

Full Length Research Paper

Dynamical behavior of coumarin compounds in alcohol solvents

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Dynamical behavior of 3-(2-Benzimidazolyl)-7-(DiethylAmino) coumarin [coumarin7 (C7)] and 3-(2-N-Methylbenzimidazolyl)-7-N, N-diethylamino coumarin [coumarin30 (C30)] laser dyes have been examined in methanol as a function of temperature. It is observed that, the rotational motion of probe molecule in methanol solvent increases as the temperature increase. We also investigated that, C30 rotates faster than C7 in the same solvent. It is all due to the friction between solute and solvent, diffusion and hydrogen bonding establish between alcoholic group and coumarin molecule. We have also determined the excited state and ground state dipole moments in alcoholic series solvents by using Bakhshiev, Chamma-viallet equations and Quantum mechanical treatment. From the results, it is found that, excited state dipole moment is greater than the ground state dipole moment, which indicates that excited state is more polar than the ground state.

Key words: Coumarin7 (C7), coumarin30 (C30), reorientation time, fluorescence time, stokes shift, dipole moment, rotational diffusion, dielectric friction.

INTRODUCTION

Molecular orientation in a liquid is greatly influenced by its environment, as molecules are continuously interacting with each other due to their close proximity. By understanding the molecular rotation in liquids, one can get a better insight into the nature of the solute-solvent interactions, which in turn creates a lot of interest in understanding the photo physical properties of molecules.

A molecule rotating in a liquid continuously experiences friction, due to its volume, size, viscosity etc. The general approach is to measure the reorientation time of a solute molecule in a liquid experimentally and model its rotation using diffusion based theories like Stokes Einstein Debye (SED)1929; Nee and Zwanzig, 1970; Van der Zwan and Hynes, 1985; Alavi and Waldeck, 1993. Models Nee-Zwanzig and Van der Zwan-Hynes, which treat the solute as a point dipole, could not explain the observed trend qualitatively.

But Alavi-Waldeck model which treats the solutes electrostatic field as a distribution of charges is able to

explain the observed behavior qualitatively. According to SED theory, the reorientation time of solute molecule is proportional to its size, volume, viscosity and surrounding temperature. However, this reorientation of a molecule can better understand if we analyze the molecule under solvent effects. Various techniques are available, among the most popular, is the Bakhshiev's and Kawski-Chamma-Viallet's treatment, Chamma and Viallet (1970); Chamma and Viallet (1970). Coumarin dyes are very good media for efficient broadband dye laser in the blue-green region and most of the substitute coumarins are often fluorescence. The lasing properties of substituted coumarins have led to a renewed interest in their spectral characteristics, which require complete and systematic study. These compounds are widely used as a dye laser, indicators of a biophysical process, biomedical applications, optical brightener, anticoagulant, sunscreens etc.

EXPERIMENTAL

Apparatus

Electronic UV/Vis absorption measurements which are made, using Hitachi 150 - 20 spectrophotometer and Fluorescent measurements

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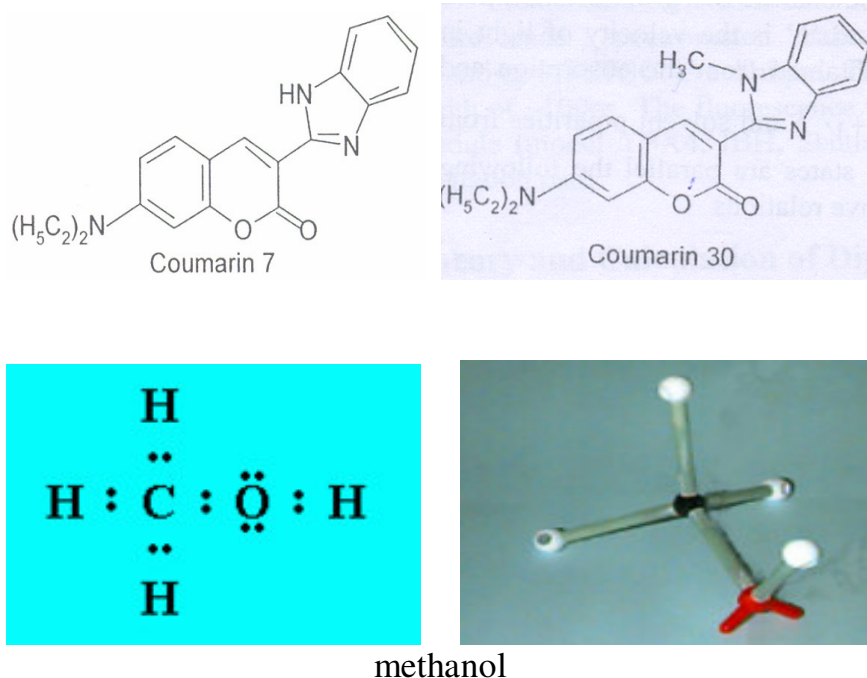


Figure 1. Structure of coumarin , coumarin 30 and methanol.

are on Hitachi F2000 spectrofluorometer at room temperature and at varying temperatures ranging from 298K to 333K.

Fluorescence life times were measured using an IBH (Scotland, UK) fluorescence spectrometer based on Time-Correlated-Single-Photon-Counting (TCPSC) technique. The sample was excited by laser with pulse width of ~100ps. The fluorescence was detected by PMT based on deflection module Pal et al. (1990) (model TBX4, IBH, Scotland, UK) placed at right angles to the excitation path.

Materials

AR-Grade coumarin7 (C7) and coumarin30 (C30) have been used in our present investigation are from Aldrich Chemical Co., without further purification. The molecular structures are given in Figure 1. All the solvents viz., methanol, ethanol, n-decanol, n-nonanol, n-octanol, n-pentanol, 2-propanol and n-propanol are of spectroscopic grade.

General procedure

Steady state reorientation times of C7 and C30 are measured, using steady state depolarization method in methanol solvent of spectroscopic grade. The steady state of anisotropy $\langle r \rangle$ is related to experimentally measured intensities by the following equation.

$$\langle r \rangle = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2GI_{\perp}} \quad (1)$$

Where I_{\parallel} and I_{\perp} are polarized fluorescence intensities parallel and perpendicular with respect to the excitation radiation. G is an instrumental factor which corrects for the polarization bias in the detection system and is given by:

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

Where I_{HV} is the fluorescence intensity in which the excitation polarizer is kept horizontal and the emission polarizer vertical and I_{HH} is the fluorescence intensity when the both the polarizers are kept horizontal.

The sample was excited at 436 nm and emission was monitored from 450 nm to 540 nm. The measurement of $\langle r \rangle$ involves with recording four spectra each for I_{\parallel} and I_{\perp} and two for the G -factor. Each anisotropy measurement was repeated 5-6 times and for every trial the G -factor was determined. The experiment was performed in the range of 298-333K. Reorientation time can be obtained from the measured steady state anisotropies by the following Perrin relation. The decay of fluorescence and the decay of anisotropy are single exponential Lackowich JR (1983).

$$\tau_r = \frac{\tau_f}{\left[\left(\frac{r_0}{\langle r \rangle} \right) - 1 \right]} \quad (3)$$

Where r_0 , τ_f and τ_r are limiting anisotropy, fluorescence life time and reorientation time respectively. The limiting anisotropy r_0 value was determined by measuring the steady state anisotropies of the probe in glycerol at low temperature (below - 15°C). As glycerol having high viscosity in this condition, all rotational motions are frozen.

Theory and calculation of dipole moment

In the present paper we have calculated the dipole moments using solvatochromic shift method. Based on the Bakhshiev's (Equation 4), Kawski-Chamma-Viallet's (Equation 5) and quantum mechanical

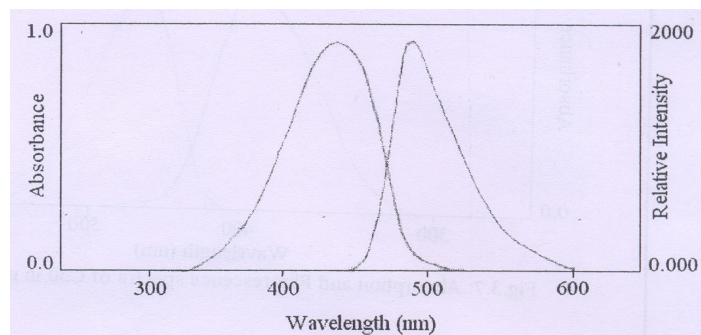


Figure 2. Absorption and fluorescence spectra of C7 in methanol.

perturbation theory of the absorption and fluorescence band shifts (in wave numbers) in the solvents of different permittivity (ϵ) and refractive index (n), the following equations are Kawski (1966); Bilot L and Kawski (1962) shown below:

$$\bar{\nu}_a - \bar{\nu}_f = m_1 f(\epsilon, n) + \text{Constant} \quad (4)$$

$$\bar{\nu}_a + \bar{\nu}_f = -m_2 [f(\epsilon, n) + 2g(n)] + \text{Constant} \quad (5)$$

Where

$$f(\epsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \quad (6)$$

$\bar{\nu}_a$, $\bar{\nu}_f$ are the absorption and fluorescence maxima (in wave numbers)

$$g(n) = \frac{3}{2} \left[\frac{n^4 - 1}{(n^2 + 2)^2} \right] \quad (7)$$

Equation 6 and 7 are called solvent polarity parameters With

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad (8)$$

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \quad (9)$$

Where μ_e and μ_g are the dipole moments of the ground and excited states respectively, h is Planck's constant and ' c ' is the velocity of light in vacuum.

The parameters m_1 and m_2 are obtained from the absorption and fluorescence band shifts ($\bar{\nu}_a - \bar{\nu}_f$ and $\bar{\nu}_a + \bar{\nu}_f$) and solvent polarities from above equations. If the ground and excited states are parallel the following expressions are obtained on the basis of above relations (Koti ASR et al., (2000); Kawaski (1992, 2002)

$$\mu_g = \frac{m_2 - m_1}{2} \left[\frac{hca^3}{2m_1} \right]^{\frac{1}{2}} \quad (10)$$

$$\mu_e = \frac{m_1 + m_2}{2} \left[\frac{hca^3}{2m_1} \right]^{\frac{1}{2}} \quad (11)$$

Or

$$\frac{\mu_e}{\mu_g} = \frac{m_1 + m_2}{m_1 - m_2} \quad (m_2 > m_1) \quad (12)$$

The Onsager radius ' a ' of the solute molecule can be determined by using atomic increment method Edward (1956).

RESULTS AND DISCUSSION

Effect of solvents on probe molecule

Figures 2 and 3 show the absorption and fluorescence emission spectra of C7 and C30 in methanol respectively. We have studied solvent effects on the positions of the absorption and emission using different solvent parameters like dielectric constant (ϵ), refractive index (n) and the solvent polarity parameter. Values are tabulated in Tables 1 and 2. Polarity parameters [such as Equations 6 and 7] are calculated and tabulated in Table 3. The value of stokes shift between absorption and emission maxima is the indication of charge transfer during an excitation. The large magnitude of the stokes shift indicates that, the excited state geometry could be different from that of the ground state. The general observation is, whenever there is an increase in the stokes shift with increasing solvent polarity, there is an increase in the dipole moment on excitation.

The wave numbers of absorption and emission maxima of C7 and C30 in various solvents are summarized in Tables 1 and 2. In order to estimate the ratio (μ_e/μ_g) of excited state to ground state dipole moments of the probe molecules, the solvent polarities $f(\epsilon, n)$ and $f(\epsilon, n) + 2g(n)$ are calculated.

Stokes shifts ($\bar{\nu}_a - \bar{\nu}_f$) versus $f(\epsilon, n)$ and ($\bar{\nu}_a + \bar{\nu}_f$) versus $f(\epsilon, n) + 2g(n)$ are plotted (Figures 4 – 7) and a linear fit was carried out using the software origin 6.1.

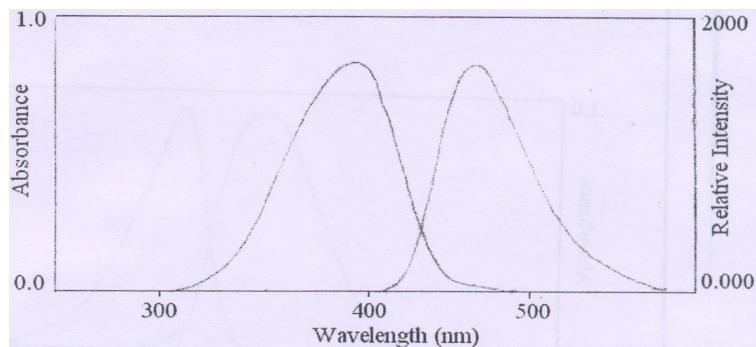


Figure 3. Absorption and fluorescence spectra of C30 in methanol.

Table 1. Solvent shift data for coumarin7

Solvent	$\bar{\nu}_a$ (in cm^{-1})	$\bar{\nu}_f$ (in cm^{-1})	$\bar{\nu}_a - \bar{\nu}_f$	$\bar{\nu}_a + \bar{\nu}_f$
methanol	22935	20325	2610	43260
Ethanol	22935	20366	2569	43301
n-decanol	23255	21052	2203	44307
n-nonanol	23094	20833	2261	43927
n-octanol	23041	20703	2338	43744
n-pentanol	23041	20618	2423	43659
2-propanol	23105	20618	2487	43723
n-propanol	22988	20449	2539	43437

Table 2. Solvent shift data for coumarin30.

Solvent	$\bar{\nu}_a$ (in cm^{-1})	$\bar{\nu}_f$ (in cm^{-1})	$\bar{\nu}_a - \bar{\nu}_f$	$\bar{\nu}_a + \bar{\nu}_f$
methanol	24331	20790	3541	45121
Ethanol	24300	20833	3466	45133
n-decanol	24331	21276	3055	45607
n-nonanol	24330	21141	3189	45471
n-octanol	24271	21008	3263	45279
n-pentanol	24271	20964	3307	45235
2-propanol	24271	20920	3351	45191
n-propanol	24271	20876	3395	45147

Table 3. Calculation of $f(\epsilon, n)$ and $f(\epsilon, n) + 2g(n)$ for chosen alcoholic solvents.

Solvent	$f(\epsilon, n)$	$f(\epsilon, n) + 2g(n)$
methanol	0.85573	1.30257
Ethanol	0.81645	1.30829
n-decanol	0.55001	1.14271
n-nonanol	0.58594	1.16537
n-octanol	0.62675	1.20882
n-pentanol	0.72044	1.27603
2-propanol	0.78073	1.29364
n-propanol	0.78266	1.30628

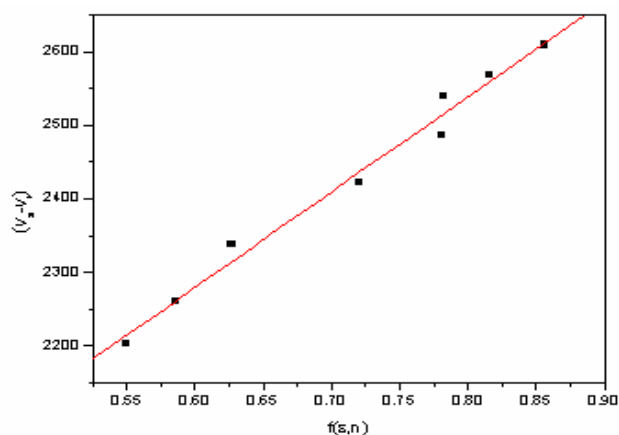
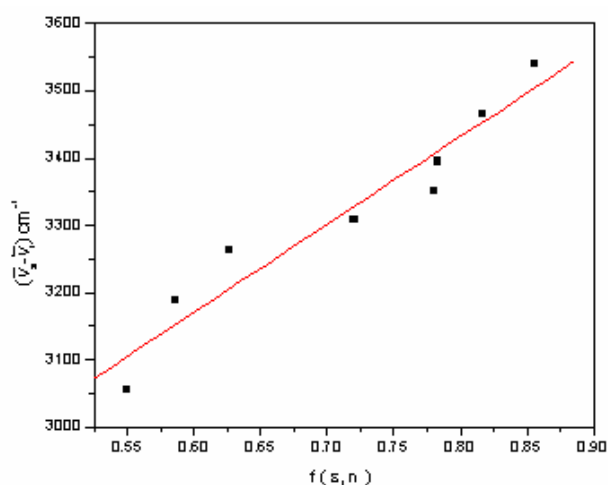
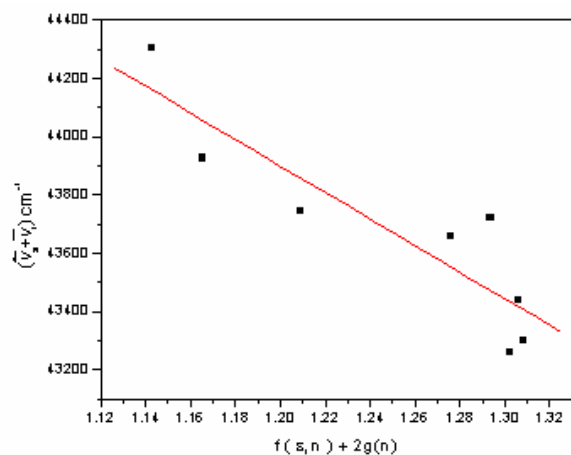
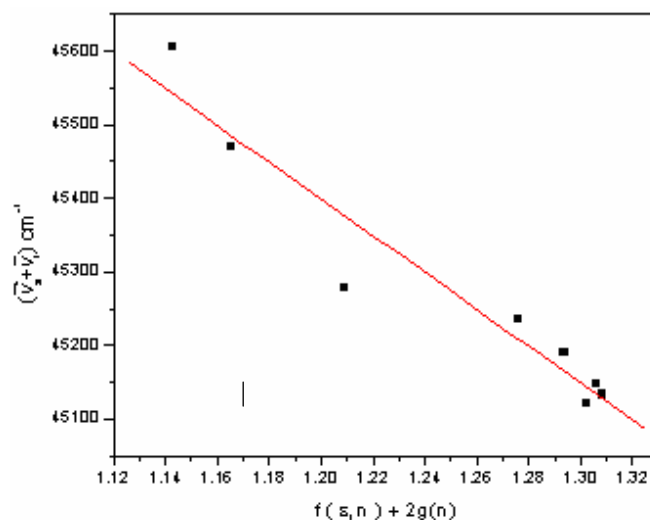
It is observed that the shifts of emission peaks with changes in solvent polarity and are more pronounced than the shifts of absorption peaks. This indicates (Table 4) that $\mu_e \gg \mu_g$, that is, the dipole moment of a molecule increases on excitation. With increasing solvent polarity red shift is observed which indicates $\pi-\pi^*$ transition. Further, it is observed that $(\mu_e)_{C7} \gg (\mu_e)_{C30}$ and $(\mu_g)_{C7} \gg (\mu_g)_{C30}$.

Effect of methanol on rotational probe

The reorientation times (τ_r) of C7 and C30 in methanol

Table 4. Dipole moments, slopes and correlation factor of coumarin7 and coumarin30 molecule for alcohol solvents.

Moleculc	Radius 'a'(A)	μ_g (D)	μ_e (D)	$\Delta\mu$ (D)	$\frac{\mu_e}{\mu_g}$	m_1 (cm^{-1})	m_2 (cm^{-1})	Correlation factor (r)
C7	4.2	3.89	6.98	3.09	1.79	1299.993	4563.119	0.993;0.895
C30	4.2	1.41	4.51	3.10	3.19	1307.903	2498.551	0.962;0.962

**Figure 4.** Plot of $(\bar{\nu}_a - \bar{\nu}_f) \text{ cm}^{-1}$ vs $f(\epsilon, n)$ of C7 in chosen solvents.**Figure 6.** Plot of $(\bar{\nu}_a - \bar{\nu}_f) \text{ cm}^{-1}$ vs $f(\epsilon, n)$ of C30 in chosen solvents.**Figure 5.** Plot of $(\bar{\nu}_a + \bar{\nu}_f) \text{ cm}^{-1}$ vs $f(\epsilon, n) + 2g(n)$ for C7 in chosen solvents.**Figure 7.** Plot of $(\bar{\nu}_a + \bar{\nu}_f) \text{ cm}^{-1}$ vs $f(\epsilon, n) + 2g(n)$ for C30 in chosen solvents.

as a function of temperature are calculated using Equation (3). The values are reported in Table 5 and 6. From the measured values of $\langle r \rangle$, r_0 and τ_f [r_0 value of C7 is 0.368 ± 0.003 and for C30 is 0.372 ± 0.003] Dutt et al. (2001), it can be seen that, fluorescence and anisotropy curves in methanol are single exponential throughout the

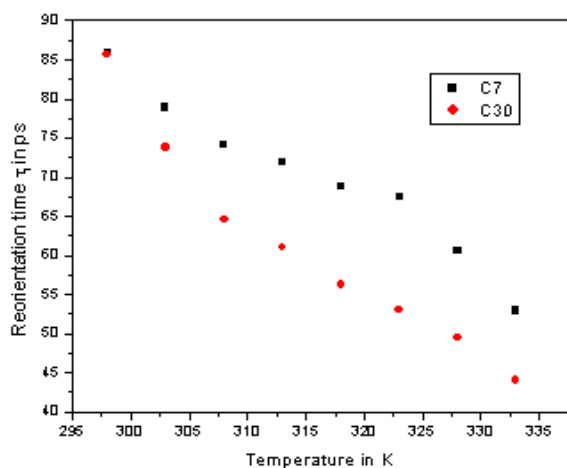
temperature range (Raikar et al., 2006), have also reported C30 in n-octanenitrile and n-butanol. Solvents at

Table 5. Fluorescence life time of C7 molecule in methanol as a function of temperature.

Temperature in K	η (mPa)	$\langle r \rangle$	τ_f /ns	τ_r /ps
298	0.793	0.0107	2.622	86.0
303	0.746	0.0101	2.556	78.9
308	0.696	0.0096	2.532	74.2
313	0.645	0.0094	2.511	72.0
318	0.595	0.0091	2.485	68.9
323	0.544	0.0090	2.462	67.5
328	0.487	0.0082	2.438	60.5
333	0.439	0.0072	2.416	52.9

Table 6. Fluorescence life time of C30 molecule in methanol as a function of temperature.

Temperature in K	η (mPa)	$\langle r \rangle$	τ_f /ns	τ_r /ps
298	0.793	0.0179	1.495	85.7
303	0.746	0.0156	1.490	73.8
308	0.696	0.0143	1.429	64.6
313	0.645	0.0140	1.377	61.0
318	0.595	0.0135	1.320	56.2
323	0.544	0.0133	1.266	53.0
328	0.487	0.0130	1.209	49.5
333	0.439	0.0121	1.160	44.0

**Figure 8.** Variation of reorientation time vs Temp of C7 and C30 in methanol.**Table 7.** Different solvents and their respective boiling points and molecular weights.

Solvent	Boiling point (°C)	Molecular weight
Methanol	64.7	32.04
Ethanol	78.5	46.07
Butanol	117.73	74.12

different temperatures follow the single exponential trend. In the present work, the fluorescence decay measurements for C7 and C30 in methanol are carried out. The values of $\langle r \rangle$, r_0 and τ_f are justified at 298 - 333K. From the measurements of reorientation times of C7 and C30 in methanol (Figure 8), it clears that C30 rotates faster than C7.

Reported readings (Table 5 and 6) indicate that the molecule experiences more friction at higher viscosity than at lower viscosities (viscosity is inversely proportional to temperature). According to hydrodynamics theory, the rotational relaxation time of the probe is proportional to the viscosity and inversely proportional to temperature (Debye, Stokes-Einstein equations). So, C7 and C30 experience less friction in methanol than in ethanol, butanol etc.

This can be explained by considering the interaction of alcohol molecule with the probe molecule, which results from hydrogen bonding. Methanol molecule can form hydrogen bonds with the probe molecule. This hydrogen bonding reduces the rotation of the solute molecule. However, larger is the strength of the stiffness of the hydrogen bonding (higher boiling point alcoholic solvent) (Table 7) and greater is the frictional force impact on the rotational probe. Hence, we conclude that, in alcoholic series solvents, larger is the strength of the hydrogen bonding (higher boiling point of solvent) and larger is the frictional force, leads to slower the probe rotation in solvent (higher relaxation time). The effects of physical properties like size, volume of the solute and solvent molecule on reorientation times cannot be neglected. The cavities formed in the network of methanol solvent, probe molecule become region of reduced friction and rotates faster at higher temperature. We reported (Raikar et al., 2006) the rotational motions in different probes are as; (C30) in methanol > (C30) in butanol (Raikar et al., 2006). C7 is having higher dipole moment than the C30, both in excited and ground state due to (CH₃) group in C30 which is more affinity to hydrogen bonding than (H) in C7 with methanol solvent at higher temperature.

Conclusion

Rotational relaxation studies of C7 and C30 molecule serve as a means of understanding solute and solvent interactions. Rotational relaxation times of C7 and C30 in methanol solvent have been measured as a function of temperature. The experimental rotational correlation time is linear as a function of temperature. In the present work we observed that C30 rotates faster than C7 in methanol solvent. Both the probes show more rotational tendency at higher temperatures. We also determined experimentally the ratio of μ_e to μ_g for C7 and C30 molecules based on Stokes shift and quantum mechanical perturbation theory and found that both probes have higher dipole moments in excited states than the ground state. This depicts that, the given probe is more polar in excited

state than in ground state.

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 C7 and C30 in methanol solvent than in other alcoholic solvents.

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