INFERENCES

This thesis investigates the rotational dynamics of non-dipolar probes in associative and non-associative solvents.

The ground and excited state dipole moments of six exalite dyes were determined using solvatochromic shift method. The dipole moments of molecules in the excited state have been measured employing two different methods. The bathochromic shift with the increasing solvent polarity observed in these dyes hints towards n-π* transition. The spectral shifts also indicate the presence of general and specific types of solvent-solute interactions.

The experimentally determined dipole moments in the excited states are found to be invariably higher than their ground state counterparts for all the six dyes and the change in dipole moments varies from 1.24 to 13.19D. The higher slopes obtained for the linear plots of emission maxima compared to those of absorption maxima as function of $E_r(30)$ function, are suggestive of the fact that solvation is larger in the excited than in the ground state.

The determination of dipole moments is useful in evaluating the dielectric friction (Nee and Zwanzing model) [1] and hence the rotational correlation times. A large difference in dipole moments in the ground and excited states is observed for these dyes. Higher values of dipole moments in the excited state suggest that the molecules may have rod like structure. This also gives additional support for modeling these molecules as prolate ellipsoids in analyzing the rotational reorientation data.
Out of the six molecules investigated above three molecules viz., E392A, E404 and E398 were chosen for the study of rotational reorientation in two types of solvents: non-associative (alkanes) and associative (alcohols). This is primarily because of the nondipolar nature of the dyes and since our interest was to understand the rotational reorientation of nondipolar solutes in polar and nonpolar solvents. The molecular structure and dimensions of these three molecules make them ideal probes for the rotational dynamics studies, modeling them as prolate ellipsoids. Rotational reorientation times of these dyes determined experimentally and those predicted from slip and stick hydrodynamic, GW [2] and DKS [3] quasihydrodynamic models lead to the following inferences:

1. The present work has been aimed at understanding rotational relaxation of three nondipolar exalite dyes in alkanes and alcohols. As already noted these exalite dyes are long-chain molecules containing 4-5 phenyl rings and have been shown to be efficient laser dyes in the uv and blue region of the electromagnetic spectrum. The rotational reorientation times are determined using steady state fluorescence anisotropy experiments and are compared with those predicted using hydrodynamic (slip and stick) and quasihydrodynamic (GW and DKS) models. The absence of any hydrogen bonding functional groups on these three molecules reduces the contribution of dielectric friction to the overall friction experienced by these molecules to almost zero. Hence, the friction experienced by these molecules is expected to arise entirely due to mechanical friction.
2. Rotational reorientation times of E392A are determined experimentally in series of alkanes ($\eta=0.214 \text{ mPas} - 3.032 \text{ mPas}$) and alcohols ($\eta=1.074 \text{ mPas} - 10.9 \text{ mPas}$). In alkanes the $\tau_r$ values increase linearly from 81 ps to 1157 ps with increasing viscosity. These values compare well with those predicted by the SED [4] hydrodynamic theory with stick boundary condition. In fact, this molecule follows stick hydrodynamics in alkanes as is normally expected of molecules of the size on this order [5]. In alcohols, $\tau_r$ increases linearly from 210 to 2314 ps and they compare very well with those predicted by the SED hydrodynamic theory with slip boundary condition. Further, $\tau_r$ values fall below the slip values for larger solvent molecules (n-heptanol to n-decanol), showing a tendency towards a sub-slip behaviour. Interestingly, the $\tau_r$ values determined in alcohols are significantly smaller than those obtained for alkanes indicating a faster rotation in alcohols which is in direct contradiction to the predictions of DKS model. This may be attributed to either structural or dynamical microscopic frictional effects. The quasihydrodynamic models of the GW and DKS are unable to predict the observed behaviour, even qualitatively. They, as a matter of fact, underestimate the friction experienced by this molecule in both alkanes as well as alcohols.

3. The second molecule E404 is 110% larger than the earlier one and rotates much slower as expected from simple hydrodynamics (15-20% in alkanes and 37-42% in alcohols). $\tau_r$ increases linearly from 112 ps to 1354 ps in alkanes for the range of viscosities studied. The trend followed by the experimental $\tau_r$ values lies between the slip and stick lines, but more inclined towards slip limit. However, in
alcohols $\tau_r$ increases linearly from 488 ps to 3934 ps as function of viscosity and the molecule almost follows slip hydrodynamic model in these solvents. Note that, the rotation of this molecule too is consistently faster in alcohols than in alkanes.

4. E398 is the largest of the three probes chosen here and also the largest molecule to be reported so far in literature. Rotational reorientation times of this dye in alkanes increase linearly from 215 to 3588 ps in alkanes and follow sub slip trend. In alcohols, $\tau_r$ ranges from 934 to 13619 ps. These values are significantly smaller than those predicted by SED model with slip boundary condition. It is very interesting to note that such a large molecule exhibits sub-slip behaviour. This could be explained by saying that the measured (macro) viscosity is greater than the microviscosity or the actual viscosity experienced by the molecule. To the best of our knowledge this is the first report on the largest molecule studied so far exhibiting sub slip behaviour. Reports on such behaviour are scarce in literature [5-7]. The molecules p-terphenyl and p-quinquephenyl followed sub-slip experimental trend in alkanes yielding substantially reduced $\tau_r$ values as observed by Canonica et al., [6]. Roy and Doraiswamy [5] noted that out of the five molecules they studied, 2,2"'-dimethyl-p-quaterphenyl, exhibited sub slip behaviour in alcohols whereas the trend lied between slip and stick limits in case of alkanes. Here too both the GW and DKS models failed to predict the observed behaviour.

Further, in a study of temperature dependence of rotational correlation times of diphenylbutadiene in a series of alcohols, Anderton and Kauffman [7] noted much faster rotation in all the solvents than that expected by the slip limit. The failure of
DKS model in this case was attributed to the fact that both the Frenkel hole theory of liquids and the Hilderbrand treatment of solvent viscosity were derived for regular solutions, which explicitly excluded alcohols. The fact that DKS model was able to explain the results in alkanes as observed in many cases also supported this argument [5, 8]. However, in the present study E398 shows sub slip behaviour in case of both alkanes as well as alcohols. The SED hydrodynamic model predicted the experimental trend in alkanes as well as alcohols.

5. The rotational reorientation times of these three dyes were measured in two solvents representing each category (alkanes and alcohols) at five different temperatures above room temperature. The two solvents, nonane and n-octanol, were specifically chosen since their molecular volumes are almost same whereas their viscosities differ by an order of magnitude i.e., the viscosity of n-octanol is ~11 times that of nonane. It is noted that the τᵣ values for the three molecules increase from E392A to E398. They decrease with increasing temperatures for all the three molecules. The predictions by the GW and DKS models could not be made for each of the temperatures studied, since B and ΔV values for the temperatures studied, are not available in literature. An important aspect that is reproduced is that the rotation is faster for all the three molecules in n-octanol compared to nonane.

6. Noteworthy aspect of the present investigation on the three nondipolar exalites (E392A, E404 and E398) is the fact that the SED hydrodynamic theory is able to qualitatively predict the rotational dynamics at room temperature.
correctly predicts linear relationship of $\tau$, and $\eta$ in all the cases. The slip and stick boundary conditions are fairly adequate in understanding the nature of solvent-solute interactions. As can be expected from molecules of the size of E392A and E404, stick and slip behaviour observed in case of alkanes and alcohols respectively, is reasonably agreeable. Many experimental studies have clearly demonstrated that as the solute size increases there is a change over from slip to stick behaviour [5, 8, 9]. This is noted in case of E392A and also to some extent for E404. However, the SED hydrodynamic theory fails to predict the observed sub slip behaviour in case of the largest probe E398. The quasihydrodynamic models of GW and DKS, which take into account the relative sizes of the solute and solvent molecules and the effects of free space in the liquid, are unable to explain the experimentally observed results, even qualitatively. In fact, they underestimate the friction experienced by these probes and predict much faster rotation both in alkanes and alcohols. In general, the DKS theory has failed to predict the observed faster rotation of all the three molecules in alcohols as compared to alkanes.

In the present investigation, though the SED hydrodynamic theory correctly predicts the linear relationship of $\tau$, with $\eta$ for all the three molecules it has failed to estimate the $\tau$, values quantitatively. The first molecule E392A appears to follow stick boundary condition in alkanes while the trend falls in between slip and stick lines in alcohols. This is in good agreement with other reports on non-polar molecules [5, 10, 11]. E404 though a bigger molecule than E92A, surprisingly
inclines towards slip limit in alkanes and exactly follows slip condition in alcohols. The largest molecule E398 shows a result that is not expected from the hydrodynamic theory. In both alkanes and alcohols, the τ, values were significantly smaller than those predicted by the slip limit. It may be noted that the GW model, which accounts for the molecular nature of the solute, fails to predict the experimental trend. The DKS theory, which takes into account the relative sizes of the solute and solvent and also the free volume available to the solute, does not predict the results correctly for all the three molecules. The results obtained here are indicative of weaker solvent-solute interaction through hydrogen bonding in alcohols where significantly faster rotation is observed. Hence, it is presumed that the friction experienced by the molecules arises entirely due to mechanical friction. The DKS model also fails to predict the faster rotation of all the three probes in alcohols as compared to alkanes.

**Conclusions:**

1. All the three molecules exhibit a linear relationship of rotational reorientation times with the viscosity of the solvent both in case of alkanes and alcohols, which is correctly predicted by the SED hydrodynamic theory. However, the quantitative agreement between theory and experiment is poor perhaps due to the fact that this model does not take into account the relative sizes of the solute and solvent molecules. The molecules being non-polar in nature and have no hydrogen bonding.
functional groups, leads to negligible contribution of dielectric friction to
the overall rotational friction experienced by these molecules.

2. The GW theory fails to predict the experimental results, even qualitatively,
for all the three molecules. It also did not predict the observed faster
rotation of the three probes in alcohols while the DKS theory predicts it
though qualitatively. It may be noted that the GW theory is adequate for
small solutes of 2-3 Å radius [5]. It considers the relative radii of the solute
and solvent molecules by considering them as a sphere and taking cube root
of their volume and the solute shape is included in the calculation through
the factor f. Thus it is suitable for spherical molecules and can be extended
to non-spherical solutes of small size only.

3. The experimentally observed fact that all the three molecules rotate faster in
alcohols than in alkanes suggest the importance of nonhydrodynamic effects
in both the solvent series. It is possible that the solvent molecules in
alcohols are forming hydrogen bonded clusters and as such the solute
molecules do not feel the full spectrum of the solvent fluctuations and the
shear viscosity of the solvent leading to a drastically reduced microscopic
friction on the probe molecule. The DKS theory qualitatively predicts the
faster rotation in alcohols. This model also approximates the solute and
solvent as sphere and uses their areas by taking square of the cube root of
their volumes. However, it incorporates the shape factor and asymmetry of
solute and solvent through ΔV and a factor φ=f C_{slip}. ΔV is a function of
lengths of axes of a model ellipsoid adopted for the solute. The variation in 
$\phi$ from solute to solute may be in adequate in determining the difference in 
friction experienced by different molecules and hence shows poor 
agreement with experimental values at higher solute radii.

Thus the present investigation extends the existing data base on non- 
dipolar molecules to a radius of 6.0 Å (volume 928 Å$^3$). The subslip 
behaviour exhibited by the largest molecule E398 is contradictory to the 
hypothesis that the increasing size of the solute leads to stick boundary 
condition. Also GW and DKS theories are unable to predict the results even 
qualitatively. Therefore it is opined that, the ability of quasihydrodynamic 
microfriction models to show a transition from microscopic to macroscopic 
hydrodynamic behaviour with increase in solute size is lacking.

Further most of the neutral non-polar molecules studied so far 
including the present ones are modeled as prolate ellipsoids. It will be 
interesting to take up the study of oblate ellipsoids to augment the data in 
this range of volumes.
References: