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Rotational Diffusion of Coumarins in Aqueous DMSO

S.R. Inamdar · B.R. Gayathri · J.R. Mannekutla

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Abstract The rotational dynamics of four structurally similar polar molecules viz., coumarin 440, coumarin 450, coumarin 466 and coumarin 151 has been studied in binary mixtures comprising of dimethyl sulphoxide and water at room temperature using the steady state fluorescence depolarization method and time correlated single photon counting technique. The binary mixtures are characterized by the fact that at a particular composition the viscosity (η) of the solution reaches a maximum value that is higher than the viscosities of either of the two co-solvents. The dielectric properties of the solution change across the composition range and the qualitative features of the solvent relaxation dynamics in complex systems are known to differ from those in simple solutions. A hook type profile of rotational reorientation time (τ_r) vs viscosity (η) is obtained for all the solutes in dipolar aprotic mixture of dimethyl sulphoxide-water, with the rotational reorientation times being longer in organic solvent-rich zone, compared to the corresponding isoviscous point in water-rich zone due to strong hydrogen bonding. Fluorescence lifetimes as well as rotational reorientation times are sensitive to the composition of the binary solvent system under study than to the viscosity suggesting the

importance of local structure. The results are discussed in the light of hydrodynamic and dielectric friction models.

Keywords Binary solvent · Hydrogen bonding · Dielectric friction · Heterogeneity · Isoviscous · Hook profile

Introduction

The study of various mechanisms by which molecules reorient in condensed phases is one of the most challenging and active fields in spectroscopy. Investigation of rotational diffusion leads to valuable information on the effects of chemical interest like solvation, aggregation, hydrogen bonding, photochemical process, etc. Several experimental techniques such as NMR, EDR, Raman, dielectric relaxation, dynamic light scattering, fluorescence depolarization, etc. have been employed in the study of molecular motion.

The molecules rotating in liquids experience friction due to their continuous interaction with neighboring molecules. The studies using polar solutes in polar solvents have enlightened the concepts such as dielectric friction [1–4] and solute-solvent hydrogen bonding [5–9] in addition to the viscous drag. The dielectric friction arises because of the inability of the solvent molecules, encircling the polar probe molecule, 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. Under such circumstances, the observed friction, which is proportional to the measured reorientation time, is generally explained as a combination of mechanical and dielectric frictions. A solute molecule may also form hydrogen bond with the solvent molecule depending on the nature of the functional groups on the solute and the solvent, which enhances the volume of the probe molecule. This may

Dedicated to Professor M.I. Savadatti on his 77th Birthday.

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further impede the rotational motion leading to longer observed reorientation time.

The mixing of polar solvents provides an important class of chemical media wherein polarity can be controlled through changes in composition. In a binary mixture, change in the composition of the ingredients leads to variation in the solubility, polarizability, viscosity and other static and dynamic properties. However, the dielectric properties of polar mixtures depart significantly [10] from those obtainable from an ideal mixing of components. In the case of hydrogen bonding systems, such as DMSO-water mixtures, intermolecular correlations are strong and the dielectric properties of the mixture are simply not related to those of the separated components.

The aqueous DMSO solutions are quite interesting systems because they show nonlinear relationship between the bulk viscosity and the solvent composition. In the case of DMSO-water binary mixture, there is a rapid rise in the viscosity with a small addition of DMSO to water and the viscosity decay profile after the post peak point is gradual. The sharp increase in the viscosity with increasing concentration of DMSO is attributed to the formation of hydrogen bonding between water and DMSO [11]. From the viscosity data, it may be seen that there are two compositions of DMSO-water for which the viscosity is nearly the same and as per hydrodynamic theory the friction experienced by a rotating probe is expected to be the same at these compositions. This dual valuedness should manifest in reasonable mirror symmetry of the rotational reorientation time (τ_r) about the viscosity peak point. The viscosity of DMSO is slightly higher than twice that of water and at 40% mole composition of DMSO, the solvent mixture has a maximum value of viscosity of about 3.75 mPas, which is 1.87 times the viscosity of DMSO and nearly 4 times that of water.

The properties of a few binary solutions have been studied using theoretical calculations and molecular dynamics (MD) simulations [12–16]. The results have shown that the dynamical features in binary solutions are very much different from neat solutions and that the dynamics can be strongly affected by the properties of the solute. The dynamic properties in a binary mixture show exotic features, which pose interesting challenges to both theoreticians and experimentalists. Amongst them, the extrema observed in the composition dependence of excess viscosity [17, 18] and the inconsistent viscosity dependence of the rotational relaxation time [19] are the commonly observed features. The anomalous features in complex systems arise from the specific intermolecular interactions due to structural heterogeneities. The non-ideal behavior of the mixtures is due to the nature of interaction between different species constituting the mixture. In DMSO-water mixture, the partial negative charge on the oxygen atom of the dimethyl sulfoxide molecule forms hydrogen bonds with water

molecules, giving rise to a non-ideal behavior of the mixture [20]. This abnormal behavior of the viscosity in the binary mixtures arises from the formation of clusters. The prominent hydrophilic nature of DMSO makes it capable of forming strong and persistent hydrogen bonds with water through its oxygen atom [20, 21–23]. This leads to the formation of DMSO-water molecular aggregates of well-defined geometry, which are often held responsible for, the strong non-ideal mixing behavior manifested as maxima or minima in several physico-chemical properties [24–28]. The largest deviation from the ideal mixing occurs around 40% mole fraction of DMSO, suggesting the existence of stoichiometrically well defined DMSO-water 1:2 complexes. A number of molecular dynamics simulation studies [20, 29–31] and neutron diffraction experiments have indeed identified the structure of the DMSO-water 1:2 complex and linked many of the structural and dynamical features of DMSO-water mixtures to the presence of such aggregates. Of late, Borin and Skaf [31] have found from molecular dynamics simulations of DMSO-rich mixtures, another distinct type of aggregate consisting of two DMSO molecules linked by a central water molecule through H-bonding, which is expected to be the predominant form of molecular association between DMSO and water. This H-bonded complex is referred to as DMSO-water 2:1 aggregate.

The molecular rotational relaxation is an important probe of inter molecular coupling. The rotational relaxation time of a solute in a neat solvent varies linearly with viscosity whereas it is not so in case of binary solvent mixture as the composition of the mixture is changed. Alavi and Waldeck [32] studied the rotational diffusion of the dye molecule oxazine 118 chloride in two binary solvent systems as a function of temperature. When temperature is varied to change the viscosity of a given solvent mixture, a linear correlation is observed for the rotational relaxation time, with η/T according to SED predictions where η is the viscosity and T is the temperature of the solvent. The change in slope of the SED plot reflects either a change in the hydrodynamic boundary condition or a change in the amount of dielectric friction. The experimental results show a nonlinear dependence of the rotational diffusion on the solvent viscosity when the solvent composition is changed.

Gudgin et al. [33] studied the rotational relaxation of structurally similar probes cresyl violet and resorufin in binary solution comprising of DMSO and water. These molecules exhibit hydrodynamic nature in hydrogen bonding solvents but show entirely different curvilinear nature in binary system. Another study of three kinds of dyes—cresyl violet (a monocation), nilered (neutral but polar), and resorufin (a monoanion) carried out in a series of binary mixtures of hexamethylphosphoramide (HMPA)-water at 298 K [34] using the picosecond fluorescence depolarization spectroscopy resulted in a hook-type profile for all

three molecules. The present study is one such effort which investigates four structurally similar dye molecules in DMSO–water binary mixture by using fluorescence depolarization method and time correlated single photon counting technique. Binary aqueous mixtures are interesting systems to test the SED theory in view of the fact that the viscosity of the binary system exhibits a bivalued profile as a function of the composition of a solvent in water and at some intermediate composition, the viscosity being much higher than that of component solvents.

In this paper, we report the rotational diffusion studies of four structurally similar coumarin dyes viz., coumarin-440 (C440), coumarin-450 (C450), coumarin-466 (C466) and coumarin-151 (C151) in binary mixture of dimethyl sulphoxide and water. C466 possesses a -N-diethyl group at the seventh position whereas all other dyes in the present study possess amino groups at the seventh position in addition to carbonyl group. These structures are expected to affect the reorientation times due to the formation of hydrogen bonds with the solvent mixture. The rotational diffusion of fluorescent molecules in solvent mixtures has not been studied as extensively as in neat solvents. Thus, the structure and structural changes in the solvent environment around the solute in the mixed solvents are not fully understood. It is therefore important and imperative to investigate the rotational relaxation characteristics that are unique to the binary solvent mixtures.

Materials and methods

The laser dyes coumarin-440 (C440) and coumarin-450 (C450) were procured from Exciton Inc. (USA). Coumarin-466 (C466) and coumarin-151 (C151) were obtained from Lambda Physik Inc. (Germany). All the four dyes were used as received. The molecular structures of C440, C450, C466 and C151 are as shown in Fig. 1. The solvent

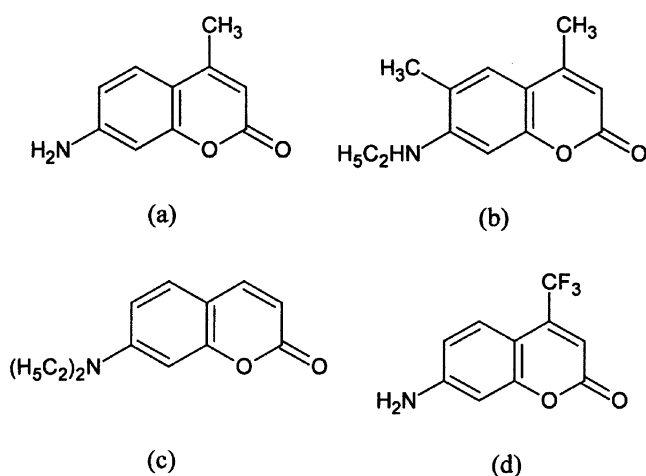


Fig. 1 The molecular structures of **a** C440, **b** C450, **c** C466 and **d** C151

dimethyl sulphoxide is obtained from Spectrochem (HPLC) and used without further purification. The triple distilled water (VITSIL, Model VQDD, India) is used for preparing aqueous mixture. The steady state absorption and emission spectra were recorded using Hitachi U-2800 UV-Vis double beam ratio spectrophotometer and Hitachi F-2000 spectrophotometer, respectively, at room temperature (298 K). The refractive indices of the solvent mixtures were measured using Abbe's refractometer (ATAGO-3T, Japan). The viscosities of the binary mixture have been measured by using Schott-Gerate viscometer (model AVS 350, Germany), as described earlier [35]. The recorded absorption and fluorescence wavelengths are accurate within ± 1 nm.

Rotational reorientation times of the probes in binary mixture were measured using steady state fluorescence depolarization technique [36]. For the vertically polarized excitation the steady state fluorescence anisotropy is defined as

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

where I_{\parallel} and I_{\perp} are the emission intensities polarized parallel and perpendicular to the excitation polarization, G is the instrumental parameter which corrects for polarization bias in the detection system and is given by $G = \frac{I_{HV}}{I_{HH}}$, 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 polarizers are maintained horizontal. If the decay of fluorescence and the decay of anisotropy are represented by single exponentials, then the reorientation time τ_r is given by

$$\tau_r = \frac{\tau_f}{\left[\left(\frac{r_0}{\langle r \rangle}\right) - 1\right]}, \quad (2)$$

where τ_f is the fluorescence lifetime and was recorded using time domain spectrometer employing time correlated single photon counting technique. r_0 is the limiting anisotropy when all the rotational motions are frozen. All the sample solutions were excited at 370 nm and anisotropy was measured at least six times before taking the average value $\langle r \rangle$.

The instrument used to measure the fluorescence lifetime has been described elsewhere [37]. In brief, the second harmonic light pulses with wavelength of 370 nm were derived from the output of a tunable Ti-sapphire (720 to 980 nm) femtosecond laser (Coherent, Mira) with a repetition rate of 3.8 MHz. The emission was collected with a resolution of 4 nm at magic angle through a monochromator equipped with a holographic grating blazed at 1,200 grooves/mm. The TCSPC system has been obtained from Edinburgh Instruments (LifeSpec-Red); the detector is a thermoelectric cooled photomultiplier tube (Hamamatsu H7422). The instrument response function

(IRF) of the TCSPC system is ~ 180 ps. The fluorescence decays were deconvoluted from the IRF using F900 software.

Theoretical models

Although a number of theories have been developed to describe the rotational diffusion kinetics of molecules in liquids, the theoretical modeling of molecular reorientation in liquids and its correlation with experimental data is far from satisfactory. The general approach is to experimentally measure the reorientation time of a solute molecule in a liquid and model its rotation using the diffusion based theories of Stokes-Einstein-Debye (SED) [38, 39]. This theory, originally proposed for macroscopic objects, has been applied with reasonable success at molecular level. According to it, the solvent is treated as a structureless continuum and is characterized by its bulk properties. This theory describes the rotational diffusion of medium sized molecules fairly accurately when the coupling between the solute and the solvent is purely mechanical or hydrodynamic in nature. SED model relates the rotational reorientation time (τ_r) of a sphere in a continuous homogeneous fluid to the macroscopic viscosity (η) of the solvent. Accordingly the reorientation time τ_r of a rotating molecule is given by

$$\tau_r = \frac{\eta V f C}{kT}, \quad (3)$$

where V is the volume of the solute molecule, T the absolute temperature, k the Boltzmann constant and f the shape factor introduced by Perrin [40] to take care of non-spherical shape of the solute molecule. The constant C determines the extent of coupling between the rotating probe molecule and solvent molecules. When both the parameters f and C are set equal to unity, Eq. (3) reduces to the original form of the SED equation. For a prolate molecule f_{stick} is given by

$$f_{stick} = \frac{2}{3} \frac{1 - \rho^4}{\left[\frac{(2-\rho^2)}{(1-\rho^2)^{1/2}} \rho^2 \ln \frac{1+(1-\rho^2)^{1/2}}{\rho} \right] - \rho^2}, \quad (4)$$

where ρ is the ratio of the semi-major axis to semi-minor axis.

Note that when the size of the rotating probe molecule is much bigger than the solvent molecule, the value of $C=1$ which implies stick boundary condition wherein it is assumed that the first layer of the solvent molecules encircling the solute sticks to it so that there is no relative velocity between them. However, when the probe molecule is of size comparable to or smaller than solvent molecule the value of C lies in the range $0 < C < 1$, which is known as slip boundary condition. The value of C for slip boundary condition can be determined from the calculations of Hu

and Zwanzig [41]. The exact value of C depends on the axial ratio of the probe molecules. Using these values of f and C in Eq. (3) rotational reorientation time can be evaluated.

Consideration of various aspects of the molecular nature of solvents yields modified values for C in the quasihydrodynamic models. The hydrodynamic theories, take into consideration only the size of the solute molecule and not that of the solvent molecules. The size effects of both solute and solvent were incorporated in the quasihydrodynamic model proposed by Gierer and Wirtz (GW) [42] which visualizes the solvent to be made up of concentric shells of spherical particles surrounding the spherical probe molecule at the center. Consequently, the liquid in each shell moves at a constant angular velocity and the velocity of the successive shells decreases with the distance from the surface of the probe molecule, as though the flow between the successive shells were laminar. The angular velocity vanishes at larger distances. The angular velocity ω_1 of the first solvation shell is related to angular velocity ω_o of the probe molecule by means of a sticking factor σ and is given by

$$\omega_1 = \sigma \omega_o \quad (5)$$

where $\sigma=1$ corresponds to stick boundary condition and σ is related to the ratio of the solute to solvent size, and is given by

$$\sigma = \left[1 + 6 \left(\frac{V_s}{V_p} \right)^{1/3} C_o \right]^{-1} \quad (6)$$

where

$$C_o = \left\{ \frac{6(V_s/V_p)^{1/3}}{[1 + 2(V_s/V_p)^{1/3}]^4} + \frac{1}{[1 + 4(V_s/V_p)^{1/3}]^3} \right\}^{-1} \quad (7)$$

V_s and V_p being the volume of the solvent and probe, respectively. According to GW theory the boundary condition, C_{GW} is obtained by considering how the angular velocity of the solvent molecules in successive shells surrounding the probe decreases as a function of distance from the probe molecule and is given by

$$C_{GW} = \sigma C_o. \quad (8)$$

Although this theory takes into consideration the size of the solvent molecules, it ignores the cavities or free spaces created by solvents around the probe molecule. These criteria were incorporated in a more recent theory proposed by Dote, Kivelson and Schwartz (DKS) [43]. If the size of the solute is comparable to free volume of the solvents the coupling between solute and solvent will become weak, resulting in decreased friction experienced by the probe

molecule. Accordingly, the solute–solvent coupling parameter C_{DKS} , is given by

$$C_{DKS} = (1 + \gamma/\phi)^{-1}, \quad (9)$$

where γ/ϕ is a measure of the ratio of the free volume of the solvent to the effective size of the solute molecule and ϕ is the ratio of the rotation time predicted by slip hydrodynamics to stick prediction for the sphere of the same volume. γ is given by

$$\gamma = \frac{\Delta V}{V_p} \left[4 \left(\frac{V_p}{V_s} \right)^{2/3} + 1 \right], \quad (10)$$

with ΔV being the smallest volume of the free space per solvent molecule and is empirically related to viscosity, Hilderbrands-Batschinski parameter B , and isothermal compressibility k_T , of the solvent by the following expression:

$$\Delta V = Bk_T\eta/kT \quad (11)$$

This expression is valid for regular solvents such as alkanes, and for associative solvents like alcohols the volume of free space ΔV is calculated empirically using the expression $\Delta V = V_m - V_s$ with V_m being the ratio of solvent molar volume to Avogadro's number and V_s the van der Waals volume of the solvent. The value of ΔV thus obtained was used to calculate C_{DKS} . However, for binary mixtures, either the molar volume or the Hilderbrands-Batschinski parameter B is not known. Therefore we have used GW theory to evaluate the reorientation times.

As the concentration of DMSO in water increases, the van der Waals volume (V_s) of the solvent mixture also increases. This volume V_s at a particular composition was calculated using the relation $V_s = \chi_{DMSO}V_{DMSO} + \chi_{water}V_{water}$, where χ_{DMSO} and χ_{water} are the mole fractions of DMSO and water, respectively, and V_{DMSO} and V_{water} are the van der Waals volumes of DMSO and water, respectively. The parameters σ and C_o were calculated using the volumes of the solvent mixture and of the probe molecule from Eqs. (6) and (7), respectively. The coupling parameter C_{GW} was obtained using Eq. (8) and the rotational reorientation time was calculated using Eq. (3) by replacing the coupling parameter C by C_{GW} .

A polar molecule dissolved in polar solvents rotates much slower than that predicted by SED theory which is explained using solventberg model that assumes that there is a specific solute–solvent interaction like hydrogen bonding causing an increase in the volume of the solute. Such an enhancement of the volume causes the molecule to automatically rotate slower. The rotational diffusion of a number of polar solutes in polar solvents has been studied to stress the importance of dielectric friction and also to test various theories of dielectric friction. Within a dielectric continuum model for the solvent,

the contribution to the rotational reorientation time due to dielectric friction, τ_{DF} is given by [34]

$$\tau_{DF} = \frac{\mu_e^2}{a_0^3 kT} \frac{\varepsilon - 1}{(2\varepsilon + 1)^2} \tau_D, \quad (12)$$

where μ_e is the dipole moment of the solute in the excited state, ε the dielectric constant, τ_D the Debye dielectric relaxation time of the solvent, k the Boltzmann's constant and T the absolute temperature. A polar molecule, rotating in a polar solvent, experiences friction due to hydrodynamic as well as dielectric effects. Hence the total rotational reorientation time for the solute can be written as

$$\tau_r = \tau_h + \tau_{DF} = \frac{\eta V_f C}{kT} + \frac{\mu_e^2}{a_0^3 kT} \frac{\varepsilon - 1}{(2\varepsilon + 1)^2} \tau_D. \quad (13)$$

If the observed rotational reorientation time differs considerably from the sum of the contributions due to hydrodynamic and dielectric frictions, then the difference should be properly attributed to solute–solvent interactions. Since the solutes used in the present work are dipolar, it is essential to include the contribution due to dielectric friction when their motions in polar solvents are being addressed. The magnitude of dielectric friction contribution to the rotational reorientation time crucially depends on the dipole moment of the dye molecule in the first excited electronic state S_1 , the cavity radius a_o , dielectric constant ε and the Debye relaxation time τ_D of the solvent.

Results and discussion

The ground and the excited state dipole moments of C440, C450, C466 and C151 were determined by employing

Table 1 The refractive index (n), coefficient of viscosity (η), dielectric constant (ε) and Debye relaxation time (τ_D) along with the volume of the solvent mixture (V_s) for different mole fraction of DMSO

Mole fraction of DMSO	V_s (\AA^3)	n	η (mPas)	ε	τ_D (ps)
1.0	72.200	1.47	2.00	48.11	25.04
0.828	63.325	1.45	2.30	54.07	26.82
0.695	56.462	1.44	2.62	58.46	33.99
0.503	46.555	1.41	3.38	64.70	47.45
0.372	39.795	1.39	3.75	68.73	49.20
0.275	34.790	1.37	3.50	71.47	44.97
0.202	31.023	1.36	2.90	73.33	38.59
0.145	28.082	1.35	2.40	74.48	31.39
0.098	25.657	1.34	1.80	76.02	26.29
0.06	23.696	1.34	1.40	77.02	19.41
0.0	20.600	1.33	0.89	77.56	9.52

Dielectric constant (ε) and Debye relaxation time (τ_D) taken from the Ref. [11]

Table 2 Experimentally determined ground and excited state dipole moments for C440, C450, C466 and C151

Solute molecule	μ_g	μ_e
	(D)	(D)
C440	4.23	7.20
C450	5.62	8.58
C466	3.15	6.35
C151	3.63	6.88

solvatochromic shift method [44] in binary solvents, comprising of dimethyl sulphoxide (DMSO) and water at room temperature. The dielectric constant ϵ and Debye relaxation time τ_D were obtained from the literature [11]. These values along with the calculated values of the volumes and measured values of viscosities of the solvent mixtures are given in Table 1.

By using experimentally determined Stokes shift and the calculated values of solvent polarity parameters the ground and excited state dipole moments were calculated. Experimentally determined values of the excited state dipole moments were used in the estimation of the dielectric friction contribution in the case of all four coumarins. The ground and excited state dipole moments obtained experimentally are presented in Table 2.

The limiting anisotropy r_0 was measured by dissolving the solutes in glycerol and by measuring the steady state anisotropy at low temperature. It gives the orientation of the absorption and emission transition dipoles with respect to each other. The values of r_0 range from -0.2 to 0.4 with r_0 being 0.4 when the absorption and emission dipoles are parallel and -0.2 when they are perpendicular. The limiting anisotropy obtained for C440, C450, C466 and C151 are

0.372 ± 0.002 , 0.357 ± 0.005 , 0.378 ± 0.002 and 0.362 ± 0.003 , respectively, indicating that the absorption and emission dipoles are at angles of 12.47° , 15.53° , 13.98° and 14.58° with respect to each other. From the anisotropy $\langle r \rangle$, the limiting anisotropy, r_0 , and lifetime, τ_f , the reorientation times were obtained using Eq. (2). The van der Waals volume, calculated using Edward's atomic increment method [45], was found to be 152 \AA^3 , 204 \AA^3 , 204 \AA^3 and 165 \AA^3 , respectively, for C440, C450, C466 and C151. The major-axes (a) of the solute molecule was taken as the distance between the two farthest atoms [46] and were found to be 4.15 \AA , 5.32 \AA , 5.11 \AA and 4.30 \AA , respectively, for C440, C450, C466 and C151. The semi-minor axes (b) of the molecules were determined by using the values of semi major axes and van der Waals volume (V_w) by taking the ellipsoid volume equal to van der Waals volume [47, 48] using $b = \sqrt{3V_w/4\pi a}$ and were found to be 2.96 \AA , 3.03 \AA , 3.09 \AA and 3.03 \AA respectively, for the above probes. Using the ratio of semi-major to semi-minor axis, the shape factor f and the friction coefficient C were evaluated. Fluorescence lifetime (τ_f) and rotational reorientation times (τ_r) determined for all the solutes are listed in Table 3.

The rotational reorientation time of a solute in a solvent is in a way an index of molecular friction. Theoretically calculated values of the rotational reorientation times are tabulated in Table 4 and Table 5. Although the rotational reorientation time due to dielectric friction is smaller than that due to mechanical friction a realistic estimation can be obtained by considering both the contributions. Figure 2(a) and (b) represent the variation of rotational reorientation time (τ_r) with viscosity (η) along with theoretical profile including the viscous and the dielectric contribution for all the probes, which clearly indicate a non-hydrodynamic

Table 3 The experimentally determined fluorescence lifetime (τ_f) and the rotational reorientation time (τ_r) of C440, C450, C466 and C151

Mole fraction of DMSO	η (mPas)	C440		C450		C466		C151	
		τ_f (ns)	τ_r (ps)	τ_f (ns)	τ_r (ps)	τ_f (ns)	τ_r (ps)	τ_f (ns)	τ_r (ps)
1.00	2.00	2.65	81±6	3.33	136±11	2.27	104±8	4.66	91±7
0.828	2.30	3.47	116±9	3.36	158±13	1.73	171±14	3.99	113±9
0.695	2.62	3.84	139±11	3.12	165±13	1.26	181±14	5.21	118±9
0.503	3.38	4.07	147±12	3.77	177±14	0.70	149±12	4.80	122±10
0.372	3.75	3.49	116±9	3.82	110±9	0.58	128±10	4.16	94±8
0.275	3.50	4.40	84±7	4.17	108±9	0.44	89±7	4.62	78±6
0.202	2.90	3.97	65±5	3.70	85±7	0.36	69±6	4.56	64±5
0.145	2.40	3.75	51±4	4.44	76±6	0.39	65±5	4.03	45±4
0.098	1.80	3.97	43±3	4.28	61±5	0.31	55±4	4.45	41±3
0.06	1.40	3.94	32±3	4.42	50±4	0.29	49±4	3.86	30±2
0.00	0.89	4.27	23±2	4.60	39±3	0.24	39±3	3.85	24±2

The error in the fluorescence lifetime (τ_f) is <10%

Table 4 Theoretically calculated rotational reorientation times for C440 and C450

Mole fraction of DMSO	η (mPas)	C440					C450				
		τ_{rstick}^{SED} (ps)	τ_{rslip}^{SED} (ps)	$\tau_{rstick+DF}^{SED}$ (ps)	$\tau_{rslip+DF}^{SED}$ (ps)	τ_r^{GW} (ps)	τ_{rstick}^{SED} (ps)	τ_{rslip}^{SED} (ps)	$\tau_{rstick+DF}^{SED}$ (ps)	$\tau_{rslip+DF}^{SED}$ (ps)	τ_r^{GW} (ps)
1.0	2.00	84	6	125	47	18	133	24	177	68	30
0.828	2.30	97	7	136	46	21	153	28	195	70	36
0.695	2.62	110	8	157	55	25	174	31	223	80	43
0.503	3.38	142	10	201	69	34	225	40	287	102	58
0.372	3.75	158	11	215	68	39	249	45	310	106	68
0.275	3.50	147	10	198	61	38	233	42	286	95	66
0.202	2.90	122	9	164	51	33	193	35	238	80	57
0.145	2.40	101	7	135	41	28	160	29	195	64	48
0.098	1.80	76	5	104	33	22	120	22	149	51	37
0.06	1.40	59	4	79	24	17	93	17	115	39	29
0.0	0.89	37	3	47	13	11	59	11	70	22	19

behavior. Experimentally obtained results of all the probes under study show a hairpin profiles bent upwards. The reorientation times gradually increases as a function of viscosity up to the peak viscous value. They decrease after the solvent mixture exhibits a reduction in viscosity after the peak value. Thus all the probes exhibit different rotational reorientation times for isoviscous points. It is interesting to note that, the reorientation times are longer in the DMSO rich region compared to the water rich zone. The experimentally obtained τ_r values at isoviscous points differ greatly in contrast to those estimated from theory where a change of less than 10–15% is noted. Also, the probes experience a greater friction in the organic solvent rich zone as against the water rich zone. This trend is clearly brought out by experimental values and all the theoretical models except the GW model. The studies of the rotational diffusion of the dye molecules in binary solvents have showed that the rotational relaxation time does not

necessarily scale linearly with viscosity when the solvent composition is changed. These observations can be seen as a manifestation of solvent structure on time scales similar to or longer than the time scale of solute rotation or as resulting from a change in the dielectric friction through the composition of solvent mixture. In some cases these observations have been interpreted as a breakdown of the hydrodynamic approximation. The rotational diffusion studies of the dye molecule oxazine 118 in two binary solvent systems as a function of temperature have showed a nonlinear dependence of the rotational diffusion on the solvent viscosity when the solvent composition is changed [19].

One of the important observations is that even though C440 possessing amino group at the seventh position with a capability of forming stronger hydrogen bond with the binary mixture rotates faster than C466 which has N-diethyl group at the seventh position. In order to explain this

Table 5 Theoretically calculated rotational reorientation times for C466 and C151

Mole fraction of DMSO	η (m Pas)	C466					C151				
		τ_{rstick}^{SED} (ps)	τ_{rslip}^{SED} (ps)	$\tau_{rstick+DF}^{SED}$ (ps)	$\tau_{rslip+DF}^{SED}$ (ps)	τ_r^{GW} (ps)	τ_{rstick}^{SED} (ps)	τ_{rslip}^{SED} (ps)	$\tau_{rstick+DF}^{SED}$ (ps)	$\tau_{rslip+DF}^{SED}$ (ps)	τ_r^{GW} (ps)
1.0	2.00	127	18	151	42	29	92	6	127	41	20
0.828	2.30	146	20	169	43	35	106	7	139	40	24
0.695	2.62	166	23	193	50	41	121	8	160	47	28
0.503	3.38	215	30	249	64	56	156	11	205	62	38
0.372	3.75	238	33	271	66	65	173	12	221	60	44
0.275	3.50	222	31	252	61	63	161	11	204	54	43
0.202	2.90	184	26	209	51	54	134	9	169	44	37
0.145	2.40	152	21	172	41	46	111	8	139	36	31
0.098	1.80	114	16	130	32	35	83	6	106	29	24
0.06	1.40	89	12	101	24	28	65	5	82	22	19
0.0	0.89	57	8	62	13	19	41	3	49	11	13

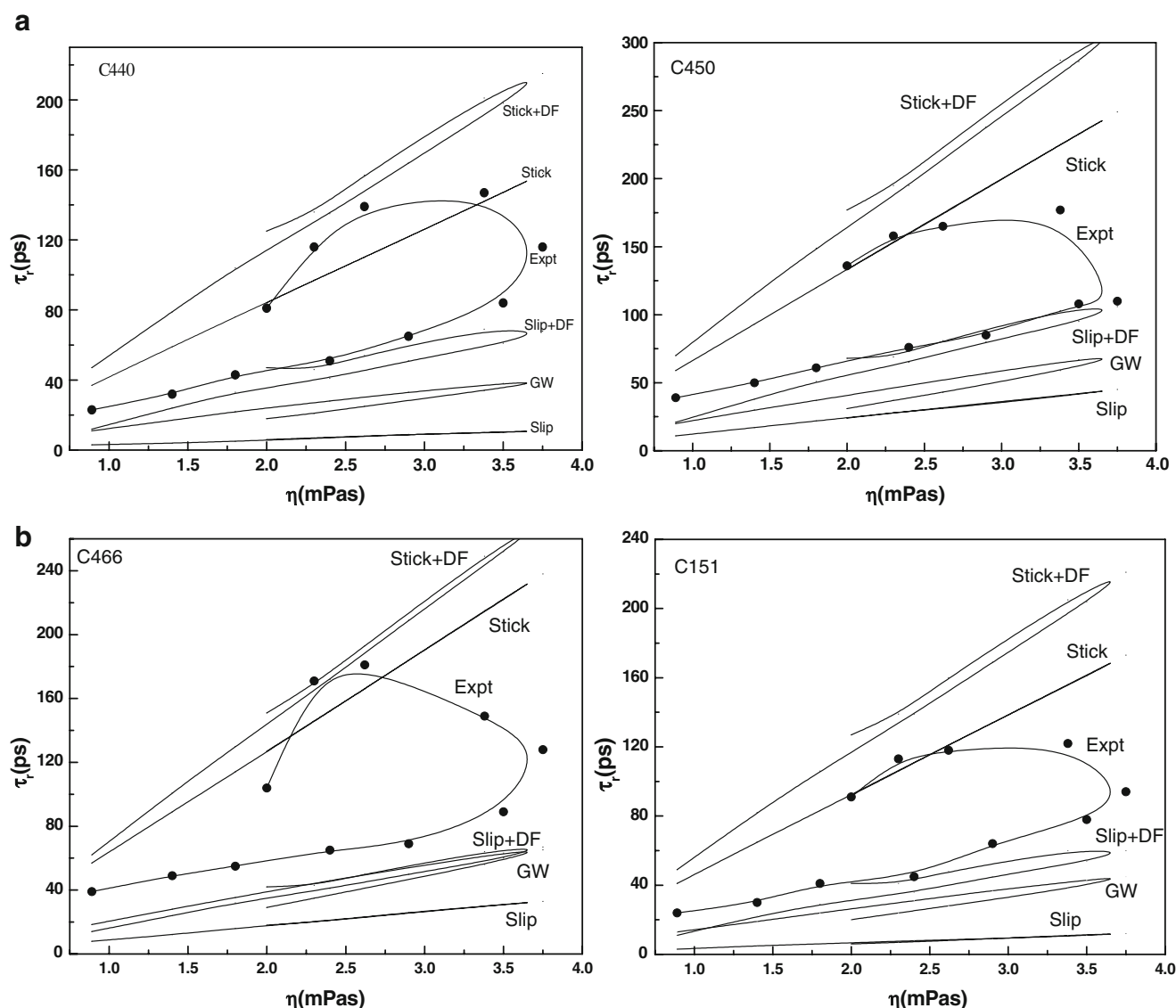


Fig. 2 **a** Plots of rotational reorientation time (τ_r) vs. viscosity (η) along with theoretical profile including the viscous and the dielectric contribution for C440 and C450 probes. **b** Plots of rotational

reorientation time (τ_r) vs. viscosity (η) along with theoretical profile including the viscous and the dielectric contribution for C466 and C151 probes

aspect, the rotational reorientation times of these two solutes were measured in aprotic solvent environment like formamide, dimethyl formamide (DMF) and in N-methyl formamide (NMF). The rotational relaxation time for C466 as a probe molecule was 138 ps in formamide, 63 ps in DMF and 223 ps in NMF, whereas for C440 the rotational relaxation time was 130 ps, 44 ps, and 58 ps, respectively, for these solvents. Experimental results thus showed that C466 rotates slower even in aprotic solvents compared to that of C440 establishing that the friction experienced by C466 is predominantly hydrodynamic compared to C440. Another interesting result is that C450 is rotating slower than C440 and C151. This may be attributed to the formation of hydrogen bonds by the primary amino group of C450 which are stronger compared to those formed by

the secondary amino group of C440 and C151 with the binary mixture. In addition to this, the size of C450 is about 25–30% more than the other two probes, which will enhance the mechanical friction resulting in slower rotation.

The linear variation of the rotational reorientation time as a function of viscosity from pure water to a composition of the binary mixture when the viscosity reaches a peak is in accordance with the SED theory, though the theory does not account for the large curvature in the profile. The theoretical SED stick line shows a sharp hairpin profile. The incorporation of the dielectric friction contribution qualitatively mimics the observed profile, with the rotational reorientation time being slightly longer in the post peak viscosity DMSO rich zone. The fact that a continuum theory without the consideration of any molecular features

could reproduce the gross features of the observed profile of τ_r vs. η , is noteworthy. However, the experimentally observed profile bent upwards indicates that the rotational reorientation times in the DMSO rich zone are considerably longer than those for the corresponding isoviscous point in the water rich zone. The theoretical models also reproduce this trend though qualitatively. However, the GW model invariably predicts a reduced friction for all the probes and depicts a hairpin profile bending downwards, thus fails to explain the observed results in the DMSO rich zone (Fig. 2(a) and (b)) and it underestimates the friction experienced by the probe. The pronounced difference in the rotational reorientation time at the isoviscous points can be explained on the basis of solvation. It is indicative of the fact that at the isoviscous points the microstructural features in the binary mixture could be different. The dual valuedness of τ_r at isoviscous points is also due to different contributions of dielectric friction at these two points.

Beddard et al. [19] have reported different rotational relaxation times of the dye cresyl violet in ethanol-water mixture at the iso-viscous points i.e., at the same viscosity but at different compositions. The observed re-entrance type behavior of the orientational relaxation time with the variation of viscosity could not be explained only in terms of non-ideality in viscosity exhibited by the binary mixture. The authors also opined that such behaviour is strongly dependent on the specific interaction of the solute with the solvents. This is because in a system where solute interacts differently with different species in a binary mixture, its rotational relaxation will depend more on the composition than on the viscosity of the binary mixture. The role of specific interaction on the orientational dynamics has been discussed and the effect has been included in the SED relation by changing the boundary condition. We find that all the probe molecules, used in our investigation show a similar re-entrance trend in the plots of τ_r vs. η . Our results are in conformity with the observations made by Beddard et al. [19]. Thus, it reaffirms that for a solute dissolved in a binary mixture, its rotational relaxation depends more on the composition than on the viscosity of the binary mixture. Further, a graph of C_{observed} (calculated from measured τ_r) v/s. % mole fraction of DMSO for all the probes is given in Fig. 3. It may be seen that C_{observed} does not vary linearly with composition, which further supports this aspect. The re-entrant type behavior strongly depends upon the interactions of the solute with the two different species in the solvent environment. The differences in the τ_r values at isoviscous points in the organic solvent and water rich zones are quite large and are more prominent in case of C466. This is possible partly due to the sensitivity of fluorescence lifetimes of this probe to the composition of the solvents. It is of interest to note that the τ_r values are higher in

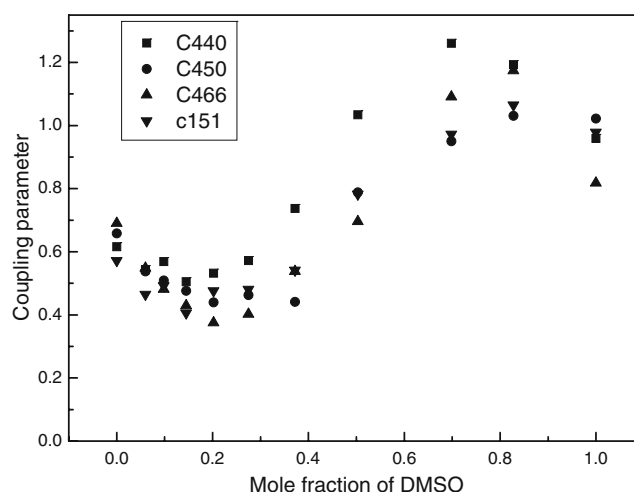


Fig. 3 Variation of coupling parameter with mole fraction of DMSO

the DMSO rich zone than in water rich zone and they systematically decrease as function of decreasing mole fraction of DMSO. The other three probes do not exhibit such an order where fluorescence lifetimes do not exhibit a specific order with respect to neither the composition nor the viscosity of the solvent system under study. Yet all the models employed in the present study fail to account for these.

Conclusion

The effects of anomalous features of dimethyl sulphoxide (DMSO) and water binary solution on the rotational diffusion of the aforesaid coumarin dyes were studied spectroscopically. The anomalous features associated with viscosity of the mixture are mostly due to the heterogeneity of the binary solution at the molecular level. We have shown that the nonlinear trend in the rotational relaxation time at a given temperature could be explained as due to a change in the hydrodynamic boundary condition. The variation of a boundary condition as a function of solvent composition was used as an alternate model to explain the rotational dynamics of a solute in binary mixtures. Our investigations confirm that the inclusion of the dielectric friction, using available models, enhances the agreement between the experiment and theory. The two different values of the rotational reorientation time at the isoviscous points near the organic solvent rich region were attributed to different contributions of dielectric friction at these two compositions as well as to strong hydrogen bonding. Solvation effects are also important in explaining the still persisting difference between the observed and theoretical values in the viscosity range studied above.

The rotational reorientation dynamics observed in the binary mixtures has no obvious correlations with the bulk viscosity of the aqueous DMSO binary solutions. The results are influenced by the local molecular structures of the binary solutions. Theoretical studies need to be taken up in this aspect by invoking the molecularity of the binary solvent systems under study. Further investigations of such binary mixtures sans a diffusing probe are likely to throw light on the properties of such highly non-ideal liquids.

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