggest that excitation of C102 simultaneously weakens and strengthens hydrogen bonding in complexes with two in equivalently bound waters [23], leading to a description of the hydrogen bond dynamics that can simultaneously accommodate both an increase in the hydrogen bond strength calculated in our laboratory and a disruption of hydrogen bonding. However, it should be noted that the Monte Carlo simulation is performed only on the ground state of C102; the suggestion of Wells and colleagues needs further examination. The hydrogen-bond cleavage and reformation also have been used to explain the rapid anisotropy decay of C460 and C153 in n-alcohols [24-25], which occurred on the order of picoseconds. According to the above discussions, it can be seen that, although a number of experimental and theoretical studies have been performed to investigate the hydrogen dynamics in the excited state of coumarin dyes in solvents, hydrogen bonds type (i) and (iii) are not widely studied and detailed mechanisms are not clear enough.

While a considerable number of works have been reported on laser dyes in various fields with view, we focus here on the rotational dynamics of coumarin laser dyes in a medium. The nature of rotational motion in solution has been a subject of long-standing interest in physical chemistry because such motions directly reflects the interactions between a solute molecule and its surroundings. For this reason, studies of rotational dynamics provide a useful for exploring the nature of solvent friction and how it influences more complex dynamics, such as chemical reaction [26-28].

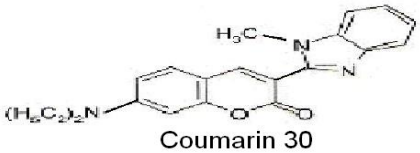
The present work reports the rotational dynamic studies of structurally similar coumarin dyes viz., coumarin 7 (C7) and coumarin 30 (C30). These structures are expected to affect the rotational reorientation times due to the formation of hydrogen bonds with the solvent. Thus, the structures and structural changes in the solvent environment around the solute in the solvent are not fully understood. There fore this study investigate the rotational reorientation characteristics.

2 EXPEMENTAL

The laser dyes C7 and C30 were procured from Aldrich Chemical Co., and used without purification as shown in Fig. 1. Steady state fluorescence anisotropies were recorded using Hitachi F2000 spectrophotometer and electronic absorption spectra are recorded on Hitachi model U-3200 spectrophotometer. The samples were excited at 436 nm (C7) and 411 nm (C30) and emission was monitored from 450 to 550 nm. Rotational reorientation times of C7 and C30 were measured using steady-state depolarization technique [27] in ethanol and n-decanol solvents of spectroscopic grade.



Coumarin 7



Coumarin 30

Fig. 1. Molecular Structure of C7 and C30.

The steady state fluorescence anisotropy <r>was measured experimentally and the quantities given by the following equation

$$< r > = \frac{I_{11} - G\, I_{\perp}}{I_{11} + 2\, G\, I_{\perp}} \qquad (1)$$

where I_{11} and $I_{\perp}$ are the polarized fluorescence intensities parallel and perpendicular with respect to the excitation respectively, G is an instrumental factor which corrects for the polarization bias in the detection system is given by

$$G = \frac{I_{HV}}{I_{HH}} \qquad (2)$$

where $I_{HV}$is the fluorescence intensity when the excitation polarizer is kept horizontal and $I_{HH}$is the fluorescence intensity when both the polarizer are kept horizontal.

The measurement of <r> involves recording four spectra, two I_{11} and $I_{\perp}$ and two for G-factor. Each anisotropy measurement was repeated 5-6 times and for every trail, the G-factor was determined. The experiments were performed in the temperature range of 298-342 ^{0}K. Rotational reorientation times can be obtained from the measured steady-state anisotropies in the following relation if the decay of fluorescence and decay of anisotropy are single exponential [29].

$$\tau_r = \frac{\tau_f}{\left[\left(\frac{r_0}{< r >}\right) - 1\right]} \qquad (3)$$

where r_0,$\tau_f$and $\tau_r$arelimiting anisotropy, fluorescence lifetime and reorientation times respectively.The limiting anisotropy $r_o$value was determined by measured steady state anisotropies of the probe molecule in glycerol at low temperature, glycerol having high viscosity under these conditions, when all the rotational motions are frozen.

Florescence lifetimes were measured using time-correlated single-photon counting technique [30] with the gated hydrogen discharge lamp as the excitation source (Edinbergh Instruments, Model EI-199) and the details have been given elsewhere [31]. The excitation wavelength was 420 nm and a cutoff filter GG455 was used to eliminate the excitation light while collecting the emission decay. In both the apparatus, the desired sample temperature was maintained within $\pm 1^0$with the help of temperature controller.

3 RESULTS AND DISCUSSION

Absorption and fluorescence emission spectra of molecules were recorded in ethanol and n-decane solvents. Figure 2 shows the typical absorption and fluorescence spectra of C7 obtained in ethanol solvent. The limiting anisotropy $r_o$was measured by dissolving the solutes in glycerol and measuring steady state anisotropy at low temperature and the values of r_o for C7 and C30 are 0.368 and 0.372. It gives the orientation of the absorption and emission transition dipoles with respect to each other. The axial radii of the molecules were estimated from the Corey-Pauling-Koltum scaled model, long axis was taken along the bond joining benzimidazole group with diethylaminocoumarin and the axis perpendicular to it was taken as the short in-plane axis. van der Waals volumes were calculated using the Edward's atomic increment method [32]. The estimated axial radii of the probes C7 or C30 are 9.5 ×3.7×1.9 (axial radii/Å^3) and van der Waals volumes are 297 (C7) and 315 (C30) V/Å^3. Both of these molecules are modeled as asymmetric ellipsoids.

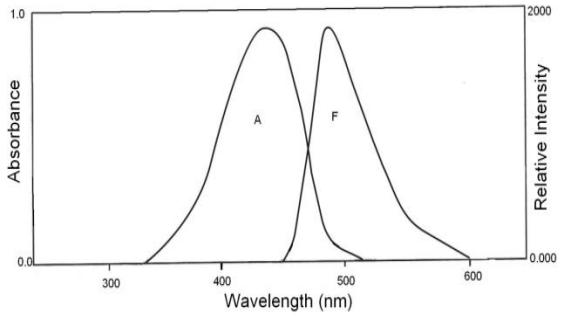


Fig. 2. Absorption (A) and Fluorescence (F) spectra of C7 in ethanol.

The reorientation times of C7 and C30 in ethanol and n-decane solvents as a function of temperature (T), which were obtained from the measured values ofr_o,$\tau_f$and τ_r using equation (3) are presented in the table 1 and 2. Anisotropy <r>

values for C7 are in the range of 0.0102 to 0.0181 and the τ_f values are in the range of 2.648 to 2.741 ns. For C30 <r> varies from 0.0088 to 0.0186, τ_f in the range of 2.150 to 2.307 ns in the temperature ranges from 298 to 342 ^{0}K. The values of anisotropy (0.008 to 0.0151), lifetime (2.481 to 2.522 ns), rotational reorientation times (55.3 to 107.9 ps) for C7 are obtained. For C30 molecule the values of anisotropy (0.0063 to 0.0131), lifetime (2.583 to 2.598 ns) and rotational reorientation times (45.4 to 94.9 ps) in the n-decane solvent in the temperature range from 298 to 342 ^{0}K. The rotational reorientation times of a probe in the solvents are the way an index of molecular friction. Fluorescence decay of both the probes in the solvents were single exponential throughout the temperature range used in the study.

Table 1. Steady-state anisotropy <r>, fluorescence lifetime (τ_f) and rotational reorientation times (τ_r) of C7 and C30 in ethanol as function of temperature.

Temp. in ^{0}K	η/ mPas	η/T *10^{-3}mPas K^{-1}	<r>	τ_f/ns	τ_r/ps	<r>	τ_f/ns	τ_r/ps
			C7			C30		
298	1.074	3.604	0.0181	2.648	137.4	0.0186	2.307	121.7
303	0.989	3.264	0.0149	2.657	112.7	0.0174	2.290	112.6
308	0.926	3.006	0.0156	2.669	118.2	0.0158	2.274	101.1
313	0.868	2.773	0.0148	2.679	112.3	0.0156	2.255	99.3
318	0.808	2.540	0.0129	2.689	97.7	0.0134	2.237	84.2
323	0.694	2.148	0.0126	2.700	96.0	0.0130	2.221	80.8
328	0.683	2.082	0.0126	2.709	96.3	0.0113	2.202	69.4
333	0.627	1.882	0.0108	2.721	82.7	0.0113	2.183	68.3
338	0.567	1.677	0.0100	2.730	76.5	0.0105	2.169	63.1
342	0.509	1.484	0.0102	2.741	78.4	0.0088	2.150	52.2

Table 2. Steady-state anisotropy <r>, fluorescence lifetime (τ_f) and rotational reorientation times (τ_r) of C7 and C30 in n-decane as function of temperature.

Temp. in ^{0}K	η/mPas	η/T *10^{-3}mPas K^{-1}	<r>	τ_f/ns	τ_r/ps	<r>	τ_f/ns	τ_r/ps
			C7			C30		
298	0.838	2.812	0.0151	2.522	107.9	0.0131	2.583	94.9
303	0.784	2.587	0.0138	2.518	98.1	0.0102	2.585	72.9
308	0.748	2.428	0.0107	2.512	75.6	0.0100	2.587	72.0
313	0.707	2.258	0.0101	2.513	71.4	0.0097	2.589	69.6
318	0.670	2.107	0.0100	2.511	70.5	0.0093	2.590	66.7
323	0.635	1.966	0.0100	2.510	70.2	0.0087	2.592	62.6
328	0.597	1.820	0.0095	2.505	66.8	0.0085	2.593	61.0
333	0.556	1.669	0.0094	2.501	66.0	0.0080	2.595	57.7
338	0.518	1.532	0.0093	2.489	64.6	0.0065	2.597	46.6
342	0.482	1.405	0.0080	2.481	55.3	0.0063	2.598	45.4

Since the present study has been carried out two probes and solvents viscosity was varied by changing the temperature, the friction experienced by the solute molecule in a given solvent remain the same throughout the temperature range. The reorientation times of these probes are more or less the same in the solvent at a particular temperature. These probes however, are experiencing more friction in DMSO and n-octanenitrile similar viscosity over temperature [33]. Moog et al. [34] observed that C102 and C153 these probes ar similar in size, shape and electronic charge distribution, one would expect nearly identical rotation times and hydrogen-bounding behavior for two solutes. Indeed the rotation times of probes rotates more slowly in alcohol solvents than alkanes.

Figure 3 gives a plot of τ_r versus of η/T for the both coumarins in ethanol solvent, although linear least-squares fits of τ_r versus of η/T for both the probes in ethanol gave positive intercepts. Positive intercepts indicating that the relationship between τ_r and η/T is linear in this solvent system. The τ_r values obtained for C7 and C30 are more or less the same within the limits of experimental error in ethanol for particular viscosity, indicating that they are experiencing identical friction. Reorientation times of the two probes are smaller in C30 compare to C7, which indicates that the probe rotating faster in C30 compare to C7. The similar trend also observed in both the molecules in n-decane solvent (Figure 4). According to general consensus, a polar molecule rotating in a polar solvent should experience dielectric friction and it is may not observed in nonpolar solvent. The higher dielectric friction experienced in ethanol solvent by the C7 molecule compared to C30 is probably the reason why the observed reorientation times of C7 are slower in ethanol at higher values of η/T. The free volume available for solute's rotation may be less in n-decane compared to ethanol, which exists as hydrogen-bonded clusters and hence facilitates faster rotation of the probes in ethanol solvent.

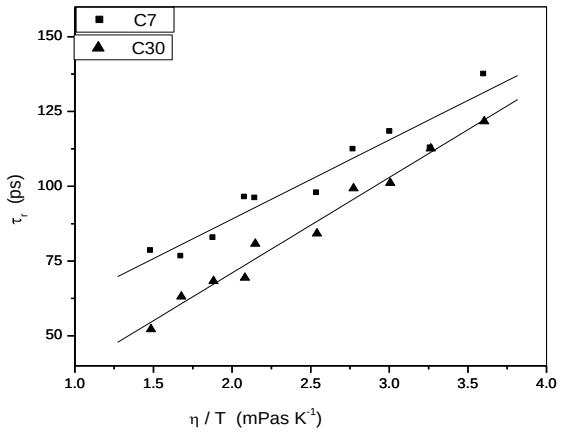


Fig.3: Plots of rotational reorientation times of C7 and C30 as function of η/T in ethanol.

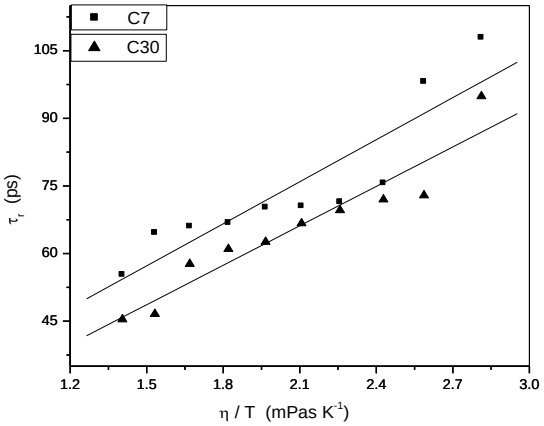


Fig.4: Plots of rotational reorientation times of C7 and C30 as function of η/T in n-decane.

4 CONCLUSION

Rotational reorientation times of two similar structures with almost identical volumes, C7 and C30 have been measured in alcohol and alkane solvents as a function of temperature. The experimental rotational correlation times are well represented as linear function of η/T. To conclude, the present results on C7 and C30 underscore the fact that we are far from having a complete understanding of how it is that the molecular details of solute-solvent interactions translate into friction on solute molecule. One of the goals for undertaking the present study is to find out which aspect is responsible for the observed trend. We may conclude that the faster rotation of molecule in the alcohol solvent is due to dielectric friction experienced by molecules in the solvent medium is responsible for the observed rotation.

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