

# Pico Second Time Resolved Emission Spectroscopy Study of DMMN Molecule in Alcohols

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**Abstract.** At the room temperature rotational re-orientations times of the probe DMMN have been studied in alcohol series, by using the Steady-State Fluorescence Depolarisation and Time-Correlated Single Photon Counting (TCSPC) techniques. Experimental observation shows DMMN probe rotates slower when solvent viscosity increases. SED stick boundary conditions matches nearly with the experimental values for lower alcohols. Quasi-hydrodynamic models (Dote-Kivelson-Schwartz and Geirer-Wirtz) were used to determine mechanical friction and found an interesting behaviour towards super stick trend.

## INTRODUCTION

Study of the molecular diffusions are of key importance because it leads to an understanding of the solvation's, photochemical process, isomerization, hydrogen bonding, dynamic interaction with surrounding molecules such as solvent-solute interactions many other. Stokes-Einstein's-Debye-Perrin equation<sup>1</sup> describes the theoretical description of the molecular rotational motion of any probe in the liquid, the rotational reorientation time ( $\tau_r$ ) of the solute is related to the solvent viscosity parameter ( $\eta$ ). Rotational reorientation dynamics are broadly classified into two categories<sup>1</sup>. Firstly, to know how the electrostatic long-range interactions, Polar probes are embedded in charged polar solvents, to understand the influence on rotational dynamics of the solute molecules. Secondly, non-polar probes embedded in non-polar or polar solvents to understand the influence solute to solvent size ratio and solute shape. Because of its continuous interactions with its surrounding media a molecule rotating in solution experience frictions. The friction has both mechanical and dielectric origins. Mechanical friction is modeled by hydrodynamics and the dielectric friction by different continuum theories. Under such conditions, the reorientation time is longer here noticed, as a result of an increase in adequate rotating probe size. According to experimentalists, the non-separability of the total friction ( $\zeta_{total}$ ) can be written as a contribution of mechanical ( $\zeta_{MeF}$ ) and dielectric ( $\zeta_{DiF}$ ) components.

$$\zeta_{total} = \zeta_{MeF} + \zeta_{DiF} \quad (1)$$

Mechanical friction origins are described by SED, Geirer Wirtz<sup>2</sup> and Dote-Kivelson Schwartz<sup>3</sup> models. For rotational reorientation a) SED theories consider only the size of the probe molecules exclusively into the study and ignoring the size of the solvents. Whereas GW and DKS take into accounts even the sizes of the solute and solvent molecules.

## MATERIALS AND EXPERIMENTAL METHODS

7-[dimethylamino]-4-methoxy-1-methyl-1,8-naphthyridine-2[1H]-one (DMMN), were purchased from Exciton Company USA (with 98% purity) and used without further purification. Optimized geometry structures are shown in Fig.1. The alcohol solvents, are commercially available from S-D Fine Chemicals Ltd, India and all are spectroscopic grade are used without further dilution. The steady-state absorption spectrum of the probe was recorded using Shimadzu UV-1800 spectrophotometer with 1.0-nm resolution. Fluorescence anisotropy ( $\langle r \rangle$ ) occurs as a result of the photo selection of fluorophore in the direction of the polarization of the excitation source. The fluorescence anisotropy of solute molecules depends on its own intrinsic property as well as on its environment. In our experiments, fluorescence anisotropies were measured with exciting light polarizer along the Z-direction. Fluorescence decay of three dye molecules in alcohol solvents were recorded using picosecond laser as an excitation source and a Time-Correlated Single Photon Counting (TCSPC) technique (Edinburgh Instruments, Model: FSP920) along with Hamamatsu PMT is used for fluorescence detector. The rotational reorientation times ( $\tau_r$ ) is found from experimentally measured using the relation by  $\tau_r = \tau_f [(\tau_0/\langle r \rangle) - 1]$ .

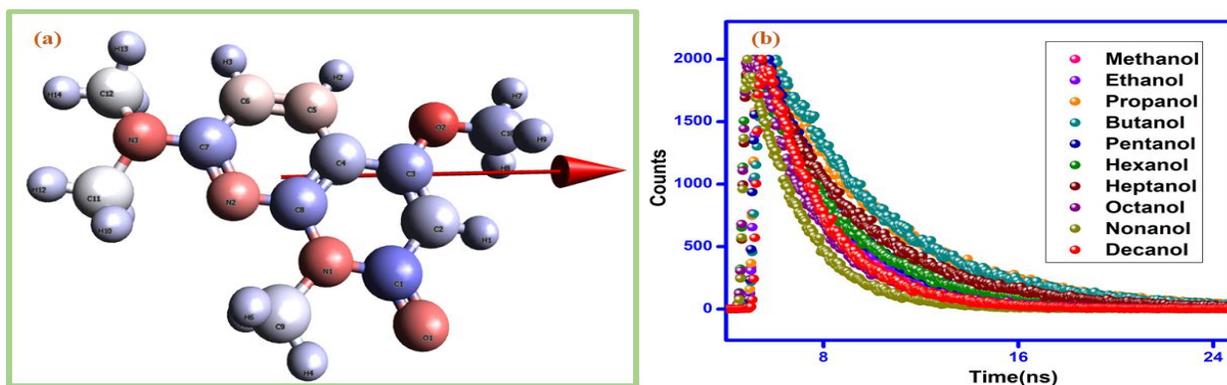


Fig.1 a) Optimized structure of DMMN b) Typical fluorescence decay curve of DMMN in all solvents

## THEORETICAL CONTEXT

### MECHANICAL FRICTIONAL THEORIES

Mechanical friction origins are described by Stokes Einstein Debye (SED) theory. The general approach is to consider the solute molecule as either asymmetric or symmetric ellipsoidal moving in a continuous, homogeneous medium characterized by its macroscopic properties such as dielectric constant and viscosity. Accordingly, the rotational reorientation times ( $\tau_r$ ) of probe molecules applying SED theory is given by

$$\tau_r = \left[ \frac{\eta V}{kT} f C \right] \quad (2)$$

Where,  $\eta$ - is viscosity of the solvent,  $K$  – Boltzmann constant,  $V$ - is the van der Waals volume of the probe,  $T$  – absolute temperature,  $f$  – shape factor,  $C$  – boundary conditions that indicate the degree of coupling in the solute and solvent. For explaining size effects on mechanical friction, two quasi-hydrodynamic theories were put forth 1) GeirerWirtz [GW] and 2) Dote-Kivelson Schwartz [DKS]. GW theory relates the ratio of solute to solvent size ( $\sigma$ ) and is expressed as

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

Where

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

where  $V_s$  – being solvent volume,  $V_p$  – probe volume,  $C_0$  – coupling parameter. The equation for the  $C_{GW}$  is given by  $C_{GW} = \sigma C_0$ .

However, GW theory ignores relatively weak contact between the solvent and solute, also the cavities of free space formed by the solvent molecules around the probe molecule. The solute-solvent coupling parameters,  $C_{DKS}$  and  $\gamma$ , according to DKS model were calculated using the given equations

$$C_{DKS} = \left[ 1 + \frac{\gamma}{\phi} \right]^{-1} \quad (5)$$

$$\gamma = \frac{\Delta V}{V_p} \left[ 4 \left( \frac{V_s}{V_p} \right)^{2/3} + 1 \right] \quad (6)$$

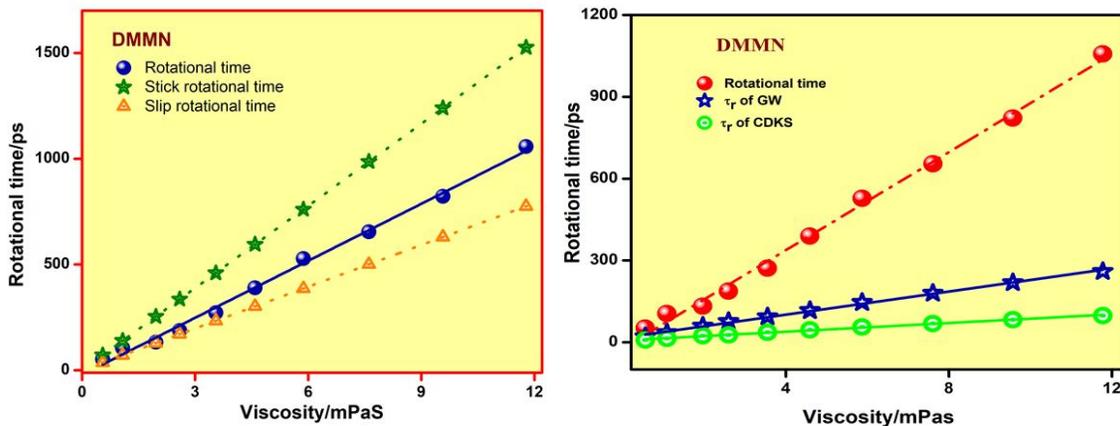
where  $\gamma/\phi$  – is the ratio of the solvent volume available free to the effective solute size,  $\phi$  – is the ratio of reorientation time obtained using slip hydrodynamic to reorientation time predicted by stick hydrodynamic theory.  $\Delta V$  – smallest free space volume available per solvent molecule and is given by  $\Delta V = V_{sm} - V_s$ , where  $V_{sm}$  – solvent molar volume /Avogadro number.

## RESULTS AND DISCUSSION

The solute parameter volume, Shape factor, slip boundary conditions parameters of the laser dye are  $213.4 \text{ \AA}^3$ , 2.498, 0.508 respectively are used to calculate the rotational reorientation times of probe molecules applying SED theory. Experimentally obtained steady-state fluorescence anisotropy ( $\langle r \rangle$ ), Fluorescence lifetime ( $\tau_f$ ) and Rotational re-orientation times ( $\tau_r$ ) of DMMN are tabulated in Table1. We can infer from the Table1, fluorescence lifetimes of the probe differ lies in the values range of 5.86-6.02 ns, limiting anisotropy ( $r_0$ ) -0.455. Average values of fluorescence anisotropy's  $\langle r \rangle$  is 0.0289. From the values of  $r_0$ ,  $\langle r \rangle$  and  $\tau_f$ , the rotation reorientation times were determined (using Eqn.2). Rotational reorientation time values are increasing linearly with increase in viscosity from methanol to decanol. A graph of  $\tau_r/v/s \eta$  is plotted for the probe in alcohols along with slip and stick lines are shown in Fig 2. The experimentally observed reorientation times for probe lies between slip and stick boundary condition lines. The  $\tau_r$  values for probe are observed to be nearly same as that predicted by the hydrodynamic slip boundary condition at lower alcohols and deviates for higher alcohols<sup>5-9</sup>. The calculated hydrodynamic friction amounts to 68% of the observed friction for the laser dye. This deviation is due to the increase in the size of the solvent molecule than solute molecule, hence dye molecule experiences a reduced mechanical friction. SED theories consider wholly the size of the probe molecules into the study and not considering the size of the solvents this deviation couldn't be successfully explained. For GW, the  $C_{GW}$  coupling (Using eqn.3,4) parameter value varies in the range of 0.16-0.23 for the probe in alcohol solvents. By comparison of experimental value to reorientation times calculated using GM theory, it is noticed that larger deviation between experimentally and theoretically calculated reorientation times of all three probes thus this model fails to explain the results even in a qualitative way<sup>10-12</sup>. For understanding this behavior of the probes we use DKS theory. The friction calculated from DKS (Using eqn.5 & 6) theory to the total friction experienced by all the probe found to be about 10-33%. Since DKS<sup>2</sup> theory takes into account the sizes of the dye as well as solvent-free space created by the solvent to calculate the contribution of the friction. The contribution of friction from DKS theory underestimates the observed experimental results by a factor of 9.13. The rotational times  $\tau_r$  for all the three probes calculated with  $C_{GW}$  and  $C_{DKS}$  theory, the values of  $\tau_r/v/s \eta$  of alcohol solvents are shown in Fig 2. From the figure 2, it is noticed that GW and DKS models fail to explain the results in a qualitative way and underestimate the contribution friction by probe molecule to a larger extent. In view of the deviations from experimental results for the probe molecule from Mechanical frictional theories it becomes imperative to verify for dielectric friction effects

**Table 1.** Steady-State anisotropy  $\langle r \rangle$ , fluorescence life time ( $\tau_f$ ) and rotational reorientation time ( $\tau_r$ ) of probe in alcohols.

Solvent	Viscosity mPa s <sup>a</sup>	$\langle r \rangle$	$\tau_f$ /ns	$\tau_r$ /ps
Methanol	0.55	0.004	5.86	51.97
Ethanol	1.08	0.008	5.89	105.41
Propanol	1.96	0.010	5.90	132.58
Butanol	2.59	0.014	5.91	187.62
Pentanol	3.55	0.020	5.91	271.72
Hexanol	4.59	0.028	5.94	389.51
Heptanol	5.87	0.037	5.96	527.56
Octanol	7.61	0.045	5.96	654.15
Nonanol	9.57	0.055	5.98	822.25
Decanol	11.78	0.068	6.02	1057.78

**Fig.2** Plot of Rotational time v/s Viscosity

## CONCLUSIONS

Rotational reorientation time values of the probe molecule increases linearly with increase in viscosity from methanol to decanol solvents. The rotational reorientation time values are found nearly same as that predicted by the hydrodynamic super slip boundary condition at lower alcohols and deviates for higher alcohols. Both GW and DKS models fail to explain the results in a qualitative way. The experimental values deviations from mechanical frictional theories it becomes essential to study for dielectric friction effects.

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