RESEARCH ARTICLE

ROTATIONAL DYNAMICS OF COUMARIN 519 IN ALCOHOLS

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ARTICLE INFO

ABSTRACT

The rotational dynamics of a polar laser dye coumarin 519 has been studied in alcohols by both steady state and time-resolved fluorescence depolarization technique at room temperature. Rotational correlation times of the probe were found to vary linearly as function of viscosity of the solvents. Results are analyzed by employing the Stokes-Einstein-Debye (SED) hydrodynamic theory to estimate the mechanical friction with slip and stick boundary conditions.

INTRODUCTION

The study of rotational motion of molecules provides useful information of chemical effects on isomerization, solvation, aggregation, hydrogen bonding, photochemical process, etc. The study of rotational motion of molecules in liquids enables one to understand the physicochemical properties of solutions and we can get a better insight into the nature of the solute-solvent interactions which is greatly influenced by its environment, since the molecules are continuously interacting with each other due to their close proximity. Accordingly, rotational relaxation in liquids is important in several branches of spectroscopy and has attracted both experimentalists and theoreticians. Rotational diffusion studies of small and medium sized molecules provide a useful means for probing these solute-solvent interactions [Blachardt *et al*., 1986, Chandrashekhar *et al*., 1995, Dutt *et al*., 2000, Flemming *et al*., 1976, Von Jena *et al*., 1981, Von Jena *et al*., 1979]. Among various experimental techniques available like, Raman, EPR, NMR, dynamic light scattering, dielectric relaxation, etc., the rotational diffusion studies are highly pragmatic for the study of solute–solvent interactions. The mechanical friction between the solute and the solvent depends on the size and shape of the solute molecules and it exists only when either the solute or the solvent is nonpolar or when both of them are nonpolar. The situation is more complicated when an excited polar solute rotating in a polar solvent polarizes the surrounding solvent medium and the response of the solvent polarization to the solute's rotation not being instantaneous. In addition to the viscous drag, dipolar-dipolar interaction [Alavi *et al*., 1991, Hartman *et al*., 1997, Templeton *et al*., 1986, Wiemers *et al*.,

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2000] between a polar solute and a polar solvent often gives rise to a retarding force. This arises because of the inability of solvent molecules, encircling the polar solute probe, to rotate synchronously with the probe. The result of this effect is the creation of an electric field in the cavity, which exerts a torque opposing the reorientation of the probe molecule. A number of studies [Dutt *et al*., 1992, Dutt *et al*., 2001, Gudgin *et al*., 1986, Kivelson *et al*., 1985, Kenney *et al*., 1988, Philips *et al*., 1985, Simon *et al*., 1990] involving polar solutes in polar solvents have been carried out and the observed friction, which is proportional to the measured reorientation time, has been conveniently explained. However, detailed investigations of reorientation dynamics have indicated the presence of another source of drag on a rotating probe molecule due to specific interactions such as hydrogen bonding between the solute and the solvent molecules. A solute molecule can form hydrogen bond [Dutt *et al*., 1999, Dutt *et al*., 2000, Fleming *et al*., 1986, Moog *et al*., 1993, Spear *et al*., 1985] with the solvent molecule depending on the nature of the functional groups on the solute and the solvent. Under such circumstances, the observed reorientation time is longer due to an increase in the effective size of the rotating probe molecule. Nevertheless, such an explanation is only qualitative. The present work deals with the study of rotational dynamics of polar molecule coumarin 519 in series of alcohols (Fig.1). The molecule possesses hydrogen bonding functional groups such as C=O and N. Normal alcohols are among the most widely used solvents as they not only offer a wide range of viscous and dielectric properties within a homologous series but also have the ability to form hydrogen bonds with the amino and carbonyl groups of the solute molecule. The reorientation time of the solute is therefore expected to reflect on the presence of an additional friction along with the mechanical friction. Regardless decades of continued investigation, the details of solute-solvent interactions, particularly in polar solute-solvent systems, remain to be understood in detail. The aim of the present investigation
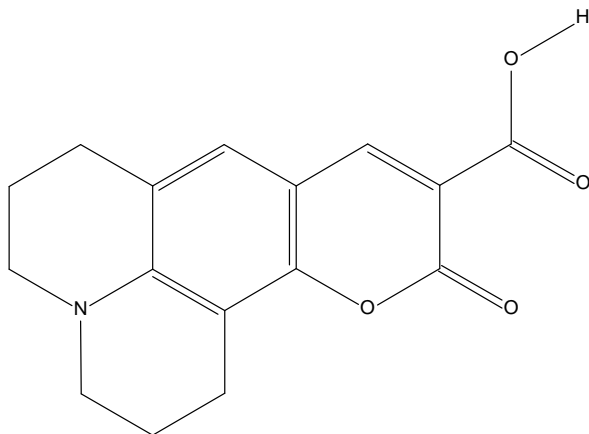
Fig.1. Molecular structure of coumarin 519

is to study the reorientation times of the probe in order to understand the mechanism underlying the rotational relaxation of the dye in alcohols. Steady-state fluorescence anisotropies of the probe molecule were measured using fluorescence depolarization technique [Lackowicz, 2006]. For vertically polarized excitation the steady-state fluorescence anisotropy is defined as

$$r = \frac{I_\| - GI_\perp}{I_\| + 2GI_\perp} \dots\dots\dots 1$$

where $I_\|$ and $I_\perp$ are the emission intensities polarized parallel and perpendicular to the excitation polarization, G is an instrumental parameter which corrects for the polarization bias in the detection system and is given by $G = I_{HV}/I_{HH}$, with I_{HV} being the fluorescence intensity when the excitation polarizer is kept horizontal and the emission polarizer vertical, and I_{HH} the fluorescence intensity when both the polarizers are maintained horizontal. The reorientation time τ_r can be obtained from the measured steady-state anisotropy r and the fluorescence lifetime τ_f using the following relation

$$\tau_r = \frac{\tau_f}{\left[\left(\frac{(r_0)}{(r)}\right) - 1\right]} \dots\dots\dots 2$$

where r_0 is the limiting anisotropy when all the rotational motions are frozen. In the present study, r_0 value was measured in glycerol (Fluka) at 213 K. The probe was excited at 436 nm and the emission was monitored in the range of 300 to 600 nm. The limiting anisotropy r_0 is related to the angle between the absorption and emission dipoles of the fluorophore under study and is given by

$$r_0 = \left(\frac{2}{5}\right)\left[\frac{3\cos^2\theta - 1}{2}\right] \dots\dots\dots 3$$

Mechanical friction on a rotating solute in solvent is computed employing Stokes-Einstein-Debye hydrodynamic theory [Debye *et al.*, 1929, Fleming *et al.*, 1986, Kievelson *et al.*, 1987] by treating the solute as a smooth sphere rotating in a continuum fluid, which is characterized by a shear viscosity. If 'a' is the radius of the molecule and 'η' the viscosity of the liquid, then according to Stokes law

$$\tau_r = \frac{\eta V}{kT} \dots\dots\dots 4$$

where V is the molecular volume. The most widely used SED hydrodynamic equation for the description of rotational dynamics of spherical molecule is given by

$$\tau_r = \frac{\eta V}{kT} + \tau_0 \dots\dots\dots 5$$

where τ_0 is the rotational reorientation time at zero viscosity. It is known that spherical approximation embedded in SED model is grossly in error and the shape of the probes is however, more

important. In reality, the exact shape of the solute molecule need not be spherical and there is a necessary to include a parameter, which should describe the exact shape of nonspherical probes. Hence, the equation for nonspherical molecule proposed by Perrin [Perrin, 1936] is given as follows

$$\tau_r = \frac{\eta V}{kT}(fC) \dots\dots\dots 6$$

where *f* is shape factor and is well specified, *C* is the boundary condition parameter dependent strongly on solute, solvent and concentration. The stick rotational reorientation time τ_{stick} can be written as [Roy *et al.*, 1993]

$$\tau_{stick} = \frac{2(\rho^2+1)(\rho^2-1)^{3/2}}{3\rho\left[(2\rho^2-1)\ln\{\rho+(\rho^2-1)^{1/2}\}-\rho(\rho^2-1)^{1/2}\right]} * \frac{\eta V}{kT} \dots\dots\dots 7$$

where ρ is the ratio of semi-major axis (*a*) to the semi-minor axis (*b*). For nonspherical molecules, *f* >1 and the magnitude of deviation of *f* from unity describes the degree of the nonspherical nature of the solute molecule. *C*, signifies the extent of coupling between the solute and the solvent and is known as the boundary condition parameter [Barbara *et al.*, 1990]. When the size of the rotating probe molecule is much bigger than that of the solvent molecule, the parameter *C*=1, signifies the stick boundary condition. In the stick limit, it is assumed that the first layer of the solvent molecules encircling the solute sticks to the solute and there is no relative velocity between them. However, when the probe molecule is of comparable size or smaller than the solvent molecule the value of *C* is in the range 0<*C*<1, which is known as slip boundary condition. The shape factor (*f*) and the coupling parameter (C) were estimated using semi-major and semi-minor axes of the probe molecule. The value of *C* for slip boundary conditions can be determined from the Tables of Hu and Zwanzig [Hu *et al.*, 1974]. The value of τ_{stick} can be calculated using Eq. 7.

MATERIALS AND METHODS

The laser dye, coumarin 519 (C519) was procured from Radiant Dyes Lasers GmbH, Germany and used as received. All the solvents employed (Aldrich, HPLC spectral grade) in this study were used without further purification. The absorption spectra of the probe were recorded using UV-Visible double beam ratio recording Spectrophotometer (Hitachi, model U-2800) and fluorescence spectra using Fluorescence Spectrophotometer (Horiba, model Fluoromax-4) at room temperature. The solute concentrations were maintained in the range of 10^{-5} to 10^{-6}M, to minimize the self absorption. The time resolved fluorescence measurements were carried out using an IBH fluorescence spectrometer (Scotland, U.K.) based on the time-correlated-single-photon-counting technique, described elsewhere [Das *et al.*, 2005]. The second harmonic (400 nm) output from the mode-locked femtosecond laser (Tsunami, Spectra Physics) was used as the excitation source. The instrument response function for TCSPC system is 50 ps. The data analysis was carried out by the software provided by IBH (DAS-6), which is based on reconvolution technique using nonlinear least-squares methods.

RESULTS AND DISCUSSION

The steady-state absorption and fluorescence spectra of the probe are shown in Fig. 2. The van der Waals volume (V) of C519 is estimated using Edward's atomic increment method [Edward *et al.*, 1970] and found to be 238.2 $Å^3$. The probe molecule is modeled as asymmetric ellipsoid since the axial radius of the respective molecule has different length. Longest end-to-end distance was taken as the long axis (2a) of the molecule and the axis perpendicular to the long axis, i.e., the short-in-plane axis (2b) of the probe was estimated using ChemSketch software. The semi-major and semi-minor axes are found to be 5.3Å and 3.7Å, respectively. The bond-to-bond distance was used to calculate the axial radius. A typical fluorescence decay
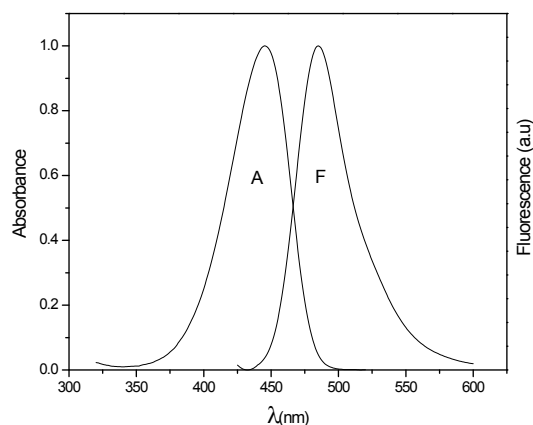
Fig. 2. Steady state absorption and fluorescence spectra of coumarin 519 in ethanol
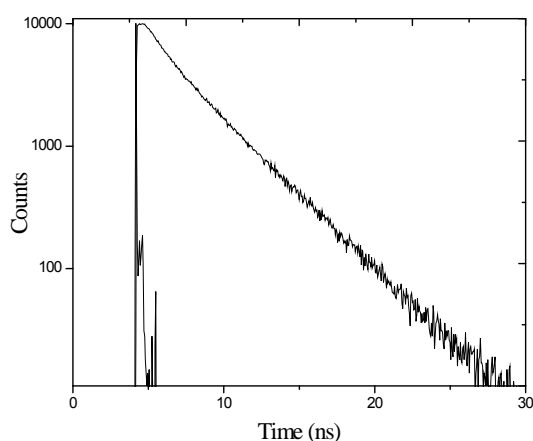

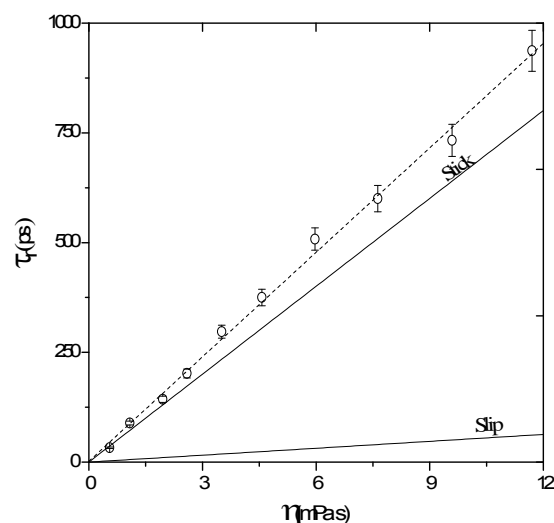**Fig. 3. Typical fluorescence decay curve of coumarin 519 in ethanol**

Fig. 4. Plot of rotational reorientation time (τ_r) of coumarin 519 as a function of viscosity (η) of the solvents. *Solid lines* **represent the theoretical stick** *(upper)* **and slip** *(lower)* **lines.** *Dashed line* **through the points** *(circles)* **with** *error bars* **represents the experimental line**

curve of C519 in ethanol is shown in Fig.3. The limiting anisotropy r_0 was measured by dissolving the solute in glycerol and by measuring the steady state anisotropy at low temperature. The limiting anisotropy (r_0) value is found to be 0.357±0.005, indicating that the absorption and emission dipole, form an angle of 15.53° with respect to each other. The experimentally determined steady-state anisotropies (r), fluorescence lifetimes (τ_f) and rotational reorientation times (τ_r) of C519 are tabulated in Table 1.

The average values of anisotropies r are in the range of 0.003 ± 0.001 to 0.072 ± 0.003 and the fluorescence lifetimes of this molecule vary in the range of 3.10–3.94 ns. From r, r_0 and τ_f, the reorientation times were obtained using Eq.2. Fig. 4 shows the variation of rotational reorientation times (τ_r) with solvent viscosity (η) for coumarin519, wherein it is seen that τ_r increases linearly with η from methanol to decanol in this case. Also it is interesting to note that τ_r values were found to be greater than those predicted by the SED hydrodynamic theory with stick boundary condition. The experimental results (Fig. 4) also indicate that C519 is rotating slower in alcohols. It may also be noted that the stick contribution increases from methanol to decanol.However there are experimental evidences of rotational re-orientation times with values higher than stick prediction i.e. super-stick behavior [Fleming *et al.*, 1976, von Jena *et al.*, 1979, von Jena *et al.*, 1981]. The super-stick behavior is generally attributed to large size of the molecules in that they experience greater friction. It is evident that such behavior of coumarin molecules of super-stick character has been observed in the earlier findings [Fleming *et al.*, 1976]. The fact that C519 rotates slower in the solvents employed establishes that the friction experienced by the probe molecule is predominantly hydrodynamic along with a share of dielectric friction. This may be attributed to the

Table 1. Steady-state anisotropy r, Fluorescence lifetime (τ_f) and rotational reorientation time (τ_r) of coumarin 519 molecule in alcohols

Solvents	$\eta(mPa\ s)^a$	$\langle r \rangle$	$\tau_f(ns)^b$	$\tau_r(ps)$
Methanol	0.55	0.003±0.001	3.93	33±05
Ethanol	1.08	0.010±0.001	3.10	89±09
Propanol	1.96	0.015±0.002	3.26	143±13
Butanol	2.59	0.021±0.002	3.24	202±18
Pentanol	3.55	0.025±0.001	3.94	297±24
Hexanol	4.59	0.035±0.002	3.45	375±31
Heptanol	5.87	0.043±0.003	3.71	508±40
Octanol	7.61	0.051±0.003	3.60	600±47
Nonanol	9.57	0.058±0.002	3.78	733±61
Decanol	11.78	0.072±0.003	3.71	937±59

[a] Viscosity data is from Ref. [Inamdar *et al.*, 2006]
[b] The error in the measured fluorescence lifetime is < 10%

presence of tertiary amino group and carboxylic groups, which are responsible for strong intermolecular hydrogen bonding and also with that of solvents enhancing the mechanical friction and resulting in slower rotation.

Conclusion

In the present paper we have studied the rotational diffusion dynamics of a polar molecule coumarin 519 in a series of alcohols by fluorescence depolarization method. On the basis of molecular dimensions, the probe is modeled as asymmetric ellipsoid. The rotational correlation times of the probe are seen to vary linearly as function of viscosity of the solvents used. The results show a tendency to follow super-stick behavior suggesting a strong interaction of the probe with surrounding solvent molecules. Hydrogen bonding between the probe and solvent molecules appears to be the predominant cause through considerable contribution from dielectric friction cannot be ruled out. Efforts to quantify the contribution of dielectric friction are underway.

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