

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Rotational Dynamics of Nonpolar and Dipolar Molecules in Polar and Binary Solvent Mixtures

Sanjeev R. Inamdar
*Laser Spectroscopy Programme,
 Department of Physics,
 Karnatak University, Dharwad
 India*

1. Introduction

The absorption of photons by a molecule leads to its excitation. An electronically excited molecule can lose its energy by emission of ultraviolet, visible, infrared radiation or by collision with the surrounding matter. Luminescence is thus the emission of photons from excited electronic energy levels of molecules. The energy difference between the initial and the final electronic states is emitted as fluorescence or phosphorescence (Lakowicz, 2006). Fluorescence is a spin-allowed radiative transition between two states of the same multiplicity (e.g., $S_1 \rightarrow S_0$) whereas; phosphorescence is a spin-forbidden radiative transition between two states of different multiplicity (e.g., $T_1 \rightarrow S_0$).

The mechanisms by which electronically excited molecules relax to ground state are given by the Jablonski diagram as shown in Fig. 1. The absorption of a photon takes a molecule from ground state (singlet state, S_0) to either first excited state (singlet state, S_1) or second

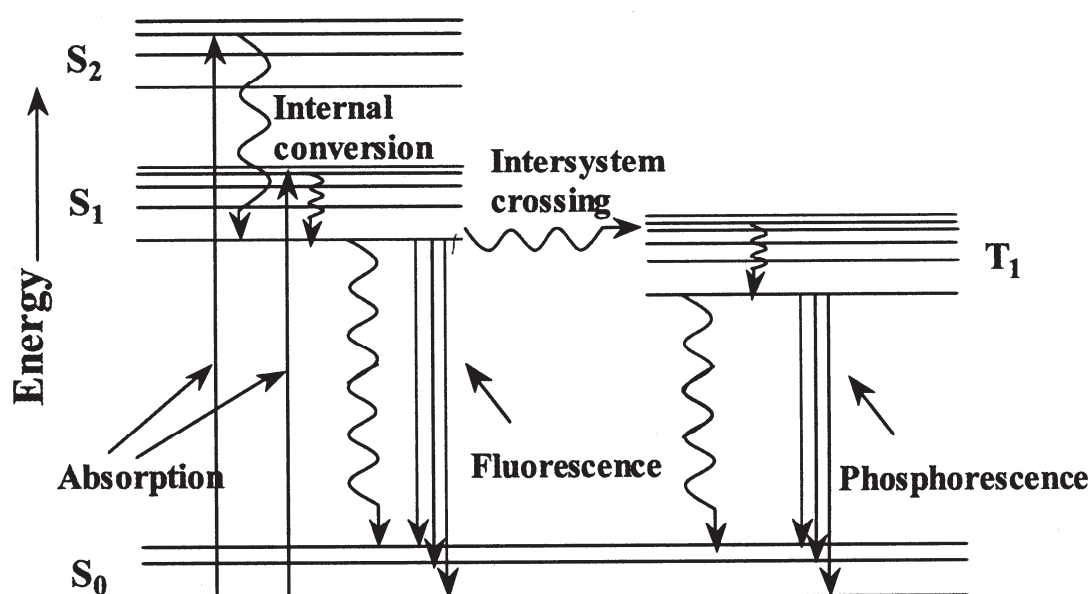


Fig. 1. Jablonski diagram of transitions among various electronic energy levels

excited state (S_2). The excited molecule then relaxes to the lowest vibronic level of the first excited state through internal conversion (IC), which generally occurs within 10^{-12} s or less. Since fluorescence lifetimes are typically near 10^{-8} s, IC is generally complete prior to emission. Now it can relax from the singlet excited state to the ground state via three mechanisms. First by emitting a photon (radiative process), second without emitting photon (nonradiative mechanism) and third it goes to a triplet state (T_1) by intersystem crossing (ISC) which also is a nonradiative process. The transition from triplet (T_1) to ground singlet state is forbidden and hence is a very slow process relative to fluorescence. Emission from T_1 is called phosphorescence and generally is shifted to longer wavelength relative to the fluorescence.

In fluorescence spectroscopy the observed spectral intensity is a function of two variables: the excitation wavelength (λ_{ex}) and the emission wavelength (λ_{em}). The fluorescence property of a compound is conventionally studied by examining both the excitation spectrum and the emission spectrum. The intensity vs. wavelength plot of the fluorescence spectrum obtained is characteristic of a fluorophore and sensitive to its local surrounding environment. It is consequentially used to probe structure of the local environment. Generally, the wavelength of maximum fluorescence intensity is shifted to longer wavelength relative to the wavelength of its absorption maximum. The difference between these two wavelengths, known as Stokes' shift, arises because of the relaxation from the initially excited state to the 'ground' vibronic level of S_1 which involves a loss of energy. Further loss of energy is due to the transitions from S_1 to higher vibrational levels of the ground state S_0 . The Stokes' shift further increases because of general solvent effects. The energy difference between the absorption maximum (ν_a) and the emission maximum (ν_f) is given by Lippert equation (Birks, 1970) in which the energy difference ($\nu_a - \nu_f$) of a fluorophore as a function of the refractive index (n) and dielectric constant (ϵ) of the solvent is related as

$$\nu_a - \nu_f \approx \frac{2}{hc} \left[\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right] \frac{(\mu^* - \mu)^2}{a^3} + const \quad (1)$$

where h is the Planck's constant, c the velocity of light and a is the radius of the cavity in which the fluorophore resides. Also, μ and μ^* are the ground and excited state dipole moments, respectively.

Fluorescence emission is generally independent of excitation wavelength. This is because of the rapid relaxation to the lowest vibrational level of S_1 prior to emission, irrespective of excitation to any higher electronic and vibrational levels. Excitation on the extreme red edge of the absorption spectrum frequently results in a red-shifted emission. The red-shift occurs because red-edge excitation selects those fluorophores which are more strongly interacting with the solvent (solvation dynamics) (Demchenko, 2002). The red-edge effect can also be thought as ground state heterogeneity, which is common in most complex systems like a probe distribution in microheterogeneous media. In the case of ground state heterogeneity or the presence of multiple species in the ground state, the fluorescence emission spectrum is dependent on the excitation wavelength and the fluorescence excitation spectrum is dependent on the emission wavelength. Also fluorescence excitation spectrum observed for a given emission wavelength differs from that of the absorption spectrum for heterogeneous system. The large spectral width of the emission spectrum compared to absorption spectral width is also due to the presence of multiple species in the excited state. Fluorescence

emission spectrum is generally a mirror image of the absorption spectrum (S_0 to S_1 transition).

1.1 Steady-state and time resolved fluorescence

Fluorescence measurements can be broadly classified into two types of measurements: steady-state and time-resolved. Steady-state measurements, the most common type, are those performed with constant illumination and observation. The sample is illuminated with a continuous beam of light, and the intensity or emission spectrum is recorded as function of wavelength. When the sample is first exposed to light steady state is reached almost immediately. Because of the ns timescale of fluorescence, most measurements employ steady-state method. The second type of measurement is time-resolved method which is used for measuring intensity decays or anisotropy decays. For these measurements the sample is exposed to a pulse of light, where the pulse width is typically shorter than the decay time of the sample. The intensity decay is recorded with a high-speed detection system that permits the intensity or anisotropy to be measured on the ns timescale.

1.2 Fluorescence anisotropy

The photoselection of fluorescent probe by polarized light offers the opportunity to study some relevant processes occurring at molecular level in heterogeneous systems. The fluorescence, emitted from the samples excited with polarized light, is also polarized. This polarization is due to the photoselection of the fluorophores according to their orientation relative to the direction of the polarized excitation. This photoselection is proportional to the square of the cosine of the angle between the absorption dipole of the fluorophore and the axis of polarization of the excitation light. The orientational anisotropic distribution of the excited fluorophore population relaxes by rotational diffusion of the fluorophores and excitation energy transfer to the surrounding acceptor molecule. The polarized fluorescence emission becomes depolarized by such processes. The fluorescence anisotropy measurements reveal the average angular displacement of the fluorophore, which occurs between absorption and subsequent emission of a photon. The degree of polarization, P , and steady state fluorescence anisotropy r , are thus respectively given by equations (Lakowicz, 2006)

$$P = \frac{I_{||} - I_{\perp}}{I_{||} + I_{\perp}} \quad (2)$$

$$r = \frac{I_{||} - I_{\perp}}{I_{||} + 2I_{\perp}} \quad (3)$$

where $I_{||}$ and I_{\perp} represent the fluorescence intensities when the orientation of the emission polarizer is parallel and perpendicular to the orientation of the excitation polarizer, respectively. The fluorescence anisotropy (r) is a measure of the average depolarization during the lifetime of the excited fluorophore under steady-state conditions. A steady-state observation is simply an average of the time-resolved phenomena over the intensity decay of the sample. But the time resolved measurements of fluorescence anisotropy using ultrafast polarized excitation source (laser) give an insight into the time dependent depolarization. The time dependent fluorescence anisotropy decay, $r(t)$, is defined as

$$r(t) = \frac{I_{||}(t) - I_{\perp}(t)}{I_{||}(t) + 2I_{\perp}(t)} \quad (4)$$

where $I_{||}(t)$ and $I_{\perp}(t)$ are the fluorescence intensity decays collected with the polarization of the emission polarizer maintained parallel and perpendicular to the polarization of the excitation source, respectively. For a fluorophore in a sample solvent, the fluorescence depolarization is simply due to rotational motion of the excited fluorophore and the decay parameters depend on the size and shape of the fluorophore. For spherical fluorophores, the anisotropy decay is a single exponential with a single rotational correlation time and is given by (Lakowicz, 2006)

$$r(t) = r_0 \exp(-t / \tau_r) \quad (5)$$

where r_0 is the initial anisotropy (anisotropy at time $t=0$ or anisotropy observed in the absence of any depolarizing processes) and τ_r is the rotational correlation time. The initial anisotropy r_0 is related to the angle (θ) between the absorption and emission dipoles of the fluorophore under study as

$$r_0 = \frac{2}{5} \left(\frac{3 \cos^2(\theta) - 1}{2} \right) \quad (6)$$

where the value r_0 can vary between 0.4 and -0.2 as the angle (θ) varies between 0° and 90° respectively. The rotational correlation times τ_r of the fluorophore is governed by the viscosity (η), temperature (T) of the solution and the molecular volume (V) of the fluorophore. This is given by Stokes-Einstein relation (Fleming, 1986) as shown below:

$$\tau_r = \frac{\eta V}{kT} \quad (7)$$

where k is the Boltzmann constant.

The relation between the steady-state anisotropy (r), initial anisotropy (r_0), rotational correlation time (τ_r) and fluorescence lifetime (τ_f) is given by Perrin equation as follows (Lakowicz, 1983)

$$\frac{r_0}{r} = 1 + \frac{\tau_f}{\tau_r} \quad (8)$$

The Perrin equation is very useful in obtaining the correlation time without the measurement of polarization dependent fluorescence decays [$I_{||}(t)$ and $I_{\perp}(t)$]. The theory developed for more complicated shapes of the fluorophore show that a maximum of five exponentials are enough to explain the fluorescence anisotropy decay (Steiner, 1991).

2. Introduction to rotational dynamics

Understanding solute-solvent interaction has been of great relevance in physico-chemical processes due to the importance of these interactions in determining properties such as chemical reaction yield and kinetics or the ability to isolate one compound from another. Interactions between the solutes and their surrounding solvent molecules are difficult to

resolve because, unlike in solids, the spatial relationship between the molecules are not fixed on time scales that can be accessed using structural measurements such as X-ray diffraction or multidimensional NMR spectrometry. Intermolecular interactions in the liquid phase are more complex than those in gas phase because of their characteristic strength, the property that gives rise to the liquid phase and at the same time prevents a simple statistical description of collisional interactions from providing adequate insight (Fleming, 1986).

Regardless of almost three and a half decades of continuous investigation, the details of solute-solvent interactions, particularly in polar solvent systems, remain to be understood in detail. Most investigations of intermolecular interactions in solution have used a “probe” molecule present at low concentration in neat or binary solvent systems. Typically, a short pulse of light is shone to establish some non-equilibrium condition in the ensemble of probe molecules, with the object of the experiment being to monitor the return to equilibrium. These studies have included fluorescence lifetime, molecular reorientation (Eisenthal, 1975; Shank and Ippen, 1975; von Jena and Lessing, 1979a; Sanders and Wirth, 1983; Templeton et al., 1985; Blanchard and Wirth, 1986; Templeton and Kenney-Wallace, 1986; Blanchard, 1987, 1988, 1989; Blanchard and Cihal, 1988; Hartman et al., 1991; Srivastava and Doraiswamy, 1995; Imeshev and Khundkar, 1995; Dutt, et al., 1995; Chandrashekhar et al., 1995; Levitus et al., 1995; Backer et al., 1996; Biasutti et al., 1996; Horng et al., 1997; Hartman et al., 1997; Laitinen et al., 1997; Singh, 2000; Dutt and Raman, 2001; Gustavsson et al., 2003; Dutt and Ghanty, 2004; Kubinyi et al., 2006), vibrational relaxation (Heilweil et al., 1986, 1987, 1989; Lingle Jr. et al., 1990; Anfinrud et al., 1990; Elsaesser and Kaiser, 1991; Hambir et al., 1993; Jiang and Blanchard, 1994a & b, 1995; McCarthy and Blanchard, 1995, 1996) and time-delayed fluorescence Stokes shift (Shapiro and Winn, 1980; Maroncelli and Fleming, 1987; Huppert et al. 1989, 1990; Chapman et al., 1990; Wagener and Richert, 1991; Fee et al., 1991; Jarzeba et al., 1991; Yip et al., 1993; Fee and Maroncelli, 1994; Inamdar et al., 1995) measurements. Of these, molecular reorientation of molecules in solution has been an important experimental and theoretical concept for probing the nature of liquids and the interactions of solvents with molecules. This has proven to be among the most useful because of the combined generality of the effect and the well-developed theoretical framework for the interpretation of the experimental data (Debye, 1929; Perrin, 1936; Chuang and Eisenthal, 1972; Hu and Zwanzig, 1974; Youngren and Acrivos, 1975; Zwanzig and Harrison, 1985). Though, the effect of solute-solvent interactions on the rotational motion of a probe molecule in solution has been extensively studied, these interactions are generally described as friction to probe rotational motion and can be classified into three types. The first category includes short-range repulsive forces, which dominate intermolecular dynamics during molecular collisions. These interactions are present in all liquids and lead to viscous dissipation, which is well described by hydrodynamic theories (Fleming, 1986). The second category includes long-range electrostatic interactions between a charged or dipolar probe and polar solvent molecules. As the solute turns, the induced solvent polarization can lag behind rotation of the probe, creating a torque, which systematically reduces the rate of rotational diffusion. This effect, termed dielectric friction, arises from the same type of correlated motions of solvent molecules, which is responsible for the time dependent Stokes’ shift (TDSS) dynamics of fluorescent probes (van der Zwan and Hynes, 1985; Barbara and Jarzeba, 1990; Maroncelli, 1993). The third category includes specific solute-solvent interactions. Hydrogen bonding is probably the most frequently encountered example of this kind. Strong hydrogen bonds will lead to the formation of

solute-solvent complexes of well-defined stoichiometry. These new, larger species can persist in solution for fairly long times and will rotate more slowly than the bare solute. Formation and breakage of weak H binds occurring on time scales faster than probe rotation will provide a channel for rotational energy dissipation giving rise to additional friction.

The theoretical interest in the study of rotational reorientation kinetics of molecules in liquids arises from the fact that it provides information about the intermolecular interaction in the condensed phase. However, the theoretical modeling of molecular reorientation in liquids and its correlation with experimental data is still far from satisfactory. Thus far, two kinds of approaches have been employed in understanding the rotational dynamics. In the first approach, binary collision approximation has been used to explain the rotational dynamics. With this approach, kinetic theory model for rotational relaxation has been employed for rough sphere fluids (Widom, 1960; Rider and Fixman, 1972; Chandler, 1974) and for smooth convex bodies (Evans et al., 1982; Evans and Evans, 1984; Evans, 1988). Evans model along with Enskog equation for viscosity has been employed to express rotational reorientation time (τ_r) as a function of the solvent viscosity. However, explaining rotational dynamics from such a molecular point of view is severely constrained on account of multibody interaction in a fluid. For real systems the quantitative predictions can be made about the variation of τ_r with solvent viscosity. The second approach is the macroscopic approach of understanding the rotational dynamics, where the solvent is assumed to be a structureless continuum and the rotational motion of solutes is considered Markovian or diffusional. A considerable degree of success on the rotational dynamics arises from the Stokes-Einstein-Debye (SED) hydrodynamic theory, which forms the basis of understanding molecular rotations of medium sized molecules (few hundred Å³ volumes) in liquids (Einstein, 1906; Debye, 1929; Stokes, 1956), according to which the rotational reorientation time (τ_r) of a solute molecule is proportional to its volume (V), bulk viscosity (η) of the solvent and inversely related to its temperature (T).

Rotational dynamics of number of nonpolar and polar solutes have been carried out in homologous series of polar and nonpolar solvents. In general, the experimentally measured reorientation times of most of the nonpolar probes could be described by the SED theory with slip boundary condition. In some cases the reorientation times were found to be faster than predicted by the slip boundary condition, a situation termed as subslip behavior. However, for a given probe in a homologous series of solvents (alkanes or alcohols) the normalized reorientation times (i.e., reorientation times at unit viscosity) decrease as the size of the solvent increased. In other words, the reorientation times did not scale linearly with solvent viscosity. This behavior, known as the size effects, could not be explained with SED theory. Another observation, which the SED theory failed to explain, is that the experimentally measured reorientation times of nonpolar probes are faster in alcohols than in alkanes of similar viscosity. To explain the observed size effects two quasihydrodynamics theories have been used. The first one is a relatively old theory proposed by Geirer and Wirtz (GW) (1953), which takes into account both the size of the solute as well as that of the solvent while calculating the boundary condition. This theory visualizes the solvent to be made up of concentric shells of spherical particles surrounding the spherical probe molecule at the center. Each shell moves at a constant angular velocity and the velocity of successive shells decreases with the distance from the surface of the probe molecule, as though the flow between the shells is laminar. As the shell number increases, i.e., at large distances, the angular velocity vanishes. Although, the GW theory is successful in predicting the observed

size effects in a qualitative way, it could not explain the faster rotation of nonpolar probes in alcohols compared to alkanes. The second relatively new quasihydrodynamic theory was proposed by Dote, Kivelson and Schwartz (DKS) (1981). The DKS theory not only takes into consideration the relative sizes of the solvent and the probe but also the cavities or free spaces created by the solvent around the probe molecule. If the size of the solute is comparable to the free volumes of the solvent, the coupling between the solute and the solvent will become weak which results in reduced friction experienced by the probe molecule.

On the other hand, rotational dynamics of small and medium sized polar solutes dissolved in polar solvents experiences more friction than predicted by the hydrodynamic theories. This 'additional friction' is attributed to the solute-solvent hydrogen bonding. The first and the oldest concept of dielectric friction invoked by chemists is the 'solvent-berg' model, in which it is assumed that there is a solute-solvent interaction causing increase in the volume of the solute. Such an enhancement of the volume automatically causes the molecule to rotate slower. However, reservations against such an explanation have also been expressed (Chuang and Eisinger, 1972; Horng et al., 1997). Objections to this kind of interpretations arise from the fact that in bulk solution, the solvent molecules are expected to exchange (solute-solvent hydrogen bonding dynamics) on a much faster time scale compared to the rotational dynamics. Later, the slower reorientation times of polar molecules in polar solvents have been interpreted using dielectric friction theories (Phillips et al., 1985; Dutt et al., 1990; Alavi et al., 1991b,c; Dutt and Raman, 2001; Gustavsson et al., 2003). Dielectric friction on a rotating solute arises because the polar molecule embedded in a dielectric medium polarizes the surrounding dielectric. As the solute tries to rotate, the polarization of the medium cannot instantaneously keep in phase with the new orientation of the probe molecule and this lag exerts a retarding force on the probe molecule, giving rise to rotational dielectric friction. Although molecular theories of dielectric friction are available, at present these theories are difficult to apply because they require some knowledge of the intermolecular potential or some unavailable properties of the solvent. Continuum theories offer advantages of simplicity and the calculation of molecular friction in terms of easily accessible bulk properties of the solvent.

The SED theory has been found to describe the rotational dynamics of medium sized molecules fairly well when the coupling between the solute and solvent is purely mechanical or hydrodynamic in nature. It is documented that the SED model correctly predicts the linear dependence of the rotational reorientation times on the solvent viscosity for polar and cationic dyes dissolved in polar and non polar solvents (Chuang and Eisinger, 1971; Fleming et al., 1976; 1977; Porter et al., 1977; Moog et al., 1982; Spears and Cramer, 1978; Millar et al., 1979; von Jena and Lessing, 1979a, b; 1981; Rice and Kenney-Wallace, 1980; Waldeck and Fleming, 1981; Dutt et al., 1990; Alavi et al., 1991a, b, c; Krishnamurthy et al., 1993; Dutt et al., 1998) that have been interpreted using dielectric friction theories. The dielectric friction can be modeled using continuum theories of Nee-Zwanzig (NZ) (Nee and Zwanzig, 1970), which treats the solute as a point dipole rotating in a spherical cavity, Alavi-Waldeck (AW) (Alavi and Waldeck, 1991b; 1993) model which is an extension of the NZ theory where the solute is treated as a distribution of charges instead of point dipole and the semiempirical approach of van der Zwan and Hynes (vdZH) (van der Zwan and Hynes, 1985) in which fluorescence Stokes shift of the solute in a given solvent is related to dielectric friction. Conversely, the results of neutral and nonpolar solutes deviate

significantly from the hydrodynamic predictions at higher viscosities (Waldeck et al., 1982; Canonica et al., 1985; Phillips et al., 1985; Courtney et al., 1986; Ben Amotz and Drake, 1988; Roy and Doraiswamy, 1993; Williams et al., 1994; Jiang and Blanchard, 1994; Anderton and Kauffman, 1994; Brocklehurst and Young, 1995; Benzler and Luther, 1997; Dutt et al., 1999; Ito et al., 2000; Inamdar et al., 2006). These probes rotate much faster than predicted by the SED theory with stick boundary condition and are described by either slip boundary condition or by quasihydrodynamic theories. Slip boundary condition (Hu and Zwanzig, 1974) assumes the solute-solvent coupling parameter to be less than unity, contrary to the stick boundary condition. Quasihydrodynamic theories of Gierer and Wirtz (GW) (Gierer and Wirtz, 1953) and Dote, Kivelson and Schwartz (DKS) (Dote, Kivelson and Schwartz, 1981) attempt to improve upon SED theory by taking into consideration not only the size of the solute but also that of the solvent molecule, thereby modifying the boundary conditions. It has been argued (Ben Amotz and Drake, 1988; Roy and Doraiswamy, 1993) that as the size of the solute molecule becomes much larger than the size of the solvent molecule, the observed reorientation times approach the SED theory with the stick boundary condition.

Based on the above description, we have chosen two kinds of solutes categorized as nonpolar and polar to study their rotational reorientation dynamics in nonpolar, polar and binary mixtures of solvents. In the first case, where the nonpolar probes embedded in polar or nonpolar solvents to examine the influence of solute to solvent size ratio and the shape of the solute on the friction experienced by the probe molecule which in turn enables to test the validity of hydrodynamic and quasihydrodynamic theories. The friction experienced by these probes is purely hydrodynamic or mechanical in nature since it is dominated by short-range repulsive forces. Polar probes used in charged polar solvents with an intention of understanding how the long-range electrostatic interactions between the solute and the solvent, which are charge-dipole or dipole-dipole in nature, influence the rotational dynamics of the probe molecules. Dielectric friction on a rotating solute arises because of the polar molecule entrenched in a dielectric medium polarizes the surrounding dielectric. As the solute tries to rotate, the polarization of the medium cannot instantaneously keep in phase with the new orientation of the probe molecule and this lag exerts a retarding force on the probe molecule, giving rise to rotational dielectric friction.

2.1 Theoretical background

Among the many proposed models for the study of rotational motion, the most commonly employed is the rotational diffusion model outlined by Debye (Debye, 1929), in which the reorientation is assumed to occur in small angular steps. On account of high frequency collisions, a molecule can rotate through a very small angle before undergoing another reorienting collision. The rotational diffusion equation solved to obtain the rotational correlation time τ_r of the density function $\rho(\theta, \phi)$ is given by (Lackowicz, 2006)

$$\frac{\partial \rho}{\partial t} = D \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left[\frac{1}{\sin \theta} \frac{\partial \rho}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2 \rho}{\partial \phi^2} \right] \quad (9)$$

where D is the rotational diffusion coefficient. For spherical particles ρ satisfies the form $C_1(t) Y_{l,m}(\theta, \phi)$ in isotropic liquids, where $Y_{l,m}(\theta, \phi)$ are the Legendre polynomials and the coefficient $C_1(t)$ is essentially the same as the correlation function. Substitution of $\rho = C_1(t) Y_{l,m}(\theta, \phi)$ gives an ordinary differential equation for C as

$$\frac{dC_1}{dt} = -Dl(l+1)C_1 \quad (10)$$

This implies that the correlation function decays exponentially, e^{-t/τ_l} and the correlation time $\tau_l = [l(l+1)D]^{-1}$. In fluorescence depolarization experiments, one measures the anisotropy decay which is $l=2$ correlation and hence $\tau_r = (6D)^{-1}$.

The rotational diffusion co-efficient of a solute is given by the Stokes-Einstein model (Lakowicz, 2006) as

$$D = \frac{kT}{\zeta} \quad (11)$$

where ζ is the friction coefficient and kT is the thermal energy. It is this friction, which is of great importance in theoretical as well as experimental studies. A molecule rotating in liquid experiences friction on account of its continuous interaction with its neighbors and the desire to understand has been a motivating force in carrying the experimental measurements of rotational reorientation in liquids.

2.1.1 Hydrodynamic theory

Mechanical friction on a rotating solute in solvent is computed employing hydrodynamic theory 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 (Stokes, 1956)

$$\zeta = 8\pi a^3 \eta \quad (12)$$

Eqn. (11) reduces to

$$D = \frac{kT}{8\pi\eta a^3} \quad (13)$$

The rotational correlation time (τ_r) is given by

$$\tau_r = \frac{1}{6D} = \frac{\zeta}{6kT} \quad (14)$$

substitution of Eqn. (12) in (14) gives

$$\tau_r = \frac{\eta V}{kT} \quad (15)$$

where V is the molecular volume. The most widely used Stokes-Einstein-Debye (SED) hydrodynamic equation for the description of rotational dynamics of spherical molecule is given by

$$\tau_r = \frac{\eta V}{kT} + \tau_0 \quad (16)$$

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

more important. In reality, the exact shape of the solute molecule is need not be a 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

$$\tau_r = \frac{\eta V}{kT} (fC) \quad (17)$$

where f is shape factor and is well specified, C is the boundary condition parameter dependent strongly on solute, solvent and concentration. The shapes of the solute molecules are usually incorporated into the model by treating them as either symmetric or asymmetric ellipsoids. 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 and Jarzeba, 1990). In the two limiting cases of hydrodynamic stick and slip for a nonspherical molecule, the value of C follows the inequality, $0 < C \leq 1$ and the exact value of C is determined by the axial ratio of the probe.

It is observed that the experimentally measured rotational reorientation times of number of the nonpolar solutes (Waldeck et al., 1982; Canonica et al., 1985; Phillips et al., 1985; Courtney et al., 1986; Ben Amotz and Drake, 1988; Roy and Doraiswamy, 1993; Williams et al., 1994; Jiang and Blanchard, 1994; Anderton and Kauffman, 1994; Brocklehurst and Young, 1995; Benzler and Luther, 1997; Dutt et al., 1999; Ito et al., 2000; Inamdar et al., 2006) could be described by the SED theory with slip boundary condition (subslip behavior). For a homologous series of solvents such as alcohols or alkanes, the normalized reorientation times decreased as the size of the solvent is increased. In other words, the reorientation times did not scale linearly with solvent viscosity.

2.1.2 Quasihydrodynamic theories

While the SED hydrodynamic theory takes only the size of the solute molecule into account leaving solvent size aside, one needs to consider the size of the solute as well as solvent molecules. Quasihydrodynamic theories consider these and modify the boundary condition accordingly. To explain such observation of size effects, two quasihydrodynamic theories by Gierer and Wirtz (GW) and Dote, Kivelson and Schwartz (DKS) have been used.

i. Gierer and Wirtz theory (GW)

The first and the relatively old theory proposed by Gierer and Wirtz (GW) in 1953, takes into account both the size of the solute as well as that of the solvent while calculating the boundary condition. It visualizes the solvent to be made up of concentric shells of spherical particles surrounding the spherical probe molecule at the center. Each shell moves at a constant angular velocity and the velocity of successive shells decreases with the distance from the surface of the probe molecule, as though the flow between the shells is laminar. As the shell number increase, i.e., at large distances, the angular velocity vanishes. The angular velocity ω_1 of the first solvation shell is related to the angular velocity ω_0 of the probe molecule by means of a sticking factor σ .

$$\omega_1 = \sigma \omega_0 \quad (18)$$

When $\sigma = 1$, it gives the stick boundary condition and σ is related to the ratio of the solute to solvent size, as

$$\sigma = \left[1 + 6 \left(\frac{V_s}{V_p} \right)^{\frac{1}{3}} C_0 \right]^{-1} \quad (19)$$

where

$$C_0 = \left\{ \frac{6(V_s/V_p)^{1/3}}{\left[1 + 2(V_s/V_p)^{1/3} \right]^4} + \frac{1}{\left[1 + 4(V_s/V_p)^{1/3} \right]^3} \right\}^{-1} \quad (20)$$

V_s and V_p are the volumes of the solvent and probe, respectively. The expression for C_{GW} is given by

$$C_{GW} = \sigma C_0 \quad (21)$$

C in Eqn. (17) should be replaced with C_{GW} obtained from Eqn. (21) for calculating the reorientation times with GW theory. When the ratio V_s/V_p is very small C_{GW} reduces to unity and the SED equation with stick boundary condition is obtained.

ii. The Dote-Kivelson-Schwartz theory (DKS)

Although, the GW theory is successful in predicting the observed size effects in a qualitative way, it could not explain the faster rotation of nonpolar probes in alcohols compared alkanes. Hence, the second relatively new quasihydrodynamic theory, was proposed by Dote, Kivelson and Schwartz (DKS) in 1981. This theory not only takes into consideration the relative sizes of the solvent and the probe but also the cavities or free spaces created by the solvent around the probe molecule. If the size of the solute is comparable to the free volumes of the solvents, the coupling between the solute and the solvent will become weak which results in reduced friction experienced by the probe molecule. According to DKS theory the solute-solvent coupling parameter, C_{DKS} is given by (Dote, Kivelson and Schwartz, 1981)

$$C_{DKS} = (1 + \gamma / \phi)^{-1} \quad (22)$$

where γ / ϕ is the ratio of the free volume available for the solvent to the effective size of the solute molecule, with

$$\gamma = \frac{\Delta V}{V_p} \left[4 \left(\frac{V_p}{V_s} \right)^{2/3} + 1 \right], \quad (23)$$

and ϕ is the ratio of the reorientation time predicted by slip hydrodynamics to the stick prediction for the sphere of same volume. ΔV is the smallest volume of free space per solvent molecule and some discretion must be applied while calculating this term (Dutt et al., 1988; Anderton and Kauffman, 1994; Dutt and Rama Krishna, 2000). ΔV is empirically related to the solvent viscosity, the Hilderbrand-Batchinsky parameter B and the isothermal compressibility k_T of the liquid by

$$\Delta V = Bk_T\eta kT \quad (24)$$

Since the Frenkel hole theory and the Hilderbrand treatment of solvent viscosity were developed for regular solutions (Anderton and Kauffman, 1994), Equation (24) may not be a valid measure of the free space per solvent molecule for associative solvents like alcohols and polyalcohols. Hence, for alcohols ΔV is calculated using

$$\Delta V = V_m - V_s \quad (25)$$

where V_m is the solvent molar volume divided by the Avogadro number.

2.1.3 Dielectric friction theories

The simple description of hydrodynamic friction arising out of viscosity of the solvent becomes inadequate when the motion concerning rotations of polar and charged solutes desired to be explained. A polar molecule rotating in a polar solvent experiences hindrance due to dielectric friction (ζ_{DF}), in addition to, the mechanical (ζ_M) or hydrodynamic friction. In general, the dielectric and mechanical contributions to the friction are not separable as they are linked due to electrohydrodynamic coupling (Hubbard and Onsager, 1977; Hubbard, 1978; Dote et al., 1981; Felderhof, 1983; Alavi et al., 1991c; Kumar and Maroncelli, 2000). Despite this nonseparability, it is common to assume that the total friction experienced by the probe molecule is the sum of mechanical and dielectric friction components, i.e.,

$$\zeta_{Total} = \zeta_M + \zeta_{DF} \quad (26)$$

Mechanical friction can be modeled using both hydrodynamic (Debye, 1929) and quasihydrodynamic (Gierer and Wirtz, 1953; Dote et al., 1981) theories, whereas, dielectric friction is modeled using continuum theories.

The earliest research into dielectric effects on molecular rotation took place in the theoretical arena. Initial investigations were closely intertwined with the theories of dielectric dispersion in pure solvents (Titulaer and Deutch, 1974; Bottcher and Bordewijk, 1978; Cole, 1984). Beginning with the first paper to relate the dielectric friction to rotational motion published by Nee and Zwanzig in 1970, a number of studies have made improvements to the Nee-Zwanzig approach (Tjai et al, 1974; Hubbard and Onsager, 1977; Hubbard and Wolynes, 1978; Bordewijk, 1980; McMahon, 1980; Brito and Bordewijk, 1980; Bossis, 1982; Madden and Kivelson, 1982; Felderhof, 1983; Nowak, 1983; van der Zwan and Hynes, 1985; Alavi et al, 1991a,b,c; Alavi and Waldeck, 1993). These have included the electrohydrodynamic treatment which explicitly considers the coupling between the hydrodynamic (viscous) damping and the dielectric friction components.

i. The Nee-Zwanzig theory

Though not the first, the most influential early treatment of rotational dielectric friction was made by Nee and Zwanzig (NZ) (1970). These authors examined rotational dynamics of the same solute/solvent model in the simple continuum (SC) description i.e., they assumed an Onsager type cavity dipole with dipole moment μ and radius a embedded in a dielectric continuum with dispersion $\epsilon(\omega)$. Motion was assumed to be in the purely-diffusive (or Smoluchowski) limit. Using a boundary condition value calculation of the average reaction field, Nee and Zwanzig obtained their final result linking the dielectric friction contribution in the spherical cavity as

$$\tau_{DF}^{NZ} = \frac{\mu^2}{9a^3kT} \frac{(\epsilon_\infty + 2)^2(\epsilon_0 - \epsilon_\infty)}{(2\epsilon_0 + \epsilon_\infty)^2} \tau_D \quad (27)$$

where ϵ_0 , ϵ_∞ and τ_D are the zero frequency dielectric constant, high-frequency dielectric constant and Debye relaxation time of the solvent, respectively.

If one assumes that the mechanical and dielectric components of friction are separable, then

$$\tau_r^{obs} = \tau_{SED} + \tau_{DF} \quad (28)$$

Therefore, the observed rotational reorientation time (τ_r^{obs}) is given as the sum of reorientation time calculated using SED hydrodynamic theory and dielectric friction theory.

$$\tau_r^{obs} = \frac{\eta V f C}{kT} + \frac{\mu^2}{9a^3kT} \frac{(\epsilon + 2)^2(\epsilon_0 - \epsilon_\infty)\tau_D}{(2\epsilon_0 + \epsilon_\infty)^2} \quad (29)$$

It is clear from the above equation that for a given solute molecule, the dielectric friction contribution would be significant in a solvent of low ϵ and high τ_D . However, if the solute is large, the contribution due to dielectric friction becomes small and the relative contribution to the overall reorientation time further diminishes due to a step increase in the hydrodynamic contribution. Hence, most pronounced contribution due to dielectric friction could be seen in small molecules with large dipole moments especially in solvents of low ϵ and large τ_D .

ii. The van der Zwan-Hynes theory (vdZH)

A semiempirical method for finding dielectric friction proposed by van der Zwan and Hynes (1985), an improvement over the Nee and Zwanzig model, provides a prescription for determining the dielectric friction from the measurements of response of the solute in the solvent of interest. It relates dielectric friction experienced by a solute in a solvent to solvation time, τ_s , and solute Stokes shift, S . According to this theory the dielectric friction is given by (van der Zwan and Hynes, 1985)

$$\tau_{DF} = \frac{\mu^2}{(\Delta\mu)^2} \frac{S\tau_s}{6kT} \quad (30)$$

where $\Delta\mu$ is the difference in dipole moment of the solute in the ground and excited states and

$$S = h\nu_a - h\nu_f \quad (31)$$

where $h\nu_a$ and $h\nu_f$ are the energies of the 0-0 transition for absorption and fluorescence, respectively. The solvation time is approximately related to the solvent longitudinal relaxation time, $\tau_L = \tau_D(\epsilon_\infty / \epsilon_0)$ and is relatively independent of the solute properties. Hence, τ_L can be used in place of τ_s in Eqn. (30).

Assuming the separability of the mechanical and dielectric friction components, the rotational reorientation time can be expressed as

$$\tau_r^{obs} = \frac{\eta V f C}{kT} + \frac{\mu^2}{(\Delta\mu)^2} \frac{hc \Delta\nu}{6kT} \tau_s \quad (32)$$

where the first term represents the mechanical contribution and the second the dielectric contribution.

iii. The Alavi and Waldeck theory (AW)

Alavi and Waldeck theory (Alavi and Waldeck, 1991a), proposes that it is rather the charge distribution of the solute than the dipole moment that is used to calculate the friction experienced by the solute molecule. Not only the dipole moment of the solute, but also the higher order moments, contribute significantly to the dielectric friction. In other words, molecules having no net dipole moment can also experience dielectric friction. AW theory has been successful compared to NZ and ZH theories in modeling the friction in nonassociative solvents (Dutt and Ghanty, 2003). The expression for the dielectric friction according to this model is given by (Alavi and Waldek, 1991a)

$$\tau_{DF} = P \frac{(\epsilon_0 - 1)}{(2\epsilon_0 + 1)^2} \tau_D \quad (33)$$

where

$$P = \frac{4}{3akT} \sum_{j=1}^N \sum_{i=1}^N \sum_{L=1}^{L_{\max}} \sum_{M=1}^L \left(\frac{2L+1}{L+1} \right) \frac{(L-M)!}{(L+M)!} \times$$

$$M^2 q_i q_j \left(\frac{r_i}{a} \right)^L \left(\frac{r_j}{a} \right)^L P_L^M(\cos \theta_i) P_L^M(\cos \theta_j) \cos M \phi_{ji} \quad (34)$$

where $P_L^M(x)$ are the associated Legendre polynomials, a is the cavity radius, N is the number of partial charges, q_i is the partial charge on atom i , whose position is given by (r_i, θ_i, ϕ_i) , and $\phi_{ji} = \phi_j - \phi_i$. Although the AW theory too treats solvent as a structureless continuum like the NZ and vdZH theories, it provides a more realistic description of the electronic properties of the solute.

3. Experimental methods

The experimental techniques used for the investigation of rotational reorientation times mainly consist of steady-state fluorescence spectrophotometer and time resolved fluorescence spectrometer employing time correlated single photon counting (TCSPC).

3.1a Steady-state measurements

For vertical excitation, the steady-state fluorescence anisotropy can be expressed as (Dutt et al., 1999; Lakowicz, 1983)

$$\langle r \rangle = \frac{I_{||} - GI_{\perp}}{I_{||} + 2GI_{\perp}} \quad (35)$$

where $I_{||}$ and I_{\perp} denote the fluorescence intensities parallel and perpendicular polarized components with respect to the polarization of the exciting beam. G ($= 1.14$) is an instrumental factor that corrects for the polarization bias in the detection system (Inamdar et al., 2006) and is given by

$$G = \frac{I_{HV}}{I_{HH}} \quad (36)$$

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

3.1b Time-resolved fluorescence measurements

The fluorescence lifetimes of all the probes were measured with time correlated single photon counting technique (TCSPC) using equipment described in detail elsewhere (Selvaraju and Ramamurthy, 2004). If the decay of the fluorescence and the decay of the anisotropy are represented by single exponential, then the reorientation time τ_r is given by (Lakowicz, 1983)

$$\tau_r = \frac{\tau_f}{(r_0 / \langle r \rangle - 1)} \quad (37)$$

where r_0 is the limiting anisotropy when all the rotational motions are frozen and τ_f is the fluorescence lifetime.

In case of a prolate-ellipsoid model, the parameter f_{stick} is given by (Anderton and Kauffman, 1994)

$$f_{stick} = \frac{2(\rho^2 + 1)(\rho^2 - 1)^{3/2}}{3\rho[(2\rho^2 - 1)\ln\{\rho + (\rho^2 - 1)^{1/2}\} - \rho(\rho^2 - 1)^{1/2}]} \quad (38)$$

where ρ is the ratio of major axis (a) to the minor axis (b) of the ellipsoid. This expression is valid for stick boundary condition.

3.2 Fluorescent probes used in the study

Nonpolar probes

A variety of the nonpolar fluorescent probe molecules have been studied extensively in the recent past. Most of the nonpolar probes so far studied have the radii of 2.5 Å to 5.6 Å (Inamdar et al., 2006) and a transition towards stick boundary condition is evident with increase in size of the solute. Most of the medium sized neutral nonpolar molecules rotate faster in alcohols compared to alkanes, which is in contrast to that of smaller neutral solutes. It is also noted that the quasihydrodynamic description is adequate for small solutes of 2-3 Å radius in case of GW theory whereas, the DKS model with experimental value in alcohols fail beyond the solute radius of 4.2 Å. Our earlier work on rotational dynamics of exalite probes E392A ($r = 5.3$ Å), and E398 ($r = 6.0$ Å), yielded striking results (Inamdar et al., 2006), in that, these large probes rotated much faster than slip hydrodynamics and followed subslip trend in alcohols.

The quest to understand the influence of size of solute on rotational dynamics is continued with three nonpolar solutes viz., Exalite 404 (E404), Exalite 417 (E417) and Exalite 428 (E428), which may further fill the gap between the existing data. These probes have an anisotropic shape and a dipole emission along their long rod-like backbones. The rod like or cylinder shape is a macromolecular model of great relevance. A number of biopolymers including

some polypeptides, proteins, nucleic acids and viruses, under certain conditions exhibit the typical rod-like conformation and their hydrodynamic properties can therefore be analyzed in terms of cylindrical models. Surprisingly, not much is studied about the motion of these highly anisotropic rod-like molecules in liquids, neither experimentally nor by any simulation studies. These exalite dyes have found applications in many areas of research. When pumped by XeCl-excimer laser, Ar⁺ and Nd:YAG laser, provide tunable lasers in the ultraviolet-blue range (Valenta et al., 1999). E428 has been used to generate circularly polarized light in glassy liquid crystal films (Chen et al., 1999). Exalites are mixed with plastic scintillators (PS) to form new scintillaors, which are for superficial and diagnostic applications (Kirov et al., 1999).

Polar probes

Rotational diffusion of medium-sized molecules provides a useful means to probe solute-solvent interactions and friction. By modeling this friction using various continuum-based theories (NZ, AW and ZH) one can get better insight into the nature of solute-solvent interactions. In order to understand the effect of polar solvents on the reorientational dynamics of the polar solutes, one must unravel the effects of mechanical friction, dielectric friction and specific short-range solute-solvent interactions. To address this issue, rotational dynamics of three polar laser dyes: coumarin 522B (C522B), coumarin 307 (C307) and coumarin 138 (C138) having identical volumes and distinct structures have been carried out in series of alcohols and alkanes. These coumarins are an important class of oxygen heterocycles, which are widespread in plant kingdom and have been extensively used as laser dyes. Their chemical structures can be looked upon as arising out of the fusion of a benzene ring to pyran-2-one, across the 5- and 6-positions in skeleton. In the present coumarins, the two free substituents at 6 and 7 positions, ethylamino and methyl for C307 in comparison with the analogous model substrate C522B wherein, there is no free substituent rather they are joined by ends to obtain piperidino moiety. These two probes are looked upon as polar due to the presence of electron donating amino group and electron withdrawing CF₃ group. In C138, this CF₃ group is replaced by an alkyl group making it less polar compared to C522B and C307.

The rotational diffusion studies of the following two sets of structurally similar molecules dyes: (i) coumarin-440 (C440), coumarin-450 (C450), coumarin 466 (C466) and coumarin-151 (C151) and (ii) fluorescein 27 (F27), fluorescein Na (FNa) and sulforhodamine B (SRB) in binary mixtures of dimethyl sulphoxide + water and propanol + water mixtures, respectively. Among coumarins, C466 possess N-diethyl group at the fourth position whereas, other three dyes possess amino groups at the seventh position in addition to carbonyl group. This structure is expected to influence molecular reorientation due to possible hydrogen bonding with the solvent mixture. The spectroscopic properties of fluorescein dyes are well known with the dyes having applications ranging from dye lasers to tracers in flow visualization and mixing studies. SRB has been used to measure drug-induced cytotoxicity and cell proliferation for large-scale drug-screening applications (Koochesfahani and Dimotakis, 1986; Dahm et al., 1991; Karasso and Mungal, 1997; Voigt, 2005). Both F27 and FNa are neutral polar molecules each containing one C = O group, F-27 has two Cl and FNa has two Na groups. The anionic probe SRB possesses N (C₂H₅), N⁺ (C₂H₅) groups and sulfonic groups SO₃Na and SO₃ at positions 3, 6, 4' and 2', respectively. The laser grade nonpolar probes Exalites (E404, E417 and E428), nonpolar probes (i) coumarin derivatives (C522B, C307 and C138) and (ii) F27, FNa and SRB (all from Exciton Chemical Co., USA) were used as received. For steady-state experiments, all the samples

were excited at 375 nm and the emission was monitored from 403-422 nm from alkanes to alcohols for Exalites. All the solvents (Fluka, HPLC grade) were used without further purification. The concentration of all the solutions was kept sufficiently low in order to reduce the effects of self-absorption. All the measurements were performed at 298 K.

3.2.1 Rotational dynamics of non-polar probes

The molecular structures of the non-polar probes exalite 404 (E404), exalite 417 (E417) and exalite 428 (E428) chosen for the study are shown in Fig.2. The absorption and fluorescence spectra of the probes in methanol are shown in Fig.3. These probes are approximated as prolate ellipsoids (Inamdar et al., 2006) with molecular volumes 679, 837 and 1031 Å³, respectively, for E404, E417 and E428. The rotational reorientation times (τ_r) calculated using Eqn. (4.43), are tabulated in Table 1 and 2, respectively.

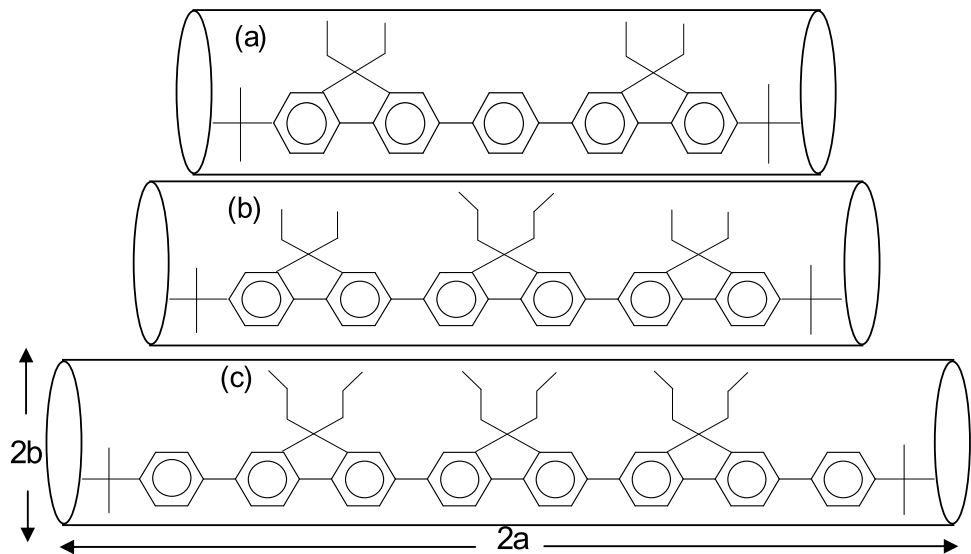


Fig. 2. Molecular structures of (a) E404, (b) E417 and (c) E428

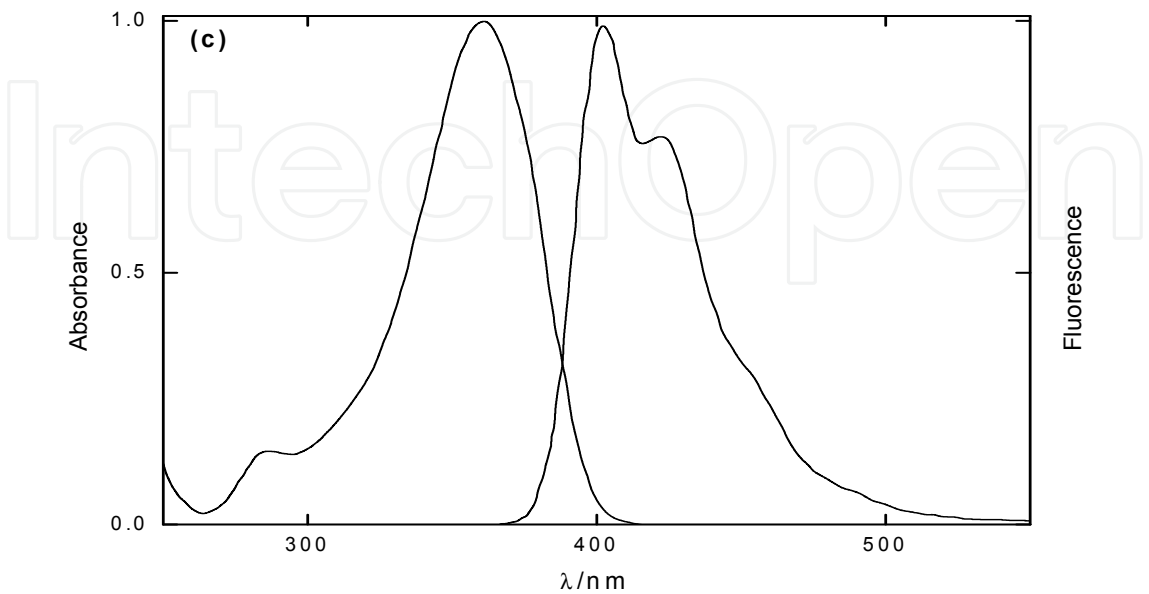


Fig. 3. Absorption and Fluorescence spectra of E404

Solvents	<div>E404E417E428</div>			
	η / mPa s ^a	τ_r / ps	τ_r / ps	τ_r / ps
Pentane	0.23	114±10	169±14	315±28
Hexane	0.29	153±14	223±18	413±40
Heptane	0.41	199±16	319±22	517±50
Octane	0.52	275±25	401±30	687±65
Nonane	0.66	322±25	523±45	814±78
Decane	0.84	417±35	677±55	1060±101
Dodecane	1.35	634±55	1002±88	1493±141
Tridecane	1.55	718±60	1137±100	1726±155
Pentadecane	2.81	1262±115	1740±120	2261±200
Hexadecane	3.07	1362±113	2080±140	2520±220

^a Viscosity data is from Inamdar et al., 2006

Table 1. Rotational reorientation times (τ_r) of Exalites in alkanes at 298K

Solvents	η / mPa s ^a	<div>E404E417E428</div>		
		τ_r / ps	τ_r / ps	τ_r / ps
Methanol	0.55	319±32	675±54	694±63
Ethanol	1.08	494±48	860±70	1244±110
Propanol	1.96	896±73	1153±99	1890±172
Butanol	2.59	1008±89	1710±150	2223±220
Pentanol	3.55	1185±100	1815±155	2750±225
Hexanol	4.59	1514±120	2244±201	3178±300
Heptanol	5.87	2070±182	2363±210	3627±345
Octanol	7.63	2669±255	2859±250	4130±380
Nonanol	9.59	3879±315	3099±292	4541±410
Decanol	11.80	4038±330	3702±340	4800±400

^a Viscosity data is from Inamdar et al., 2006

Table 2. Rotational reorientation times (τ_r) of Exalites in alcohols at 298K

i. Rotational reorientation times of Exalite 404 (E404)

Fig. 4 gives the plot of τ_r vs η in alkanes and alcohols for E404 shows that τ_r values increase linearly with η both in alkanes and alcohols, following slip hydrodynamic and subslip behavior, respectively. This clearly indicates that the rotational dynamics of E404 follows SED hydrodynamics with slip boundary condition. Further, E404 rotates slower in alkanes compared to alcohols by a factor of 1 to 1.3. It may be recalled that E392A followed SED hydrodynamics near stick limit in alkanes (Inamdar et al., 2006). E404 is larger than E392A by a factor of 1.1, and exhibits an opposite behavior to that of E392A following slip behavior in alkanes. Interestingly, the rotational dynamics of both these probes follow subslip behavior in higher alcohols.

Theoretical justification for this approach is provided by the microfriction theories of Geirer-Wirtz (GW) and Dote-Kivelson-Schwartz (DKS) wherein the solvent size as well as free spaces is taken into account. However, there is a large deviation of experimentally measured reorientation times from those calculated theoretically.

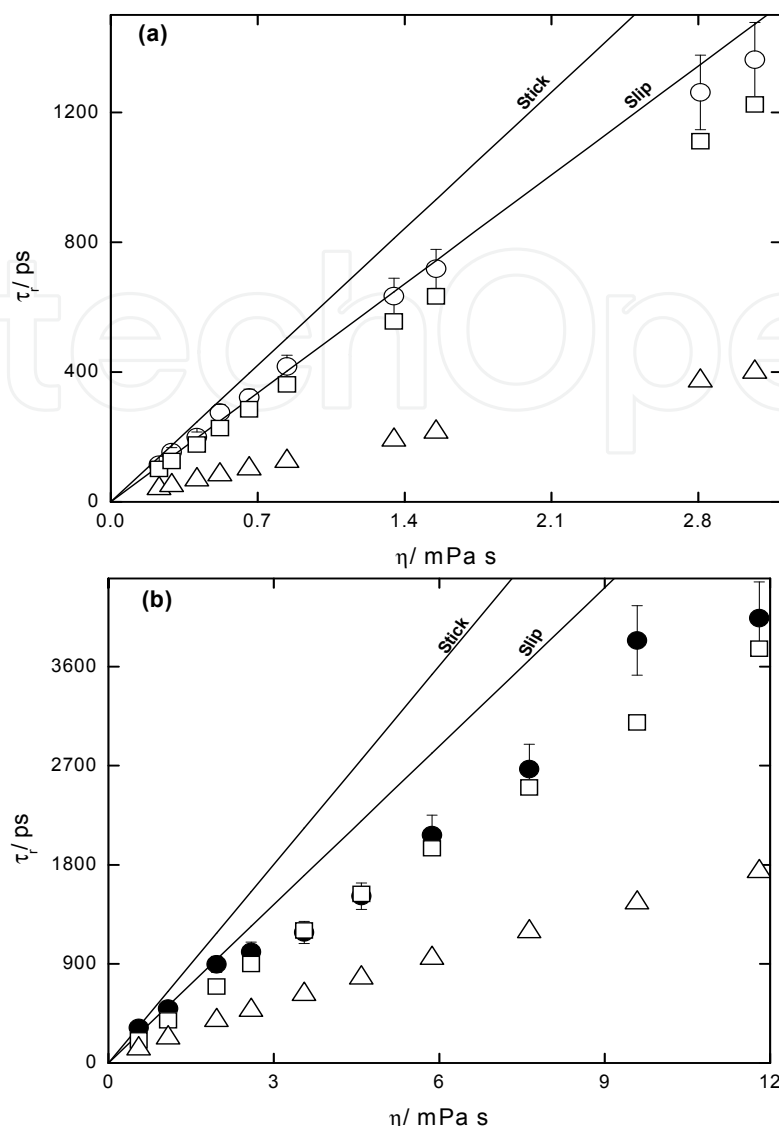


Fig. 4. Plot of rotational reorientation times of E404 as function of viscosity in (a) alkanes and (b) alcohols. The symbols (\circ , \bullet) represent experimentally measured reorientation times. The stick and slip lines calculated using hydrodynamic theory are represented by solid lines. GW and DKS theories are represented using the symbols Δ and \square respectively.

ii. Rotational reorientation times of Exalite 417 (E417)

The rotational reorientation times of E417 scale linearly with η (Fig. 5) and exhibits subslip behavior in alcohols. A large nonlinearity is observed on increasing solvent viscosity. In alkanes, the rotational reorientation times follow slip hydrodynamic boundary condition, similar to E404. GW theory is unable to explain experimental results while DKS theory is in fairly good agreement with experiment and slip hydrodynamics in case of alkanes.

iii. Rotational reorientation times of Exalite 428 (E428)

E428 is the largest probe studied so far in literature. In alcohols the τ_r values for E428 increase linearly with η from methanol to butanol and follows slip boundary condition, and from pentanol to decanol a large deviation from the linearity is observed resulting in subslip behavior (Fig. 6). However, in alkanes the measured reorientation times, clearly follow slip hydrodynamics up to tridecane, whereas in higher alkanes pentadecane and hexadecane

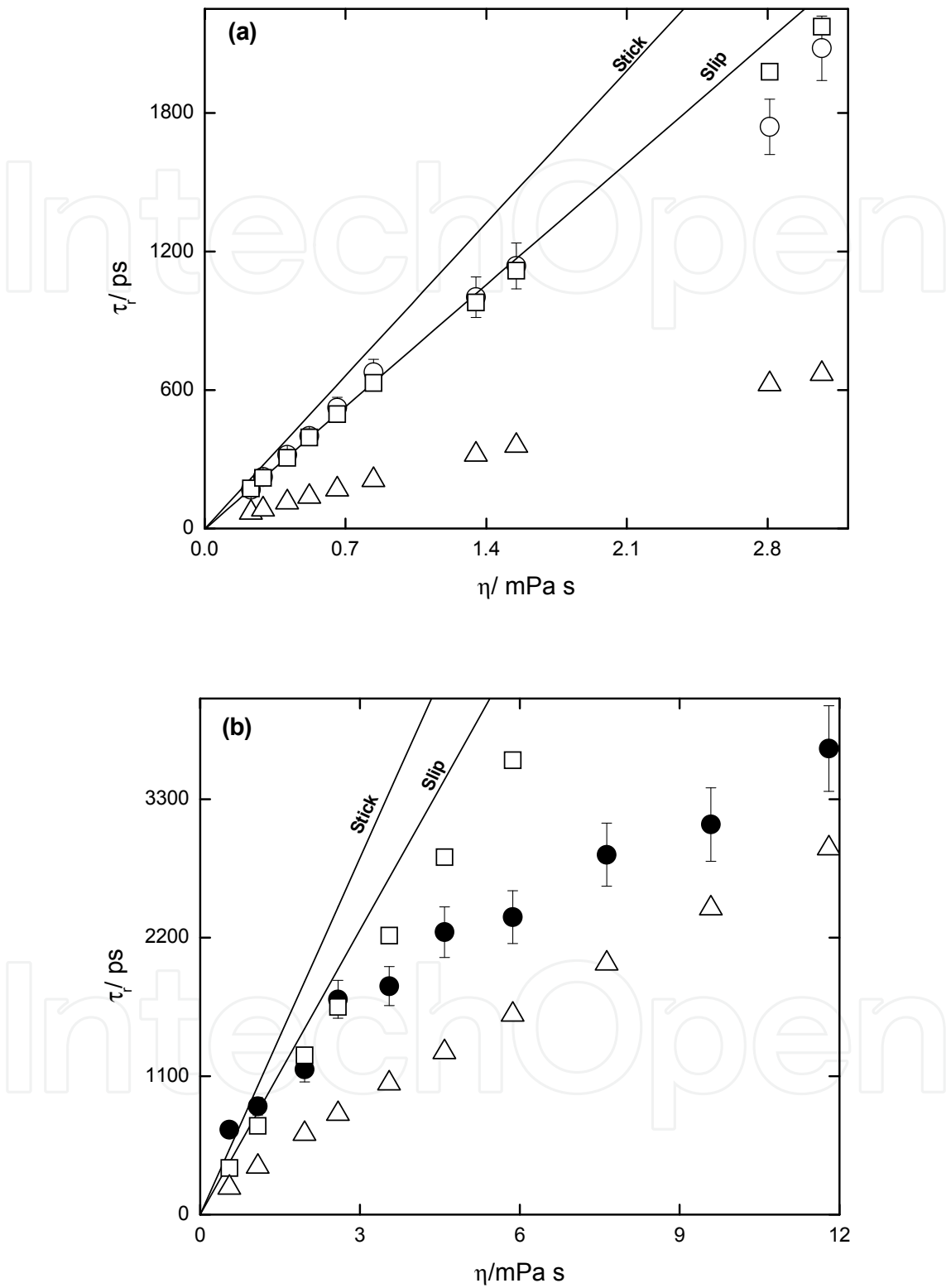


Fig. 5. Plot of rotational reorientation times of E417 as function of viscosity in (a) alkanes and (b) alcohols. The symbols (\circ, \bullet) represent experimentally measured reorientation times. The stick and slip lines calculated using hydrodynamic theory are represented by solid lines. GW and DKS quasihydrodynamic theories are represented using the symbols Δ and \square respectively.

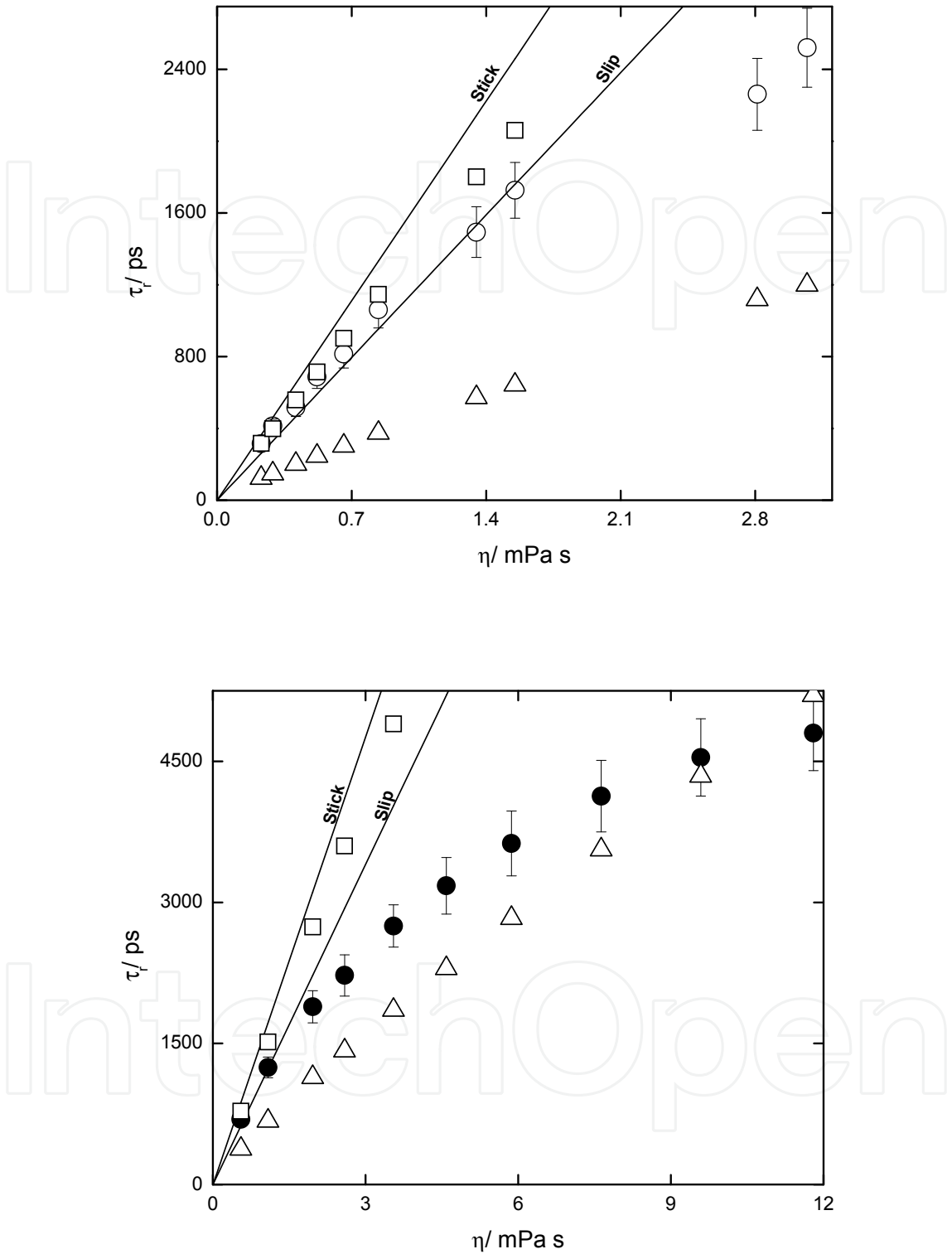


Fig. 6. Plot of rotational reorientation times of E428 as function of viscosity in (a) alkanes and (b) alcohols. The symbols (\circ, \bullet) represent experimentally measured reorientation times. The stick and slip lines calculated using hydrodynamic theory are represented by solid lines. GW and DKS quasihydrodynamic theories are represented using the symbols Δ and \bullet respectively.

subslip behavior is observed. It is interesting to note that, all the three probes rotate much faster in alcohols compared to alkanes. This can be explained as due to large interstitial gaps that may be formed in the solvent medium and because of the possible elastic nature of the spatial H-bonding network of large alcohol molecules constituting a supramolecular structure. The elasticity of the spatial network is a driving force for solvophobic interaction, which is important for the larger probes. Presumably these exalite molecules will be located mainly in these solvophobic regions. The probe molecules, thus, can rotate more freely in these gaps as they experience reduced friction due to a decreased viscosity at the point of contact. This actual viscosity is highly localized and cannot be measured easily. In such a situation the coupling parameter C can be much smaller than C_{slip} predicted by slip hydrodynamic boundary condition. One of the plausible reasons is also due to the Brownian motion, which results from the fluctuating forces in the liquid, is behind and diffusive process.

Ben-Amotz and Scott (1987) opined that processes, which are slow compared to solvent fluctuations, would see the full spectrum of the fluctuations and thus the shear viscosity of the solvent. For example, the fluctuations in n -alcohols occur roughly on the 100 ps/mPa s time scale – precisely the time scale of the Debye absorption in these solvents. On the other hand, processes, which are extremely fast, do not experience Brownian fluctuating force and are not viscously damped. Thus one expects a reduction in microscopic friction for probe molecules, which diffuse at a rate comparable to or faster than the solvent fluctuations. This is exactly the type of effect, which could explain the faster rotational diffusion of exalites in n -alcohols than in n -alkanes. Further, the subslip behavior observed for these probes in polar solvents indicates the existence the nonhydrodynamic forces and the straightforward relation between the probe size and the nature of their behavior may not be appropriate.

Table 3 and 4 contain selected data for various neutral solute molecules (including exalites), whose rotational times in alkanes and alcohols have been measured experimentally. There are many reports on rotational diffusion of small neutral molecules which follow subslip behavior. Garg and Smyth (1965) have attributed these alcohol molecules to be associated

Solute	Volume (Å ³)	Radius (Å)	Axial ratio	T _r (ps/ cP)	T _{slip} (ps/ cP)	T _{stick} (ps/ cP)	T _r /T _{stick}	References
Biphenyl	152	3.31	2.26	24	20	63	0.38	Bauer et al., 1974
Stilbene	180	3.50	2.82	38	41	94	0.40	Courtney et al., 1986
DPB	208	3.38	3.40	66	71	140	0.47	Waldeck et al., 1982
PTP	224	3.77	3.03	54	59	128	0.42	Philips et al., 1985; Kim et al., 1989
Binaphthyl	237	3.84	2.36	51	35	102	0.50	Bowman et al., 1988
PQP	296	4.13	3.77	112	124	226	0.50	Ben Amotz & Scott, 1987
DPA	312	4.15	2.55	78	56	147	0.53	Ben Amotz & Scott, 1987
BMQ	325	4.27	2.65	131	95	241	0.54	Roy and Doraiswamy, 1993
TMQ	359	4.41	2.10	149	71	265	0.56	Roy and Doraiswamy, 1993
DMQ	376	4.48	1.82	194	54	282	0.68	Roy and Doraiswamy, 1993
TMI	429	4.68	2.43	294	145	416	0.71	Roy and Doraiswamy, 1993
E392A	609	5.26	3.59	384	347	435	0.88	Inamdar et al., 2006
QUI	639	5.38	2.09	454	147	554	0.82	Roy and Doraiswamy, 1993
E404	679	5.45	4.21	437	362	601	0.73	Present work
BTBP	733	5.59	3.50	430	269	507	0.85	Ben Amotz & Drake, 1988
E417	837	5.85	5.00	636	623	944	0.67	Present work
E428	1031	6.27	6.18	749	1134	1587	0.47	Present work

Table 3. List of normalized rotational diffusion parameters of neutral nonpolar solutes in alkanes, at 25±5⁰ C

Solute	τ_r (ps/ cP)	τ_r/τ_{stick}	References
Stilbene	10	0.10	Courtney et al., 1986
PTP	39	0.30	Ben Amotz & Scott, 1987
Binaphthyl	36	0.35	Bowman et al., 1988
DPA	50	0.34	Ben Amotz & Scott, 1987
BMQ	87	0.36	Roy and Doraiswamy, 1993
TMQ	117	0.44	Roy and Doraiswamy, 1993
DMQ	137	0.49	Roy and Doraiswamy, 1993
TMI	194	0.47	Roy and Doraiswamy, 1993
E392A	196	0.45	Inamdar et al., 2006
QUI	436	0.79	Roy and Doraiswamy, 1993
E404	349	0.58	Present work
BTBP	430	0.85	Ben Amotz & Drake, 1988
E417	259	0.27	Present work
E428	357	0.22	Present work

Table 4. List of normalized rotational diffusion parameters of neutral nonpolar solutes in alcohols, at 25±5° C

with hydrogen bridges in temporary microcrystalline structures. These structures are in fact not stable, and at a given instant each of these has a finite length. At each instance some hydrogen bonds are ruptured and others are formed.

The first dispersion region is connected with the molecules in these microcrystalline structures. The dielectric relaxation process involves the breaking and reforming of the hydrogen bonds with the orientation of dipole moment, and the rate of breaking off is a determining factor for the relaxation time. In order to check whether there is any dielectric friction on these large nonpolar probes in alcohols, we have also calculated dielectric friction contribution to the rotating probe molecule. The dipole moment values in the excited states were obtained using solvatochromic shift method (Inamdar et al., 2003; Nadaf et al., 2004; Kawski et al., 2005). It is noted that summing up the contribution due to hydrodynamic and dielectric friction will not affect the subslip trend exhibited by the rotational reorientation times. Hence, we attribute this unhindered faster rotation due to strong hydrogen bonding among the solvent molecules leading to supramolecular structures.

There are several reports in literature where the reorientation times of neutral nonpolar solutes have been measured as a function of solute size and the transition from slip to stick hydrodynamics has been observed experimentally. Ben-Amotz and Drake (Ben-Amotz and Drake, 1988) have reported the rotational dynamics of the neutral large sized probe BTBP ($V=733 \text{ \AA}^3$) in series of alcohols and alkanes, and observed that rotational correlation times followed stick boundary condition. Though, BTBP contain the electronegative groups like -O and -N, which are capable of forming hydrogen bond with any solvent, they attributed, stick condition to its volume which is much larger than that of all the solvent molecules studied. Later, Roy and Doraiswamy (Roy and Doraiswamy, 1993) have studied the rotational dynamics of series of nonpolar solutes, which do not contain any electronegative groups like -O or -N. They observed transition towards the stick boundary condition on increasing the solute size from BMQ ($V = 325 \text{ \AA}^3$) to QUI ($V = 639 \text{ \AA}^3$). It is clear from the above two findings that a stick transition arises due to increase in the solute size, when compared to that of the solvent. Thus, one can expect stick or superstick behavior in case of exalites (E404, E417 and E428) as these are larger than QUI by a factor of 1.1, 1.3 and 1.6, respectively. The present situation, where the largest probe E428 follows subslip in alcohols

is surprising in the light of above studies. In such a situation the microscopic friction of the solvent molecules reduces well below the macroscopic value, which may result from either dynamic or structural features of the macroscopic solvation environment-giving rise to faster rotation in hydrogen bonding solvents. On the other hand, rotational reorientation times of these exalite nonpolar probes bequeath interesting results following slip boundary condition in alkanes. It is observed from the Table 5 that there is a difference in slope for the two solvent types. Therefore, it is evident that the rotational reorientation times of these exalites are shorter in alcohols than alkanes of comparable viscosity. This difference is an indication of nonhydrodynamic effects in one or both of the solvents. It is unlikely that nonhydrodynamic behavior resulting from frequency dependence of the solvent friction occurs in alkanes on the 100 ps to 1 ns time scale (Hynes, 1986). These times are much longer than dynamic memory effects in the solvent arising from molecular collisions. These collisional events manifest themselves in the viscoelastic relaxation time, which for an *n*-alkane is estimated to lie in the subpicosecond to single picosecond time domain (Hynes, 1986).

Solutes	Alcohols	Alkanes
Slope	Slope (ps/ mPa s)	(ps/ mPa s)
E404	349 360*	437 454*
E417	259 362*	636 677*
E428	357 510*	749 901*

* Second entry for solute is a slope of the best fit line made to pass through the origin.

Table 5. Linear regression results of rotational reorientation of exalites in series of alcohols, alkanes and binary mixture

Thus one would expect rotational times to be well described by the SED relation with the appropriate boundary condition and the solute shape factor (Ben Amotz and Scott, 1987) in *n*-alkanes. The internal mobility also allows the solute molecule to slip better through the surrounding solvent molecules than for a rigid molecular backbone (Alavi et al., 1991b,c). Waldeck et al. (1982) have also argued for the probe DPB, that the slip boundary condition is entirely reasonable for an uncharged nonpolar molecule in nonpolar solvents. E428 is about 5 times larger than DPB and from the Table 3; it is evident that τ_r/τ_{stick} ratio is same for both these probes in alkanes, which suggests the fact that the rotation of these probes can be well explained by slip hydrodynamics. Similarly, the studies of the neutral dye BBOT (Fleming et al., 1977), an approximate prolate top, found that this molecule followed slip boundary condition. It was anticipated that neutrals would not strongly interact with the solvent, and slip boundary condition were thus more appropriate. Others have argued (Porter et al., 1977) that the faster rotation observed for BBOT might also be due to the internal mobility of the dye. This may be one of the possible reasons for the faster rotation observed for the large exalite probes. Both GW and DKS models were tested for a quantitative prediction of τ_r of solutes in alkanes. The GW model predicts very low τ_r values in alkanes as well as in the case of alcohols and fails to satisfactorily explain the observed results. Also, the *C* values are nearly invariant of the size of the solute. It has

been evidenced that the GW theory correctly predicts the observed results for a solute with ~ 2.5 Å radius. Therefore, the GW model is adequate for very small solutes that show subslip behavior, viz., I_2 and NCCCCN (Goulay, 1983). Though, DKS theory is found to be in good agreement with the experimentally observed trend up to decane in case of E404 and up to nonane for E428, a better agreement is found in alkanes for E417. It has been noted that the rotational reorientation times in alkanes is reproduced quantitatively for solutes with radius up to 4.2 Å only, beyond which the theory tends to show poor agreement with experimental values [93]. Our experimental results are indicative of the fact the DKS theory also holds well even for larger probes up to a radius of 6.3 Å in alkanes and brings out the subtle variations in the observed data.

3.2.2 Rotational dynamics of polar probes

The rotational dynamics studies using polar solutes in polar solvents have shed lights on concepts such as dielectric friction and solute-solvent hydrogen bonding. In addition to viscous drag, polar-polar interaction between a polar solute and a polar solvent gives rise to an additional retarding force often termed as dielectric friction. This arises because of the inability of the 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. Under such circumstances, the observed friction, which is proportional to the measured reorientation time, has been explained as a combination of mechanical and dielectric frictions. However, many experimental investigations of reorientation dynamics have indicated that there is another source of drag on a rotating probe molecule due to hydrogen bonding between the solute and the solvent molecules. A solute molecule can 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 further impedes the rotational motion and thus the observed reorientation time becomes longer than that observed with the bare solute molecule.

Molecular structures of the three coumarin dyes chosen under the category of polar probes are shown in Fig. 7. The reorientation times of C522B, C307 in alcohols and alkanes and C138 in alcohols (Mannekutla et al., 2010) are summarized in Tables 6 and 7. The τ_r values obtained in alkanes clearly show that C522B rotates faster compared to C307. In alcohols, it is interesting to note that, the probe C138 rotates faster almost by a factor of 1:2 from propanol to decanol compared to C522B and C307, respectively. In other words, C138 experiences a reduced mechanical friction i.e., almost same as C522B and twice as C307 from propanol to decanol. This is because C307 shows greater interaction owing to its greater polarity.

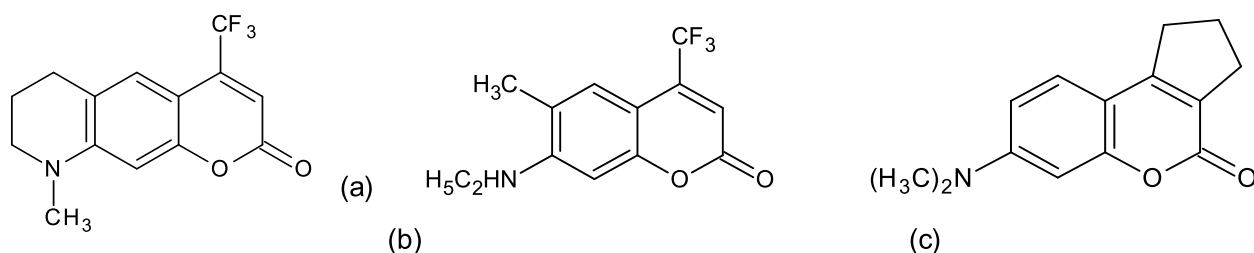


Fig. 7. Molecular structures of (a) C522B, (b) C307 and (c) C138

Solvents	η (mPa s ^a)	C522B			C307			C138		
		$\langle r \rangle$	τ_f (ns)	τ_r (ps)	$\langle r \rangle$	τ_f (ns)	τ_r (ps)	$\langle r \rangle$	τ_f (ns)	τ_r (ps)
Methanol	0.55	0.004±0.001	4.87	53±13	0.003±0.001	5.10	42±14	0.003±0.001	3.63	30±10
Ethanol	1.08	0.006±0.001	5.02	83±14	0.006±0.001	5.12	84±14	0.006±0.002	3.63	61±20
Propanol	1.95	0.009±0.001	5.05	126±14	0.011±0.002	5.13	157±29	0.009±0.002	3.64	92±20
Butanol	2.59	0.011±0.002	5.08	156±28	0.016±0.002	5.14	232±29	0.011±0.001	3.64	113±10
Pentanol	3.51	0.013±0.002	5.09	186±29	0.021±0.003	5.14	309±44	0.015±0.003	3.64	156±31
Hexanol	4.57	0.017±0.002	5.09	246±29	0.027±0.002	5.14	405±30	0.020±0.002	3.65	212±21
Heptanol	5.97	0.022±0.003	5.10	323±44	0.034±0.003	5.15	521±46	0.025±0.002	3.65	268±21
Octanol	7.63	0.027±0.002	5.10	403±30	0.041±0.003	5.15	642±47	0.035±0.004	3.68	390±45
Nonanol	9.59	0.033±0.003	5.10	501±46	0.051±0.003	5.18	828±49	0.037±0.002	3.74	422±23
Decanol	11.74	0.042±0.003	5.12	658±47	0.065±0.002	5.18	1104±34	0.047±0.003	3.77	477±35

^a Viscosity data is from Inamdar et al., 2006

Table 6. Steady-state anisotropy ($\langle r \rangle$), fluorescence lifetime (τ_f) and rotational reorientation time (τ_r) of coumarins in alcohols at 298K (the maximum error in the fluorescence life times is less than ±50 ps) (Mannekutla et al., 2010)

Solvents	η / mPa s ^a	C522B			C307		
		$\langle r \rangle$	τ_f / ns	τ_r / ps	$\langle r \rangle$	τ_f / ns	τ_r / ps
Pentane	0.23	-	-	-	0.003±0.001	4.23	35±12
Hexane	0.29	-	-	-	0.003±0.001	4.28	35±12
Heptane	0.41	0.002±0.001	3.98	22±11	0.004±0.001	4.37	48±12
Octane	0.52	0.003±0.001	4.11	34±11	0.004±0.001	4.51	49±12
Nonane	0.66	0.004±0.001	4.17	46±12	0.005±0.001	4.63	63±13
Decane	0.84	0.005±0.001	4.20	58±12	0.006±0.001	4.60	76±13
Dodecane	1.35	0.006±0.001	4.26	70±12	0.007±0.002	4.79	92±26
Tridecane	1.55	0.007±0.001	4.31	83±12	0.008±0.002	4.80	106±27
Pentadecane	2.81	0.009±0.001	4.38	110±12	0.009±0.002	4.80	120±27
Hexadecane	3.07	0.010±0.001	4.52	126±13	0.010±0.002	4.86	135±27

^a Viscosity data is from Inamdar et al., 2006

Table 7. Steady-state anisotropy ($\langle r \rangle$), fluorescence lifetime (τ_f) and rotational reorientation time (τ_r) of coumarins in alkanes at 298K for C522B and C307 (the maximum error in the fluorescence life times is less than ±50 ps) (Mannekutla et al., 2010)

The probes C522B and C138 have shown coincidentally similar interactions. In C138, aminomethyl group being free contributes more to the charge separation through resonance- whereas in C522B this resonance contribution is sluggish, comparatively. However, the presence of -CF₃ in C522B increases the charge separation, which leads to better interaction with the hydrogen bonding solvents. Replacement of -CF₃ by cyclic alkyl group in C138 would not have any great contribution towards its polarity. Hence, the presence of two different groups with contradicting properties leads to the coincidental similarities in reorientation dynamics of C522B and C138.

The normalized rotational reorientation times (at unit viscosity) are smaller in alkanes compared to alcohols, which indicates that the probes C522B and C307 rotate faster in alkanes compared to alcohols. The reorientation times of the three probes thus obtained in alcohols follow the trend: $\tau_r^{C307} > \tau_r^{C522B} \geq \tau_r^{C138}$.

Fig. 8 gives a typical plot of τ_r vs η for all the three probes in alcohols and in alkanes along with the stick and slip lines. Note that the experimentally measured reorientation times lie between slip and stick hydrodynamic in case of alcohols. However, in alkanes we observe, as the size of the solvent molecule becomes equal to and bigger than the size of the solute molecule, the probe molecule experiences a reduced friction. Benzler and Luther (1977) measured the reorientation time of biphenyl ($V=150 \text{ \AA}^3$) and *p*-terphenyl ($V=221 \text{ \AA}^3$) in *n*-alkanes. For biphenyl a nonlinearity was observed in the plot of τ_r vs η from decane and from tetradecane, in case of *p*-terphenyl. Singh [24] studied reorientation times of the probe neutral red ($V=234 \text{ \AA}^3$) which experienced a reduced friction from tetradecane to hexadecane following subslip behavior. C522B (223 \AA^3) and C307 (217 \AA^3) have nearly identical volumes as compared to neutral red and *p*-terphenyl and thus a similar rotational relaxation in alkanes may be expected.

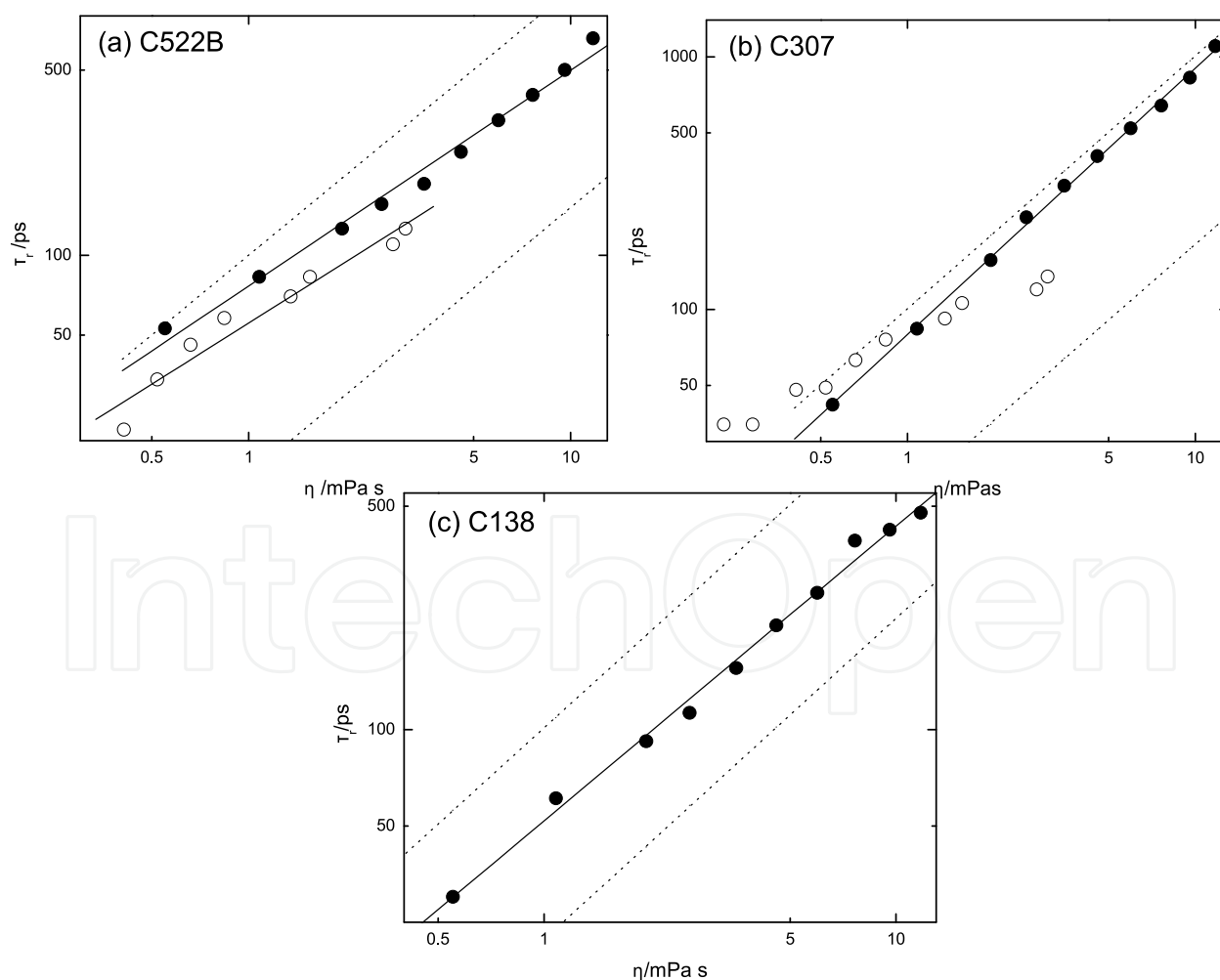


Fig. 8. Plots of τ_r vs η for the three coumarins in alcohols (\circ), and alkanes (\bullet) in case of C522B and C307

Note that the probes experience reduced friction as the size of the solvent increases. A number of probes have been studied (Phillips et al., 1985; Courtney et al., 1986; Ben Amotz and Drake, 1988; Roy and Doraiswamy, 1993; Williams et al., 1994; Jiang and Blanchard, 1994; Anderton and Kauffman, 1994; Brocklehurst and Young, 1995) in alcohols and alkanes, wherein faster rotation of the probe in alcohols is observed compared to alkanes, which has been explained as due to higher free volume in alcohols compared to alkanes with the help of DKS theory. If there were no electrical interaction between the coumarins and alcohols, a faster rotation of the coumarins would have been observed in alcohols compared to alkanes, but an opposite trend has been observed that indicates the presence of electrical friction (Dutt and Raman, 2001). Before evaluating the amount of dielectric friction, the contribution due to mechanical friction must be estimated with a reasonable degree of accuracy. SED theory with a slip hydrodynamic boundary condition is often used to calculate the mechanical friction in case of medium-sized solute molecules. However, in the present study the solvent size increases by more than 5 times in alcohols from methanol to decanol. Hence, DKS quasihydrodynamic theory is found to be more appropriate, when size effect is taken into account as compared with GW. Eqn. 25 is used to calculate ΔV in associative solvents like alcohols, because C_{DKS} obtained in this manner gave a better agreement with the experimental results (Hubbard and Onsager, 1977; Anderton and Kauffman, 1996; Dutt et al., 1999; Dutt and Raman, 2001).

In summary, a faster rotation of the probes is observed in case of C522B and C138 in alcohols compared to C307. In spite of the distinct structures, almost similar rotational reorientation times are observed for C522B and C138 in alcohols from propanol to decanol. Further studies of dielectric friction in alcohols, the observed reorientation times of these coumarins could not follow the trend predicted by the theories of Nee-Zwanzig and van der Zwan-Hynes. Dielectric frictions obtained experimentally and theoretically using NZ and ZH theories, do not agree well.

3.2.3 Rotational dynamics of polar probes in binary solvents

Binary mixtures of polar solvents represent an important class of chemical reaction media because their polarity can be controlled through changes in composition. In a binary mixture, altering the composition of one of the ingredients can lead to a change in solubility, polarizability, viscosity and many other static and dynamic properties. Yet, it is often found that the dielectric properties of polar mixtures depart significantly from what one might expect on the basis of ideal mixing. In hydrogen-bonding systems, such as alcohol-water mixtures, intermolecular correlations are strong, and consequently, the dielectric properties of the mixture are usually not simply related to those of the separated components. Recently, the properties of some binary solutions were studied using theoretical calculations and molecular dynamics (MD) simulations (Chandra and Bagchi, 1991; Chandra, 1995; Skaf and Ladanyi, 1996; Day and Patey, 1997; Yoshimori et al., 1998; Laria and Skaf, 1999). The results showed that the dynamical features of binary solutions are very much different from those of neat solutions, and the dynamics can be strongly affected by the properties of the solute probe. The binary mixtures show exotic features which pose interesting challenges to both theoreticians and experimentalists. Amongst them, the extrema observed in the composition dependence of excess viscosity (Qunfang and Yu-Chun, 1999; Pal and Daas, 2000) and the anomalous viscosity dependence of the rotational relaxation time (Beddard et al., 1981) are significant. The anomalous features in the complex systems arise from specific

intermolecular interactions due to structural heterogeneities. 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. The non-ideality of mixtures depends on the nature of interaction between the different species constituting the mixture. Traube suggested that the anomalous behavior of viscosity in binary mixtures arises from the formation of clusters (Traube, 1886). The prominent hydrophilic nature of DMSO renders it capable of forming strong and persistent hydrogen bonds with water through its oxygen atom (Safford et al., 1969; Martin and Hanthall, 1975; De La Torre, 1983; Luzar and Chandler, 1993). This leads to the formation of DMSO-water molecular aggregates of well-defined geometry which are often responsible for the strong nonideal behavior manifested as maxima or minima (Cowie and Toporowski, 1964; Packer and Tomlinson, 1971; Fox and Whittingham, 1974; Tokuhito et al., 1974; Gordalla and Zeidler, 1986; 1991; Kaatz et al., 1989). The largest deviations from the ideal mixing occur around 33% mole of DMSO, thus suggesting the existence of stoichiometrically well defined 1DMSO:2water complexes. Recently, a number of MD simulations (Vaisman and Berkowitz, 1992; Soper and Luzar, 1992; 1996; Luzar and Chandler, 1993; Borin and Skaf, 1998; 1999) and neutron diffraction experiments have indeed identified the structure of the 1DMSO:2water 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 (Borin and Skaf, 1998; 1999) have found from MD simulations, 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 in DMSO-rich mixtures. This H-bonded complex is referred to as 2DMSO:1water aggregate.

The rotational diffusion studies of the following two sets of structurally similar molecules dyes: coumarin-440 (C440), coumarin-450 (C450), coumarin 466 (C466) and coumarin-151 (C151) and fluorescein 27 (F27), fluorescein Na (FNa) and sulforhodamine B (SRB) (Fig. 9) in binary mixtures of dimethyl sulphoxide + water and propanol + water mixtures, respectively. Among coumarins, C466 possess N-diethyl group at the fourth position whereas, other three dyes possess amino groups at the seventh position in addition to carbonyl group. This structure is expected to affect the reorientation times due to the formation of hydrogen bond with the solvent mixture.

The photo-physics of fluorescent molecules in solvent mixtures has not been studied as extensively as those in neat solvents. Thus the structure and structural changes in the solvent environment around the solute in the mixed solvents have not been fully understood. It is therefore important to investigate the photophysical characteristics that are unique to the binary solvent mixtures.

DMSO is miscible with water in all proportions and aqueous DMSO solutions are quite interesting systems, as there exists a nonlinear relationship between the bulk viscosity and the composition of the solvent mixture. In DMSO-water binary mixture, there is a rapid rise in viscosity with a small addition of DMSO to water and viscosity decay profile after the post peak point is gradual. The sharp increase in the viscosity of the binary mixture with increasing DMSO concentration may be attributed to significant hydrogen bonding effects between water and DMSO molecules. Beyond around 15% composition of DMSO, there exist two DMSO compositions for which viscosity is same. This dual valuedness should manifest in reasonable mirror symmetry of the rotational reorientation time (τ_r) about the

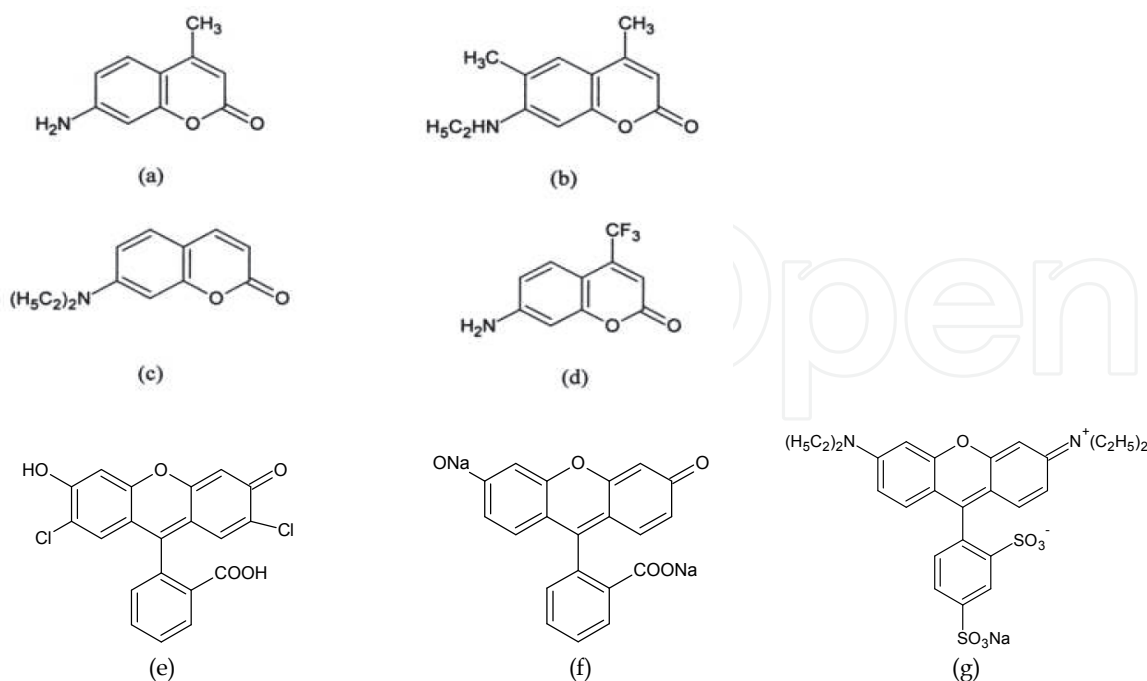


Fig. 9. The molecular structures of (a) C440, (b) C450, (c) C466, (d) C151, (e) F27, (f) FNa and (g) SRB.

viscosity peak point. The viscosity of DMSO is slightly more than twice that of water. At about 40% mole composition of DMSO, the solvent mixture has a maximum value of viscosity of 3.75 m Pas which is 1.87 times that of DMSO and nearly 4 times that of water. From the viscosity profile it may be seen that there are four distinct compositions of DMSO for which the viscosity is nearly the same and as per hydrodynamic theory the friction experienced by a rotating probe molecule is expected to be the same.

Fig. 10 (a and b) represent the variation of τ_r with η along with theoretical profile including the viscous and the dielectric contribution for all the probes, which clearly indicates a non-hydrodynamic behavior. The rotational reorientation time of a solute in a solvent is in a way an index of molecular friction. 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 and interestingly these values further increase even after the solvent mixture exhibits reduction in viscosity after the peak value. Thus all the probes exhibit different rotational reorientation values for isoviscous points. Note that, reorientation times are longer in the DMSO region compared to the water rich zone. The studies of the rotational diffusion of the dye molecules in binary solvents showed that the rotational relaxation time does not necessarily scale linearly with viscosity when the solvent composition is changed. These observations have been interpreted 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 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 showed a nonlinear dependence of the rotational diffusion on the solvent viscosity when the solvent composition is changed (Williams et al., 1994).

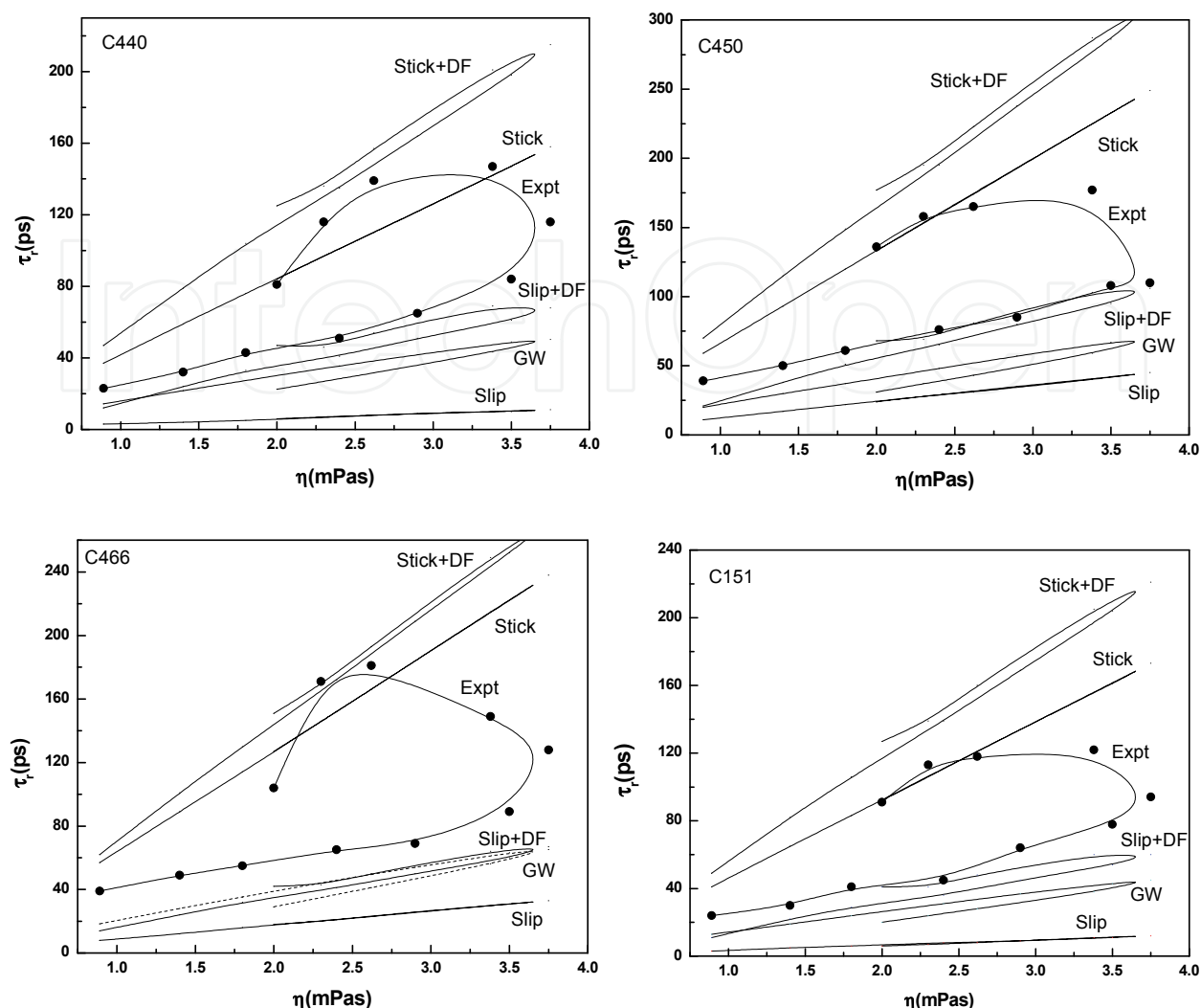


Fig. 10. Plot of rotational reorientation time with viscosity along with theoretical profile including the viscous and the dielectric contribution for C440, C450, C466 and C151 probes (Inamdar et al., 2009)

The linear variation of the τ_r as a function of η from pure water to the composition of the binary mixture when the viscosity reaches its peak is in accordance with the SED theory, though it does not account for the large curvature in the profile. The theoretical SED stick line shows a sharp hairpin profile. Incorporation of the dielectric friction contribution qualitatively mimics the observed profile, with the τ_r being slightly larger 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. The experimentally observed profile bent upwards yields considerably higher τ_r in the DMSO rich zone than the corresponding isoviscous point in the water rich zone. This is also reproduced by the theoretical models qualitatively. The pronounced difference in the rotational reorientation times at the isoviscous points can be explained only on the basis of solvation. It is possible that at the isoviscous points the microstructural features in the binary mixture could be different. The dual values of τ_r at isoviscous points in the DMSO rich zone are also due to the contributions of dielectric friction at these two points being different.

Beddard et al. (1981) reported different rotational relaxation times of the dye cresyl violet in ethanol water mixture by varying the ethanol water composition i.e., at the same viscosity but at different compositions. The observed re-entrance type behavior of the orientational relaxation time when plotted against viscosity could not be explained only in terms of non-ideality in viscosity exhibited in a binary mixture. Beddard et al. also reported that the re-entrance behavior is strongly dependent on the specific interaction of the solute with the solvents. This is because in a system where solute interacts with few different species in a binary mixture in a different manner, 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 often been discussed in relation to changing boundary conditions (Fleming, 1986). We find that the orientational relaxation time of the probe molecules when plotted against the solvent viscosity does indeed show re-entrance. Our study here re-affirms that for a solute dissolved in a binary mixture, its rotational relaxation will depend more on the composition than on the viscosity of the binary mixture and thus the re-entrant type behaviour is strongly dependent on the interactions of the solute with the two different species in the solvent.

The rotational dynamics of two kinds of medium sized three dyes-Fluorescein 27(F27) and Fluorescein Na(FNa) (both neutral but polar), and Sulforhodamine B(SRB) (anion) has been studied in binary mixtures comprising of 1-Propanol and water at room temperature using both steady-state and time resolved fluorescence depolarization techniques. Alcohols have both a hydrogen-bonding -OH group and a hydrophobic alkyl group. The latter affects the water structure. The objective in studying two neutral and an anion dyes is to compare and contrast the rotational dynamics as a function of charge. A nonlinear hook-type profile of rotational reorientation times of the probe (τ_r) as a function of viscosity (η) is observed for all three dyes in this binary system, with the rotational reorientation times being longer in organic solvent rich zone, compared to the corresponding isoviscous point in water rich zone. This is attributed to strong hydrogen bonding between the solute and propanol molecules.

The increase in viscosity as 1-propanol is added to water is sharp with the peak value of 2.70 mPa s being reached at about 30% mole composition of 1-propanol. The viscosity of 1-propanol is 1.96 mPa s, the decrease after the post peak point is linear but gradual. The dielectric friction contribution in water, amides, and dipolar aprotics is minimal while it goes on increasing in alcohols (Krishnamurthy et al, 1993).

At isoviscous points there are two different τ_r values and this duality results from different values of dielectric frictions at the isoviscous points (Fig. 11). It is seen that both the neutral dyes F27 and FNa clearly produce the hook-type profile bent upwards and qualitatively mimic the nonhydrodynamic behavior. The reorientation times gradually increase as a function of viscosity up to the peak viscous value. τ_r values decrease after the solvent mixture exhibits a reduction in viscosity after the peak value. Note that the reorientation times are longer in propanol rich region compared to the water rich zone. In case of SRB though it exhibits hook type profile, surprisingly τ_r values longer in water rich zone in the beginning and later probe rotates faster in the intermediate viscous region. In propanol rich zone SRB shows similar τ_r values as those of water rich zone. This may be due to both amino groups of SRB are ethylated and the rotational diffusion of this dye was slightly more rapid than predicted. Theoretical models mimic this trend qualitatively, though GW & DKS models invariably predict a reduced friction and illustrate a hairpin - bending downwards. Thus, these models underestimate the friction experienced by the probe. The dual

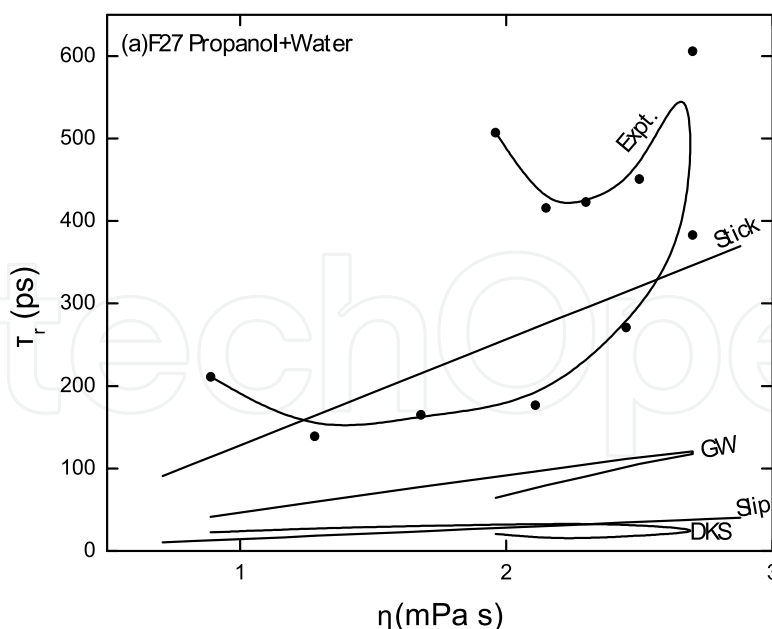


Fig. 11. Plot of rotational reorientation time with viscosity along with theoretical profile including viscous contribution for F27

valuedness of τ_r at isoviscous points near the organic solvent rich zone were attributed to different contributions of dielectric friction at these compositions and to strong hydrogen bonding.

General conclusion and summary

In this article, an attempt has been made to understand solute-solvent interactions in various situations using the powerful fluorescence spectroscopic techniques. The interesting observation of faster rotation of nonpolar probes in alcohols compared to alkanes can be attributed to large interstitial gaps that may be formed in the solvent medium and because of the possible elastic nature of the spatial H-bonding network of large alcohol molecules constituting a supramolecular structure. Presumably the exalite molecules will be located mainly in these solvophobic regions and thus, can rotate more freely in these gaps and experience reduced friction due to decreased viscosity at the point of contact. This actual viscosity is highly localized and cannot be measured easily. In such a situation the coupling parameter C can be much smaller than C_{slip} predicted by slip hydrodynamic boundary condition. Also, the largest probe E428 following subslip trend in alcohols is surprising. In such a situation the microscopic friction of the solvent molecules reduces well below the macroscopic value, which may result from either dynamic or structural features of the macroscopic solvation environment-giving rise to faster rotation in hydrogen bonding solvents. The experimental results indicate that DKS theory also holds well even for larger probes up to a radius of 6.3 Å in alkanes.

In case of polar probes, a faster rotation of the probes is observed for C522B and C138 in alcohols compared to C307. In spite of the distinction in structure a coincidental similar rotational reorientation times is observed in case of C522B and C138 in alcohols from propanol to decanol. Further studies of dielectric friction in alcohols, the observed reorientation times of these coumarins could not follow the trend predicted by the theories of Nee-Zwanzig and van der Zwan-Hynes. Experimentally and theoretically obtained dielectric frictions using NZ and ZH theories, do not agree well.

A nonlinear hook-type profile of rotational reorientation times of the probe as a function of viscosity is observed for all the dyes in binary mixtures, with the rotational reorientation times being longer in organic solvent rich zone, compared to the corresponding isoviscous point in water rich zone. This is attributed to strong hydrogen bonding between the solutes and DMSO or propanol molecules. Theoretical models mimic this trend qualitatively, though GW & DKS models invariably predict a reduced friction and illustrate a hairpin profile bending downwards. Thus they underestimate the friction experienced by the probe. The dual valuedness of τ_r at isoviscous points near the organic solvent rich zone were attributed to different contributions of dielectric friction at these compositions and to strong hydrogen bonding.

In general, the theoretical models: hydrodynamic as well as those based on dielectric friction do not adequately and precisely describe the experimental observations. The theoretical description of solute-solvent interaction to explain the experimental observations is yet to evolve. The failure of the theoretical models, to explain the experimental results quantitatively in specific cases, calls for the formulation of molecular based theories.

4. Acknowledgment

The author acknowledges the encouragement and support of Profs. M.I. Savadatti and B.G. Mulimani. Thanks are also due to Dr. James R.M., K.H. Nagachandra and M.A. Shivkumar for their timely help and financial support from Council of Scientific & Industrial Research and University Grants Commission, New Delhi.

5. References

- Alavi, D.S., Hartman, R.S. & Waldeck, D.H., 1991a, A test of continuum models for dielectric friction. Rotational diffusion of phenoxazine dyes in dimethylsulfoxide *J. Chem. Phys.* 94, 4509-20
- Alavi, D.S. & Waldeck, D.H., 1991b, Rotational dielectric friction on a generalized charge distribution *J. Chem. Phys.* 94, 6196-6202
- Alavi, D.S., Hartman, R.S. & Waldeck, D.H., 1991c, The influence of wave vector dependent dielectric properties on rotational friction. Rotational diffusion of phenoxazine dyes *J. Chem. Phys.* 95, 6770-83
- Alavi, D.S. & Waldeck, D.H., 1993, Erratum: Rotational dielectric friction on a generalized charge distribution *J. Chem. Phys.* 98, 3580-82
- Anderton, R.M. & Kauffman, J.F., 1994, Temperature-Dependent Rotational Relaxation of Diphenylbutadiene in n-Alcohols: A Test of the Quasihydrodynamic Free Space Model *J. Phys. Chem.* 98, 12117-12124
- Anfinrud, P.A., C. Han, T. Lian and R. M. Hochstrasser, 1990, Evolution of the transient vibrational spectrum following short-pulse excitation *J. Phys. Chem.* 94, 1180-84
- Backer, S.D., Dutt, G.B., Ameloot, M., Schryver, F.C.D., Müllen, K. & Holtrup, F., 1996, Fluorescence Anisotropy of 2,5,8,11-Tetra-tert-butylperylene and 2,5,10,13-Tetra-tert-butylterrylene in Alkanes and Alcohols *J. Phys. Chem.* 100, 512-518
- Barbara, P.F. & Jarzaba, W., 1990, Ultrafast Photochemical Intramolecular Charge and Excited State Solvation in *Adv. in Photochem.* Vol.15, pp. 1-68, Eds: D.H. Volman, G.S. Hammond, K. Gollnick, John Wiley & Sons, Inc., USA

- Bauer, D.R., I.I. Brauman & Pecora, R., 1974, Molecular reorientation in liquids. Experimental test of hydrodynamic models *J. Am. Chem. Soc.* 96, 6840-43
- Beddard, G.S., Doust, T. & Hudales, J. 1981, Structural features in ethanol-water mixtures revealed by picoseconds fluorescence anisotropy *Nature* 294,145-46
- Ben Amotz, D. & Scott, T.W., 1987, Microscopic frictional forces on molecular motion in liquids. Picosecond rotational diffusion in alkanes and alcohols *J. Chem. Phys.* 87, 3739-48
- Ben Amotz, D. & Drake, J.M., 1988, The solute size effect in rotational diffusion experiments: A test of microscopic friction theories *J. Chem. Phys.* 89, 1019-29
- Benzler, J. & Luther, L., 1997, Rotational relaxation of biphenyl and *p*-terphenyl in *n*-alkanes: the breakdown of the hydrodynamic description *Chem. Phys. Lett.* 279, 333-38
- Biasutti, M.A., Feyter, S.D., Backer, S.D., Dutt, G.B., Schryver, F.C.D., Ameloot, M., Schlichting P. & Müllen K., 1996, *Chem. Phys. Lett.* 248, 13-19
- Birks, J.B., 1970, *Photophysics of Aromatic Molecules*, John Wiley & Sons, New York
- Blanchard, G.J. & Wirth, M.J., 1986, Anomalous temperature-dependent reorientation of cresyl violet in 1-dodecanol *J. Phys. Chem.* 90, 2521-25
- Blanchard, G.J., 1987, Picosecond spectroscopic measurement of a solvent dependent change of rotational diffusion rotor shape *J. Chem. Phys.* 87, 6802-08
- Blanchard, G.J. & Cihal, C.A. 1988, Orientational relaxation dynamics of oxazine 118 and resorufin in the butanols. Valence- and state-dependent solvation effects *J. Phys. Chem.* 92, 5950-54
- Blanchard, G.J. 1988, A study of the state-dependent reorientation dynamics of oxazine 725 in primary normal aliphatic alcohols *J. Phys. Chem.* 92, 6303-07
- Blanchard, G.J. 1989, State-dependent reorientation characteristics of Methylene Blue: the importance of dipolar solvent-solute interactions *J. Phys. Chem.* 93, 4315-19
- Blanchard, G.J. 1989, Detection of a transient solvent-solute complex using time-resolved pump-probe spectroscopy *Anal. Chem.* 61, 2394-98
- Bordewijk, P., 1980, *Z. Naturforsch.* 35A, 1207-17
- Borin, I.A. & Skaf, M.S., 1998, *Chem. Phys. Lett.* 296, 125-30; 1999, Molecular association between water and dimethyl sulfoxide in solution: A molecular dynamics simulation study *J. Chem. Phys.* 110, 6412-20
- Bossis, G., 1982, The dynamical Onsager cavity model and dielectric friction *Mol. Phys.* 46, 475-80
- Bottcher, C.F.J. & Bordewijk, P., 1978, *Theory of Electric polarization*, 78th Edn., Vol. 11, Elsevier, Amsterdam
- Bowman, R.M., Eissenthal, K.B. & Millar, D.P., 1988, Frictional effects on barrier crossing in solution: Comparison with the Kramers' equation *J. Chem. Phys.* 89, 762
- Brito, P. & Bordewijk, P., 1980, Influence of dielectric friction on molecular reorientations *Mol. Phys.* 39, 217-226
- Brocklehurst, B. & Young, R.N., 1995, Rotation of Perylene in Alkanes: Nonhydrodynamic Behavior *J. Phys. Chem.* 99, 40-43
- Canonica, S., Schmid, A. & Wild, U.P., 1985, The rotational diffusion of *p*-terphenyl and *p*-quaterphenyl in non-polar solvents *Chem. Phys. Lett.* 122, 529-34
- Chandler, D., 1974, Translational and rotational diffusion in liquids. I. Translational single-particle correlation functions *J. Chem. Phys.* 60, 3500-07; Translational and rotational diffusion in liquids. II. Orientational single-particle correlation functions *ibid* 3508-12

- Chandra, A. & Bagchi, B., 1991, Molecular theory of solvation and solvation dynamics in a binary dipolar liquid *J. Chem. Phys.* 94, 8367-77
- Chandra, A., 1995, Ion solvation dynamics in binary dipolar liquids: theoretical and simulation results for mixtures of Stockmayer liquids *Chem. Phys. Lett.* 235, 133-39
- Chandrashekhar, K., Inamdar, S.R., Patil, D.C. & Math, N.N., 1993, Orientational relaxation of aminocoumarins by time-resolved dichroism with picosecond pulses *Spectrosc. Lett.* 28, 153-65
- Chapman, C.F., Fee, R.S. & Maroncelli, M., 1990, Solvation dynamics in N-methylamides *J. Phys. Chem.* 94, 4929-35
- Chen, S.H., Katsis, D., Schmid, A.W., Mastrangelo, J.C., Tsutsui, T. & Blanton, T.N., 1999, Circularly polarized light generated by photoexcitation of luminophores in glassy liquid-crystal films *Nature*, 397, 506
- Chuang, J.T. & Eisinger, K.B., 1971, Studies of effects of hydrogen bonding on orientational relaxation using picosecond light pulses *Chem. Phys. Lett.* 11, 368-70
- Chuang, T.J. & Eisinger, K.B., 1972, Theory of Fluorescence Depolarization by Anisotropic Rotational Diffusion *J. Chem. Phys.* 57, 5094-97
- Cole, R.H., 1984, in *Molecular Liquids-Dynamics and Interactions*, Eds: A. J. Barnes, W. J. Orville-Thomas and J. Yarwood, pp. 59-100, Reidel, Dordrecht
- Courtney, S.H., Kim, S.K., Canonica, S. & Fleming, G.R., 1986, Rotational diffusion of stilbene in alkane and alcohol solutions *J. Chem. Soc. Faraday Trans.* 82, 2065-72
- Cowie, M.G. & Toporowski, P.M., 1961, Association in the binary liquid system dimethyl sulphoxide - water *Can. J. Chem.* 39, 2240-43
- Dahm, W.J.A., Southerland, K.B. & Buch, K.A. 1991, Direct, high resolution, four-dimensional measurements of the fine scale structure of $Sc \gg 1$ molecular mixing in turbulent flows *Phys Fluids A* 3, 1115-1127
- Day, T.J.F. & Patey, G.N., 1997, Ion solvation dynamics in binary mixtures *J. Chem. Phys.* 106, 2782-91
- De la Torre, J.C., 1983, Biological actions and medical applications of dimethyl sulfoxide *Ann. N.Y. Acad. Sci.* 411, xi-xi
- Debye, P., 1929, *Polar molecules*, Dover Publications, London
- Demchenko, A.P., 2002, The red-edge effects: 30 years of exploration *Luminescence* 17, 19-42
- Dote, J.L., Kivelson, D. & Schwartz, R.N., 1981, A molecular quasi-hydrodynamic free-space model for molecular rotational relaxation in liquids *J. Phys. Chem.* 85, 2169-80
- Dutt, G.B., Doraiswamy, S., Periasamy, N. & Venkataraman, B., 1990, Rotational reorientation dynamics of polar dye molecular probes by picosecond laser spectroscopic technique *J. Chem. Phys.* 93, 8498-8513
- Dutt, G.B., Konitsky, W. & Waldeck, D.H., 1995, Nonradiative relaxation of 2-phenylindene in solution and its implications for isomerization of stilbenes *Chem. Phys. Lett.* 245, 437-40
- Dutt, G.B., Singh, M.K. & Sapre, A.V., 1998, Rotational dynamics of neutral red: Do ionic and neutral solutes experience the same friction? *J. Chem. Phys.* 109, 5994-5603
- Dutt, G.B., Srivatsavoy, V.J.P. & Sapre, A.V., 1999, Rotational dynamics of pyrrolopyrrole derivatives in alcohols: Does solute-solvent hydrogen bonding really hinder molecular rotation? *J. Chem. Phys.* 110, 9623-29
- Dutt, G.B. & Rama Krishna, G., 2000, Temperature-dependent rotational relaxation of nonpolar probes in mono and diols: Size effects versus hydrogen bonding *J. Chem. Phys.* 112, 4676-82

- Dutt, G.B. & Raman, S., 2001, Rotational dynamics of coumarins: An experimental test of dielectric friction theories *J. Chem. Phys.* 114, 6702-13
- Dutt, G.B. & Ghanty, T.K. 2003, Rotational Diffusion of Coumarins in Electrolyte Solutions: The Role of Ion Pairs *J. Phys. Chem B.* 107, 3257-64
- Dutt, G.B. & Ghanty, T.K., 2004, Is molecular rotation really influenced by subtle changes in molecular shape? *J. Chem. Phys.* 121, 3625-31
- Einstein, A., 1906, On the Theory of Brownian Motion (Zur Theorie der Brownschen Bewegung) *Ann. Phys.* 19, 371-81
- Eisenthal, K. B. 1975, Studies of chemical and physical processes with picosecond lasers *Acc. Chem. Res.* 8, 118-24
- Elsaesser, T. & Kaiser, W., 1991, Vibrational and Vibronic Relaxation of Large Polyatomic Molecules in Liquids *Annu. Rev. Phys. Chem.* 42, 83-107
- Evans, G.T., Cole, R.G. & Hoffman, D.K., 1982, A kinetic theory calculation of the orientational correlation time of a rotorlike molecule in a dense fluid of spheres *J. Chem. Phys.* 77, 3209-20
- Evans, G.T. & Evans, D.R., 1984, Kinetic theory of rotational relaxation in liquids: Smooth spherocylinder and rough sphere models *J. Chem. Phys.* 81, 6039-43
- Evans, G.T., 1988, Translational and rotational dynamics of simple dense fluids *J. Chem. Phys.* 88, 5035-41
- Fee, R.S. & Maroncelli, M., 1994, Estimating the time-zero spectrum in time-resolved emission measurements of solvation dynamics *Chem. Phys.* 183, 235-47
- Fee, R.S., Milsom, J.A. & Maroncelli, M., 1991, Inhomogeneous decay kinetics and apparent solvent relaxation at low temperatures *J. Phys. Chem.* 95, 5170-81
- Felderhof, B.U., 1983, Dielectric friction on a polar molecule rotating in a fluid *Mol. Phys.* 48, 1269-81; Dielectric friction on an ion rotating in a fluid *Mol. Phys.* 48, 1283-88
- Fleming, G.R., Morris, J.M. & Robinson, G.W., 1976, Direct observation of rotational diffusion by picosecond spectroscopy *Chem. Phys.* 17, 91-100
- Fleming, G.R., Knight, A.E.W., Morris, J.M., Robbins, R.J. & Robinson, G.W., 1977, Rotational diffusion of the mode-locking dye dodci and its photoisomer *Chem. Phys. Lett.* 49, 1-7
- Fleming, G.R., 1986, *Chemical Applications of Ultrafast Spectroscopy*, Oxford University Press: New York
- Fox, F. & Whittingham, K.P., 1974, Component interactions in aqueous dimethyl sulphoxide *J. Chem. Soc., Faraday Trans.* 75, 1407-12
- Garg, S.K. & Smyth, C.P., 1965, Microwave Absorption and Molecular Structure in Liquids. LXII. The Three Dielectric Dispersion Regions of the Normal Primary Alcohols *J. Phys. Chem.* 69, 1294-1301
- Geirer, A. & Wirtz, K., 1953, Molecular theory of microfriction *Z. Naturforsch.* A8, 532-38
- Gordalla, B.C. & Zeidler, M.D., 1986; Molecular dynamics in the system water-dimethylsulphoxide *Mol. Phys.* 59, 817-28; 1991, NMR proton relaxation and chemical exchange in the system H₁₆ 2O/H₁₇ 2O-[2H₆]dimethylsulphoxide, *Mol. Phys.* 74, 975-84
- Goulay, A.M., 1983, Rotational relaxation of OCS in n-alkanes: Collective and collisional effects *J. Chem. Phys.* 79, 1145-53
- Gustavsson, T., Cassara, L., Marguet, S., Gurzadyan, G., van der Meulen, P., Pommeret, S. & Mialocq, J.-C., 2003, *Photochem. Photobiol. Sci.* 2, 329

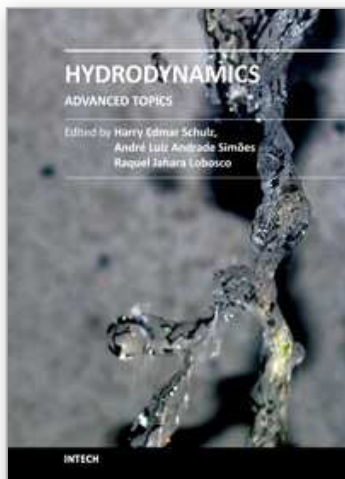
- Hambir, S.A., Y. Jiang & Blanchard, G.J., 1993, Ultrafast stimulated emission spectroscopy of perylene in dilute solution: Measurement of ground state vibrational population relaxation *J. Chem. Phys.* 98, 6075-82
- Hartman, R.S., Alavi, D.S. and Waldeck, D.H., 1991, An experimental test of dielectric friction models using the rotational diffusion of aminoanthraquinones *J. Phys. Chem.* 95, 7872-80
- Hartman, R.S., Konitsky, W.M., Waldeck, D.H., Chang, Y.J. & Castner, Jr, E.W., 1997, Probing solute-solvent electrostatic interactions: Rotational diffusion studies of 9,10-disubstituted anthracenes *J. Chem. Phys.* 106, 7920-30
- Heilweil, E.J., Casassa, M.P., Cavanagh, R.R. & Stephenson, J.C., 1986, Population lifetimes of OH($v=1$) and OD($v=1$) stretching vibrations of alcohols and silanols in dilute solution *J. Chem. Phys.* 85, 5004-18
- Heilweil, E.J., R. R. Cavanagh and J. C. Stephenson, 1987, Population relaxation of CO($v = 1$) vibrations in solution phase metal carbonyl complexes *Chem. Phys. Lett.* 134, 181-88
- Heilweil, E.J., Casassa, M.P., Cavanagh, R.R. & Stephenson, J.C. 1989, Picosecond Vibrational Energy Transfer Studies of Surface Adsorbates *Annu. Rev. Phys. Chem.* 40, 143-71
- Heilweil, E.J., Cavanagh, R.R. & Stephenson, J.C., 1989, CO($v=1$) population lifetimes of metal-carbonyl cluster compounds in dilute CHCl₃ solution *J. Chem. Phys.* 89, 230-39
- Horng, M.-L., Gardecki, J.A. & Maroncelli, M., 1997, Rotational Dynamics of Coumarin 153: Time-Dependent Friction, Dielectric Friction, and Other Nonhydrodynamic Effects *J. Phys. Chem. A* 101, 1030-47
- Hu, C.M. & Zwanzig, R., 1974, Rotational friction coefficients for spheroids with the slipping boundary condition *J. Chem. Phys.* 60, 4354-57
- Hubbard, J.B. & Onsager, L., 1977, Dielectric dispersion and dielectric friction in electrolyte solutions. I. *J. Chem. Phys.* 67, 4850-57
- Hubbard, J.B., 1978, Friction on a rotating dipole *J. Chem. Phys.* 69, 1007-09
- Hubbard, J.B. & Wolynes, P.G., 1978, Dielectric friction and molecular reorientation *J. Chem. Phys.* 69, 998-1006
- Huppert, D., Ittah, V. & E. Kosower, 1989, Static and dynamic electrolyte effects on excited-state behavior *Chem. Phys. Lett.* 159, 267-75
- Huppert, D., Ittah, V. & Kosower, E., 1990, Static and dynamic electrolyte effects on excited large dipole solvation: high dielectric constant solvents *Chem. Phys. Lett.* 173, 496-502
- Hynes, J.T., 1986, Chemical reaction rates and solvent friction *J. Stat. Phys.* 42, 149-168 and references therein
- Imeshev, G. & Khundkar, L.R., 1995, Inhomogeneous rotational dynamics of a rodlike probe in 1-propanol *J. Chem. Phys.* 103, 8322-28
- Inamdar, S.R., Chandrashekhar, K., Patil, D.C., Math, N.N. & Savadatti, M.I., 1995, Picosecond time-resolved laser emission of coumarin 102: Solvent relaxation, *Pramana, J. Phys.*, 45, 279-290
- Inamdar, S.R., Nadaf, Y.F. & Mulimani, B.G., 2003, Ground and excited state dipole moments of exalite 404 and exalite 417 uv laser dyes determined from solvatochromic shift of absorption and fluorescence spectra *J. Mol. Struct. (Theochem)*, 624, 47-51
- Inamdar, S.R., Mannekutla, J.R., Mulimani, B.G. & Savadatti, M.I., 2006, Rotational dynamics of nonpolar laser dyes *Chem. Phys. Lett.* 429, 141- 46
- Inamdar, S.R., Gayathri, B.R. & Mannekutla, J.R., 2009, Rotational diffusion of coumarins in aqueous DMSO *J. Fluoresc.* 19, 693-703

- Ito, N., Kajimoto, O. & K. Hara, 2000, Picosecond time-resolved fluorescence depolarization of *p*-terphenyl at high pressures *Chem. Phys. Lett.* 318, 118-24
- Jarzeba, W., Walker, G.C., Johnson, A.E. & Barbara, P.F., 1991, Nonexponential solvation dynamics of simple liquids and mixtures *Chem. Phys.* 152, 57-68
- Jiang, J. & Blanchard, G.J., 1994, Rotational Diffusion Dynamics of Perylene in n-Alkanes. Observation of a Solvent Length-Dependent Change of Boundary Condition *J. Phys. Chem.* 98, 6436-40; Vibrational Population Relaxation of Perylene in n-Alkanes. The Role of Solvent Local Structure in Long-Range Vibrational Energy Transfer, *ibid*, 9411-16; Vibrational Population Relaxation of Perylene in Its Ground and Excited Electronic States *ibid*, 9417-21
- Jiang Y. & Blanchard, G.J., 1995, Vibrational Population and Orientational Relaxation Dynamics of 1-Methylperylene in n-Alkanes. The Effective Range of Dipolar Energy Relaxation in Solution *J. Phys. Chem.* 99, 7904-12
- Kaatze, K., Pottel, R. & Schaefer, M., 1989, Dielectric spectrum of dimethyl sulfoxide/water mixtures as a function of composition *J. Phys. Chem.* 93, 5623-27
- Karasso, P.S. & Mungal, M.G., 1997, PLIF measurements in aqueous flows using the Nd:YAG laser *Exp Fluids* 23, 382-387
- Kawski, A., Kuklinski, B. & Bojarski, P., 2005, Dipole moment of aniline in the excited S_1 state from thermochromic effect on electronic spectra *Chem. Phys. Lett.* 415, 251-55
- Kirov, A.S., Hurlbut, C., Dempsey, J.F., Shrinivas, S.B., Epstein, J.W., Binns, W.R., Dowkontt, P.F. & Williamson, J.F., 1999, Radiation Therapy Physics: Towards two-dimensional brachytherapy dosimetry using plastic scintillator: New highly efficient water equivalent plastic scintillator materials *Med. Phys.* 26, 1515-23
- Koochesfahani, M.M. & Dimotakis, P.E., 1986, Mixing and chemical reactions in a turbulent liquid mixing layer *J Fluid Mech.* 170, 83-112
- Krishnamurthy, M., Khan, K.K. & Doraiswamy, S., 1993, Rotational diffusion kinetics of polar solutes in hexamethylphosphoramide-water systems *J. Chem. Phys.* 98, 8640-47
- Kubinyi, M., Grofcsik, A., Kárpáti, T. & Jones, W.J., 2006, Rotational reorientation dynamics of ionic dye solutes in polar solvents with the application of a general model for the solvation shell *Chem. Phys.* 322, 247-54
- Kumar, P.V. & Maroncelli, M., 2000, The non-separability of "dielectric" and "mechanical" friction in molecular systems: A simulation study *J. Chem. Phys.* 112, 5370-81
- Lakowicz, J.R., 1983, *Principles of Fluorescence Spectroscopy*, Plenum Press, New York
- Lakowicz, J. R., 2006, *Principles of fluorescence spectroscopy*, Springer: New York
- Laitinen, E., Korppi-Tommola, J. & Linnanto, J., 1997, Dielectric friction effects on rotational reorientation of three cyanine dyes in n-alcohol solutions *J. Chem. Phys.* 107, 7601-12
- Laria, D. & Skaf, M., 1999, Solvation response of polar liquid mixtures: Water-dimethylsulfoxide *J. Chem. Phys.* 111, 300-09
- Levitus, M., Negri, R.M. & Aramenda, P.F., 1995, Rotational Relaxation of Carbocyanines. Comparative Study with the Isomerization Dynamics *J. Phys. Chem.* 99, 14231-39
- Lingle Jr. R., Xu, X., Yu, S.C., Zhu, H. & Hopkins, J.B., 1990, Ultrafast investigation of condensed phase chemical reaction dynamics using transient vibrational spectroscopy: Geminate recombination, vibrational energy relaxation, and electronic decay of the iodine A' excited state *J. Chem. Phys.* 93, 5667-80
- Luzar, A. & Chandler, D., 1993, Structure and hydrogen bond dynamics of water-dimethyl sulfoxide mixtures by computer simulations *J. Chem. Phys.*, 98, 8160-73

- Madden, P. & Kivelson, D., 1982, Dielectric friction and molecular orientation *J. Phys. Chem.* 86, 4244-56
- Mannektla, J.R., Ramamurthy, P., Mulimani, B.G. & S.R. Inamdar, 2007, Rotational dynamics of UVITEX-OB in alkanes, alcohols and binary mixtures *Chem. Phys.*, 340, 149-57
- Mannektla, J.R., S. R. Inamdar, B. G. Mulimani and M. I. Savadatti, 2010, Rotational diffusion of coumarins: A Dielectric friction study *J Fluoresc.* 20, 797-808
- Maroncelli, M., 1993, The dynamics of solvation in polar liquids. *J. Molec. Liq.* 57, 1-37
- Maroncelli, M. & Fleming, G.R., 1987, Picosecond solvation dynamics of coumarin 153: The importance of molecular aspects of solvation *J. Chem. Phys.* 86, 6221-39
- Martin, D. & Hanthall, H., 1975, *Dimethyl Sulfoxide*; John Wiley & Sons, Inc., New York
- McCarthy, P.K. & Blanchard, G.J., 1995, Vibrational Population Relaxation of Tetracene in n-Alkanes. Evidence for Short-Range Molecular Alignment *J. Phys. Chem.* 99, 17748-53
- McCarthy, P.K. and Blanchard, G.J., 1996, Solvent Methyl Group Density Dependence of Vibrational Population Relaxation in 1-Methylperylene: Evidence for Short-Range Organization in Branched Alkanes *J. Phys. Chem.* 100, 5182-87
- McMahon, D.R.A., 1980, Dielectric friction and polar molecule rotational relaxation *J. Chem. Phys.* 72, 2411-24
- Millar, D.P., Shah, R. & Zewail, A.H., 1979, Picosecond saturation spectroscopy of cresyl violet: rotational diffusion by a "sticking" boundary condition in the liquid phase *Chem. Phys. Lett.* 66, 435-40
- Moog, R.S., Ediger, M.D., Boxer, S. G. & Fayer, M.D., 1982, Viscosity dependence of the rotational reorientation of rhodamine B in mono- and polyalcohols. Picosecond transient grating experiments *J. Phys. Chem.* 86, 4694-4700
- Nadaf, Y.F., Mulimani, B.G., Gopal, M. & Inamdar, S.R., 2004, Ground and excited state dipole moments of some exalite dyes from solvatochromic method using solvent polarity parameters *J. Mol. Struct. (Theochem)* 678, 177-81
- Nee, T.W. & Zwanzig, R., 1970, Theory of Dielectric Relaxation in Polar Liquids *J. Chem. Phys.* 52, 6353-63
- Nowak, E., 1983, Dielectric friction and energy dissipation in polar fluids *J. Chem. Phys.* 79, 976-81
- Packer, K.J. & Tomlinson, D.J., 1971, Nuclear spin relaxation and self-diffusion in the binary system, dimethyl sulphoxide (DMSO)+ water *J. Chem. Soc., Trans. Faraday* 67, 1302-14
- Pal, A. & Daas, G., 2000, Excess molar volumes and viscosities of binary mixtures tetraethylene glycol dimethyl ether (tetraglyme) with chloroalkanes at 298.15K *J. Mol. Liq.* 84, 327-37
- Papazyan, A. & Maroncelli, M., 1995, Rotational dielectric friction and dipole solvation: Tests of theory based on simulations of simple model solutions *J. Chem. Phys.* 102, 2888-2919
- Perrin, F., 1936, Mouvement brownien d'un ellipsoïde (II). Rotation libre et depolarisation des fluorescences. Translation et diffusion de molécules ellipsoïdales, *J. Phys. Radium* 7, 1-11
- Phillips, L.A., Webb, S.P. & Clark, J.H., 1985, High-pressure studies of rotational reorientation dynamics: The role of dielectric friction *J. Chem. Phys.* 83, 5810-21
- Porter, G., Sadkowski, P.J. & Tredwell, C.J., 1977, Picosecond rotational diffusion in kinetic and steady state fluorescence spectroscopy *Chem. Phys. Lett.* 49, 416-20

- Qunfang, L. & Yu-Chun, H., 1999, Correlation of viscosity of binary liquid mixtures. *Fluid Phase Equilibria* 154, 153-163 and references therein
- Rice, S.A. & Kenney-Wallace, G.A., 1980, Time-resolved fluorescence depolarization studies of rotational relaxation in viscous media *Chem. Phys.* 47, 161-70
- Rider, K.L. & Fixman, M., 1972, Angular Relaxation of the Symmetrical Top. II. The Rough Sphere *J. Chem. Phys.* 57, 2548-59
- Roy, M. & Doraiswamy, S., 1993, Rotational dynamics of nonpolar solutes in different solvents: Comparative evaluation of the hydrodynamic and quasihydrodynamic models *J. Chem. Phys.* 98, 3213-23
- Sanders, M.J. & Wirth, M.J., 1983, Evidence for solvation structural dependence of rotational diffusion anisotropy *Chem. Phys. Lett.* 101, 361-66
- Safford, G.J., Schaffer, P.C., Leung, P.S., Doebbler, G.F., Brady G.W. & Lyden, E.F.X. 1969, Neutron Inelastic Scattering and X-Ray Studies of Aqueous Solutions of Dimethylsulphoxide and Dimethylsulphone *J. Chem. Phys.* 50, 2140-59
- Shapiro, S.L. & Winn, K.R., 1980, Picosecond time-resolved spectral shifts in emission: dynamics of excited state interactions in coumarin 102 *Chem. Phys. Lett.* 71, 440-44
- Sceats, M.G. & Dawes, J.M., 1985, On the viscoelastic properties of n-alkane liquids *J. Chem. Phys.* 83, 1298-1304
- Selvaraju, C. & Ramamurthy, P., 2004, Excited-State Behavior and Photoionization of 1,8-Acridinedione Dyes in Micelles *Chem. Eur. J.* 10, 2253-62
- Shank, C.V. & Ippen, E.P., 1975, Anisotropic absorption saturation with picosecond pulses *Appl. Phys. Lett.* 26, 62-63
- Singh, M.K., 2000, Rotational Relaxation of Neutral Red in Alkanes: Effect of Solvent Size on Probe Rotation *Photochem. Photobiol.* 72, 438-43
- Skaf, M. & Ladanyi, B.M., 1996, Molecular Dynamics Simulation of Solvation Dynamics in Methanol-Water Mixtures *J. Phys. Chem.* 100, 18258-68
- Soper, A.K. & Luzar, A., 1996, Orientation of Water Molecules around Small Polar and Nonpolar Groups in Solution: A Neutron Diffraction and Computer Simulation Study *J. Phys. Chem.* 100, 1357-67
- Soper, A.K. & Luzar, A., 1992, A neutron diffraction study of dimethyl sulphoxide-water mixtures *J. Chem. Phys.* 97, 1320-31
- Spears, K.G. and L. E. Cramer, 1978, Rotational diffusion in aprotic and protic solvents *Chem. Phys.* 30, 1-8
- Srivastava, A. & Doraiswamy, S., 1995, Rotational diffusion of rose bengal *J. Chem. Phys.* 103, 6197-6205
- Steiner, R.F., 1991, in *Topics in Fluorescence Spectroscopy*, Vol. 2., J. R. Lakowicz (Ed.), Plenum Press, New York
- Stokes, G., 1856, *Trans. Cambridge Philos. Soc.* 9, 5
- Templeton, E. F. G., Quitevis, E. L. & Kenney-Wallace, G. A., 1985, Picosecond reorientational dynamics of resorufin: correlations of dynamics and liquid structure *J. Phys. Chem.* 89, 3238-43
- Templeton, E.F.G. & Kenney-Wallace, G.A., 1986, Picosecond laser spectroscopic study of orientational dynamics of probe molecules in the dimethyl sulfoxide-water system *J. Phys. Chem.* 90, 2896-2900
- Titulaer, U.M. & Deutch, J.M., 1974, Analysis of conflicting theories of dielectric relaxation *J. Chem. Phys.* 60, 1502-13

- Tjai, T.H., Bordewijk P. & Bottcher, C.F.J., 1974, On the notion of dielectric friction in the theory of dielectric relaxation *Adv. Mol. Relax. Proc.* 6, 19-28
- Tokuhiro, T., Menafrá L. & Szmant, H.H., 1974, Contribution of relaxation and chemical shift results to the elucidation of the structure of the water-DMSO liquid system *J. Chem. Phys.* 61, 2275-82
- Traube, J., 1886, *Ber. Dtsch Chem. Ges.* B.19, 871-892
- Vaisman, I.I. & Berkowitz, M.L., 1992, Local structural order and molecular associations in water-DMSO mixtures. Molecular dynamics study *J. Am. Chem. Soc.* 114, 7889-96
- van der Zwan, G. & Hynes, J.T., 1985, Time-dependent fluorescence solvent shifts, dielectric friction, and nonequilibrium solvation in polar solvents *J. Phys. Chem.* 90, 4181-88
- Valenta, J., Dian, J., Hála, J., Gilliot, P. & Lévy, R., 1999 Persistent spectral hole-burning and hole-filling in CuBr semiconductor nanocrystals *J. Chem. Phys.* 111, 9398-403
- Voigt, W., 2005, Sulforhodamine B assay and chemosensitivity *Methods Mol. Med.* 110, 39-48
- von Jena, A. & Lessing, H. E., 1979a, Rotational-diffusion anomalies in dye solutions from transient-dichroism experiments *Chem. Phys.* 40, 245-56
- von Jena, A. & Lessing, H. E., 1979b, Rotational Diffusion of Prolate and Oblate Molecules from Absorption Relaxation *Ber. Bunsen-Ges. Phys. Chem.* 83, 181-91
- von Jena, A. & Lessing, H.E., 1981, Rotational diffusion of dyes in solvents of low viscosity from transient-dichroism experiments *Chem. Phys. Lett.* 78, 187-93
- Wagener, A. & Richert, R., 1991, Solvation dynamics versus inhomogeneity of decay rates as the origin of spectral shifts in supercooled liquids *Chem. Phys. Lett.* 176, 329-34
- Waldeck, D.H. and G. R. Fleming, 1981, Influence of viscosity and temperature on rotational reorientation. Anisotropic absorption studies of 3,3'-diethyloxadicyanone iodide *J. Phys. Chem.* 85, 2614-17
- Waldeck, D.H., Lotshaw, W.T., McDonald, D.B. & Fleming, G.R., 1982, Ultraviolet picosecond pump-probe spectroscopy with a synchronously pumped dye laser. Rotational diffusion of diphenyl butadiene *Chem. Phys. Lett.* 88, 297-300
- Widom, B., 1960, Rotational Relaxation of Rough Spheres, *J. Chem. Phys.* 32, 913-23
- Wiemers, K. & Kauffman, J. F., 2000, Dielectric Friction and Rotational Diffusion of Hydrogen Bonding Solutes *J. Phys. Chem. A* 104, 451-57
- Williams, A.M., Jiang, Y. & Ben-Amotz, D., 1994, Molecular reorientation dynamics and microscopic friction in liquids *Chem. Phys.* 180, 119-29
- Yip, R.W., Wen, Y. X. & Szabo, A.G., 1993, Decay associated fluorescence spectra of coumarin 1 and coumarin 102: evidence for a two-state solvation kinetics in organic solvents *J. Phys. Chem.* 97, 10458-62
- Yoshimori, A., Day, T.J.F. & Patey, G.N., Theory of ion solvation dynamics in mixed dipolar solvents *J. Chem. Phys.* 109, 3222-31
- Youngren, G.K. & Acrivos, A., 1975, Rotational friction coefficients for ellipsoids and chemical molecules with the slip boundary condition *J. Chem. Phys.* 63, 3846-48
- Zwanzig, R. & Harrison, A.K., 1985, Modifications of the Stokes-Einstein formula *J. Chem. Phys.* 83, 5861- 62



Hydrodynamics - Advanced Topics

Edited by Prof. Harry Schulz

ISBN 978-953-307-596-9

Hard cover, 442 pages

Publisher InTech

Published online 22, December, 2011

Published in print edition December, 2011

The phenomena related to the flow of fluids are generally complex, and difficult to quantify. New approaches - considering points of view still not explored - may introduce useful tools in the study of Hydrodynamics and the related transport phenomena. The details of the flows and the properties of the fluids must be considered on a very small scale perspective. Consequently, new concepts and tools are generated to better describe the fluids and their properties. This volume presents conclusions about advanced topics of calculated and observed flows. It contains eighteen chapters, organized in five sections: 1) Mathematical Models in Fluid Mechanics, 2) Biological Applications and Biohydrodynamics, 3) Detailed Experimental Analyses of Fluids and Flows, 4) Radiation-, Electro-, Magnetohydrodynamics, and Magnetorheology, 5) Special Topics on Simulations and Experimental Data. These chapters present new points of view about methods and tools used in Hydrodynamics.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Sanjeev R. Inamdar (2011). Rotational Dynamics of Nonpolar and Dipolar Molecules in Polar and Binary Solvent Mixtures, Hydrodynamics - Advanced Topics, Prof. Harry Schulz (Ed.), ISBN: 978-953-307-596-9, InTech, Available from: <http://www.intechopen.com/books/hydrodynamics-advanced-topics/rotational-dynamics-of-nonpolar-and-dipolar-molecules-in-polar-and-binary-solvent-mixtures>

INTech
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](https://creativecommons.org/licenses/by/3.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen