Chapter I

INTRODUCTION

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1.1 INTRODUCTION

The liquid state of matter is exceedingly complex and yet far from completely understood. The molecules in a liquid are in intimate contact, and as such the intermolecular interactions become very important in determining the behavior of a liquid. Diffusion based descriptions of molecular rotation have generally been used to model the motion of medium sized (few hundred angstroms) solute molecules in liquid solutions. In this diffusion regime, measurement of solute reorientation times becomes a sensitive probe of the rotational friction. This friction will depend on both frequency and wave vector dependant solvent properties and also on the molecular characteristics of the particular solvent being examined.

Attempts to model the rotational friction use continuum based theories for the solvent and the solute properties are modeled in some specific way. The liquid is treated as a continuum characterized by it bulk properties, such as, viscosity and dielectric constant. The friction experienced by the solute molecule for rotational motion is computed within this continuum.

Appreciable effort has been made by experimentalists and theorists to describe the rotational friction for solute molecules. Quite often, the experimental results are interpreted in terms of hydrodynamics. It has been shown that [1] for a solute in a single solvent the dependence of the rotational relaxation times on the solvent viscosity is given by the hydrodynamic model, if the physical parameters such as friction and temperature are varied. On the other hand, a wide range of
reports have appeared in literature which consider variation of size, charge, and polarity. Specific molecular interactions are often used to explain these.

The theoretical interest in the study of the rotational diffusion kinetics of molecules in liquids stems from the fact that it provides information about the intermolecular interaction in the condensed medium. However, the theoretical modeling of molecular reorientation in liquids and its correlation with the experimental data is still far from satisfactory. So far, two kinds of approaches have been employed in the understanding of rotational dynamics. In one approach, binary collision approximation has been used to explain the rotational dynamics. Using this approach, kinetic theory model for rotational relaxation has been employed by Widom [3], Rider [4] and Fixman, and Chandler [5] for rough sphere fluids and by Evans et al. [6-8] for smooth convex bodies. Enskog equation for viscosity has been employed in the Evans model to express rotational reorientation times ($\tau_r$) 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 liquid. For real systems the quantitative predictions of $\tau_r$ by these models are often difficult to evaluate and only qualitative predictions can be made about the variation of $\tau_r$ with viscosity of solvents.

The second approach is the macroscopic approach of understanding the rotational dynamics wherein 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 in understanding the rotational dynamics of even
medium sized molecules [of a few hundred (Å³) volume] has been possible with the Stokes-Einstein-Debye (SED) equation [9-11], according to which the rotational reorientation time ($\tau_r$) for a spherical molecule of volume $V$ rotating in a liquid of viscosity $\eta$ at temperature $T$ is given by

$$\tau_r = \frac{\zeta}{kT} = \frac{\eta V}{kT}$$

where $\zeta$ is the rotational friction and $k$ is Boltzmann's constant. The modified equation to describe the rotational dynamics for any general molecule [12] is given by

$$\tau_r = \frac{\eta V f C}{kT} + \tau_0$$

where $f$ is referred to as a shape factor and is well specified, $C$ is the boundary condition parameter dependent strongly on solute, solvent, and concentration and $\tau_0$ is the rotational reorientation time at zero viscosity.

The interpretation of rotational diffusion in this hydrodynamic approach is done at two levels of approximation. In the first approximation, which is the stick limit, the boundary conditions on the diffusion problem are specified such that the first solvent shell coherently rotates with the probe molecule. In other words, it is understood that there is a strong coupling between solvent and solute along the surface tangent and $C$ in the above expression is set equal to unity. The stick boundary condition is valid for probe molecules whose size is considerably larger than the solvent molecules. The other level of approximation of rotational diffusion known as slip limit describes the motion of solute molecules whose size is
comparable to or less than that of solvent molecules. In the slip limit, the solvent is assumed not to rotate with the probe molecules. The resistance to the motion arises from the fact that for nonspherical molecules, some solvent molecules must be displaced as the probe molecule rotates. A sphere or a symmetric ellipsoid rotating about its symmetric axis experiences no rotational friction in the slip limit. The predicted rotational reorientation for a sphere can be significantly modified with a small degree of asymmetry in the probe molecule. In general, the rotational friction coefficient with slip is considerably smaller than for the corresponding stick case. Thus, the variation in the value of $C$ permitted by the hydrodynamic theory is between unity and $C_{\text{slip}}$. While the demarcation of the boundary conditions as stick and slip depends on the size of the solute, the transition from slip to stick as a function of solute size was shown to be feasible by Zwanzig [13] using his bumpy cylinder model.

There are experimental evidences to indicate that in some cases the observed rotational reorientation times have been either much more than stick prediction (referred to as super stick) [14-17] or much smaller than slip estimation (referred to as subslip) [18-26] and both conditions signify a deviation from hydrodynamic boundary condition. A faster rotation than predicted by $C_{\text{slip}}$ is not within the framework of hydrodynamics and it becomes necessary to invoke the molecularity of the system. The subslip scenario can be understood as follows. Large interstitial gaps, arising out of the shape and size of the solvent molecules, are supposed to be formed in the solvent medium. The probe molecules, which are
considerably smaller than the solvent molecule, can rotate almost freely in these gaps contrary to the tenets of the hydrodynamic theory according to which the viscous solvent is supposed to be in intimate contact with the probe molecule. In this picture $C$ can be smaller than $C_{\text{slip}}$ predicted by hydrodynamic theory. Alternatively, it can be said that the microviscosity ($\eta_{\mu}$) experienced by the probe is smaller than the macroscopic viscosity ($\eta_s$) and can be written as,

$$\eta_{\mu} = \eta_s C_{\text{slip}}$$

Theoretical justification for this approach is provided by the microfriction theory of Gierer and Wirtz (GW) [27] which takes into account the sizes of the solute and solvent molecules whereby a modified value for $C$ can be obtained. A deviation from the linear relation between $\tau_r$ of a solute and the shear viscosity of a solvent, through a homologous solvent series was noted in a number of studies [17-25]. This also focused the need to take into account the relative sizes of solute and solvent molecules, in understanding the rotational dynamics. A slight variant of the GW model, often referred to as "free space model," was suggested by Dote, Kiveslson, and Schwartz (DKS), that incorporates the effects of free space in the liquid as well as the relative sizes of solute and solvent [28]. Another approach for the description of free volume has been recently put forward by Song [29] but has not yielded any significant improvement over the DKS theory. Several other models have also been proposed [30, 31]. There has also been a suggestion [32] that the deviation from the SED formula should be analyzed in terms of...
environment-dependent coupling to the solvent, rather than as a breakdown of the basic formula.

In an effort to compare the solute size effect with the theoretical models, viz., Zwanzig's bumpy cylinder model and DKS free volume model, Ben Amotz and Drake [33] have compiled the observed rotational reorientation times of different neutral molecules in alkanes, determined using different techniques. Most of the neutral molecules (both nonpolar and polar) in their list had a range of radii [34] between 2.0 - 4.5 Å except one having a radius of 5.6 Å. It was observed that the rotational friction varies from a minimal value for small molecules to the near maximum hydrodynamic limit as the radius of the solute approaches 5.6 Å, with a sharp increase in the friction for molecules of size around 3.5 - 4.0 Å. They also noted that while Zwanzig's bumpy cylinder model with viscous memory correction qualitatively predicts the observed trend, the DKS theory could give a better quantitative agreement over the entire range of sizes of molecules in alkanes. However, due to some error in the calculation, their representation of the DKS theory was not fully correct [35]. The corrected results [35] maintain the general trend of agreement between the DKS model and the experimental data in alkanes up to solute radius 4.5 Å but fails at the largest solute of 5.6 Å radius. However, a categorical statement about disagreement between the DKS model and the experimental data for solute radius >4.5 Å cannot be made, as there is only one data point available at 5.6 Å solute radius.
The present work deals with the study of orientational relaxation dynamics of a series of neutral nonpolar dye molecules, in a homologous series of non-polar (alkanes) and polar (alcohols) solvents. The selected solutes have radii varying from 5.3 - 6.0 Å and it bridges the gap in the existing data in the literature. Our studies in this range have been used to effectively test (a) transition towards stick hydrodynamics with increase in solute size, (b) for any deviation from hydrodynamic theory, and (c) applicability of the quasi-hydrodynamic or microfrictional models, viz., GW and DKS. Further, our data together with that available in the literature provides a larger data set up to 6.0 Å, that can be used to test the overall agreement of the experimental data in alkanes and alcohols with GW and DKS models, and a turnover of the microscopic models to macroscopic behavior with increase in solute size.

1.2 SELECTION OF THE PROBE MOLECULES

As seen from the earlier works reported, a variety of fluorescent probe molecules were chosen in order to investigate their interaction with different solvents and the results were discussed in the light of the hydrodynamic theories. Upon excitation with polarized light, the emission from the fluorescence samples is also polarized. This polarization is a result of the photoselection of the fluoprophores according to their orientation relative to the direction of the polarized excitation. The emission can be depolarized by various phenomena depending on the sample under study. Rotational diffusion of fluorophores is one common cause...
of depolarization. The polarization or anisotropy measurements reveal the average angular displacement of the molecule, which occurs between the absorption and subsequent emission of a photon. This angular displacement depends on the rate and extent of rotational diffusion during the lifetime of the excited state. These diffusion motions in turn depend upon the viscosity of the solvent and the size and shape of the solute (or diffusing species). Hence, a change in solute will result in a change in fluorescence anisotropy. The dependence of fluorescence anisotropies upon the rotational diffusion of molecules has resulted in various applications. Different experimental investigations based on steady state and time resolved fluorescence anisotropies have dealt with variety of fluorescence probes and solvents. Physical characteristics of the probes such as size, shape and polarity are kept in mind while choosing the probes. The solvents are chosen not only on the basis of their viscosities but also depending on their dielectric properties (e.g. n, etc.).

A large number of publications in this field during the last two decades has constituted a data base for the molecules (both polar and non-polar) with radii in the range of 2 to 4.5 Å. Most experimental investigations attempt to test the validity of the hydrodynamic models and to account for any deviation from it in the above range. The present study attempts to extend this data base to molecular radii up to 6.0 Å, to test the applicability of SED model, to account for any deviations from it and the need to the modify/improve models of GW and DKS theories. With these ideas in view, we have chosen three relatively new dyes from the exalite series of
UV laser dyes. All these are non-dipolar and non-interacting solutes. These are probed in solvents of differing viscosity and nature (alkanes and alcohols).

Exalite series of dyes have been used in past to obtain laser pulses in the UV range. Exalite 392E dye was found to laser efficiently between 375-405 nm when pumped by a cw laser (Ar\textsuperscript{+} laser) [36]. Characterization of as many as 14 exalite dyes using XeCl examir laser as pump source was reported by Schneider et al. [37] and Fleitz et al. [38]. Broad band fluorescence emission ranging from 350-400 nm was observed from Exalite-377-doped sol-gel silica in bulk and thin film form, when pumped by a 1 nsec N\textsubscript{2} laser. The laser tuning curve exhibited two peaks at 360 and 378 nm [39]. Further, narrow linewidth of 4.4 GHz was obtained from exalite 377-doped sol-gel silica sample, when pumped by Nd: YAG laser pumped dye laser [40]. Exalite 351-doped sol-gel silica sample gave laser output at 352 nm when pumped by frequency doubled output of dye laser (280 nm) [41]. Generation of circularly polarized light by photoexcitation of exalite 428 dye has been reported by Chen and coworkers [42].

1.3 ORGANIZATION OF THE THESIS

The structure of the thesis is organized in the following manner:

Chapter II gives a systematic description of the instruments employed to study the steady state absorption and fluorescence and fluorescence anisotropy. The time domain fluorescence spectrometry using time correlated single photon counting technique is described in detail, which was used to determine the excited
state lifetimes of the exalite dyes chosen. The techniques and tools used to evaluate the dipole moments are also described in brief.

Chapter III is divided into 2 sections. Section A describes the detailed study of steady state absorption and fluorescence of 6 exalite dyes in polar and non-polar solvents. The results are used to evaluate the ratio of excited state dipole moment to the ground state dipole moments. The Stokes shifts are correlated to the solvent polarity and $E_T(30)$ functions. Section B deals with the experimental determination of dipole moment of these dyes in both the ground and excited state using different methods.

Chapter IV describes the rotational reorientation dynamics of selected nondipolar exalite dyes. A detailed literature survey of the topic is presented in the beginning. Theoretical aspects of different hydrodynamic and quasihydrodynamic models are discussed in detail. The results obtained in the present investigation are discussed in the light of these existing theories.

Chapter V highlights the important findings of the present work and contains the concluding remarks.
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1.4 References


34. A term average radius is evaluated from equating the van der Waals volume of a nonspherical molecule to $4\pi r^3/3$ and is generally used in describing the size of a molecule.

35. Private communication from Ben Amotz (April 1992).


Chapter I. Introduction
