

## RESEARCH ARTICLE

# Temperature-Dependent Rotational Dynamics of a Non-Polar Probe in n-Alkane Solvents: Insights from Hydrodynamic and Quasi-Hydrodynamic Model

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**ABSTRACT:** The rotational diffusion behavior of 3-(benzo[d]thiazol-2-yl)-7-(diethylamino)-2H-chromen-2-one (3BT7D2H-one) was investigated in two non-polar solvents, n-tridecane and n-hexadecane, across a range of temperatures. Steady-state and time-resolved fluorescence depolarization techniques were employed to measure the rotational reorientation times ( $\tau_r$ ) of the fluorescent probe molecule. The results demonstrate a linear dependence of  $\tau_r$  on the viscosity-to-temperature ratio ( $\eta/T$ ), highlighting that rotational dynamics are closely linked to changes in solvent viscosity. The experimental  $\tau_r$  values were compared to predictions made by both the hydrodynamic Stokes-Einstein-Debye (SED) model and quasi-hydrodynamic models, including the Gierer-Wirtz (GW) and Dote-Kivelson-Schwartz (DKS) models. In both solvents, the observed  $\tau_r$  values suggest sub-slip behavior, indicating that 3BT7D2H-one rotates with less frictional resistance than expected for a fully hydrodynamic regime. Specifically, the experimental  $\tau_r$  values in n-hexadecane were found to be higher than those in n-tridecane, corresponding to the higher viscosity of the former solvent. While the SED model with sub-slip boundary conditions provided a reasonable approximation for the rotational times, both the GW and DKS models failed to quantitatively capture the experimental behavior. These models either underestimated or overestimated the frictional interaction between the solute and solvent, suggesting that additional factors such as solute-solvent size ratio and molecular shape might need to be incorporated for more accurate predictions. This study enhances the understanding of solute-solvent coupling in non-polar environments and underscores the limitations of traditional hydrodynamic models in describing molecular rotational diffusion in complex solvent systems.

**Keywords:** Rotational diffusion, Solute-solvent coupling, Stokes-Einstein-Debye model, Quasi-hydrodynamic models.

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## 1. INTRODUCTION

The rotational dynamics of solute molecules in solution is a fundamental area of interest in chemical physics, particularly

in understanding solute-solvent interactions at the molecular level [1]. In solution, solute molecules experience friction due to continuous interactions with surrounding solvent molecules, hindering their free rotation [2]. This friction, arising from both hydrodynamic and molecular forces, significantly influences the rotational reorientation times of solute molecules, a property that can be experimentally observed and analyzed [3]. Rotational diffusion, which is governed by these frictional forces, is a critical phenomenon that helps elucidate solute-solvent coupling mechanisms, intermolecular interactions, and the viscosity-temperature dependence of molecular motion [4].

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Rotational diffusion studies provide crucial insights into the dynamic properties of molecular systems. By examining how a solute rotates within a solvent, researchers can infer important details about the forces at play between the solute and its surroundings [5]. The frictional force that a solute experiences as it rotates is key to understanding the molecular dynamics of chemical systems, and this friction can be modeled theoretically using various hydrodynamic and quasi-hydrodynamic approaches [6]. These models allow scientists to predict the behavior of molecules in solution under different conditions, such as varying temperatures or solvent viscosities, providing a theoretical framework that can be tested against experimental data [7].

Among the most widely used models to describe rotational dynamics is the Stokes-Einstein-Debye (SED) model, which is based on classical hydrodynamic theory [1-10]. The SED model assumes that the solute molecule is a rigid, spherical particle rotating within a homogeneous and continuous fluid. According to this model, the rotational reorientation time ( $\tau_r$ ), which describes the time it takes for a solute molecule to reorient itself by a specific angle, is given by the relationship:

$$\tau_r = \frac{\eta V}{kT} (fc) \quad (1)$$

where  $\eta$  is the solvent viscosity,  $V$  is the solute volume,  $T$  is the temperature,  $k$  is the Boltzmann constant, and  $f$ -shape factor,  $c$ -coupling parameter that accounts for solute-solvent boundary conditions. The coupling parameter can take values between 0 and 1, with 1 representing stick boundary conditions (where the solute fully couples with the solvent) and values between 0 and 1 corresponding to slip boundary conditions (where the solute experiences partial coupling with the solvent) [11-13].

One of the main predictions of the SED model is that the rotational reorientation time should vary linearly with the ratio of viscosity to temperature ( $\eta/T$ ) [14]. This linear relationship holds true for ideal systems where the solute-solvent interactions are well-behaved. However, experimental studies have frequently reported deviations from this theoretical prediction. These deviations arise from several factors that are not accounted for by the SED model, such as specific solute-solvent interactions, differences in solute-solvent size ratios, and the presence of dielectric friction in polar systems. As a result, researchers have sought alternative models, such as the Gierer-Wirtz (GW) and Dote-Kivelson-Schwartz (DKS) models, which incorporate quasi-hydrodynamic effects and aim to provide a more accurate description of rotational diffusion in complex systems [15-17].

The GW model introduces corrections to the SED model by considering molecular friction between the solute and solvent. It assumes that the friction experienced by a solute molecule is not uniform across its surface and that the solute's size and shape play a significant role in determining its rotational dynamics. Similarly, the DKS model accounts for the molecular interactions between the solute and solvent, particularly in systems where the solute is much smaller than

the solvent molecules [17, 18]. Both models predict rotational reorientation times that may deviate from the linear  $\eta/T$  relationship predicted by the SED model, especially when specific solute-solvent interactions, such as hydrogen bonding or van der Waals forces, become significant.

Numerous studies have explored the rotational dynamics of non-polar solutes in both polar and non-polar solvents. These studies have consistently observed several key trends: (1) non-polar solutes tend to exhibit slip boundary conditions, (2) as the size ratio between the solute and solvent increases, a transition from slip to stick boundary conditions may occur, and (3) deviations from the linear  $\eta/T$  profile, particularly in systems involving homologous series of solvents, such as alcohols and alkanes, are common. Such observations highlight the complexity of solute-solvent interactions and the limitations of purely hydrodynamic models like SED in predicting rotational diffusion accurately [19].

In the present study, we investigate the effect of temperature and viscosity on the rotational dynamics of a non-polar probe, 3-(benzo[d]thiazol-2-yl)-7-(diethylamino)-2H-chromen-2-one (3BT7D2H-one), in two non-polar n-alkane solvents, n-tridecane and n-hexadecane. These solvents have been chosen due to their varying molecular sizes and viscosities, which allow us to explore the role of solvent size and friction in determining the rotational reorientation time of the solute. To our knowledge, the rotational dynamics of this specific non-polar probe in these solvents have not been previously reported, making this an important contribution to the understanding of solute-solvent coupling in non-polar environments [17-19].

The experimental results obtained from steady-state and time-resolved fluorescence depolarization techniques are compared with predictions from the SED, GW, and DKS models. This comparison allows us to evaluate the applicability of these models in describing the rotational diffusion of non-polar solutes in non-polar solvents. Furthermore, our findings provide new insights into the temperature-viscosity dependence of rotational reorientation times in non-polar systems and highlight the importance of considering both hydrodynamic and molecular interactions in understanding solute dynamics.

## 2. EXPERIMENTAL DETAILS

The rotational re-orientation times of 3BT7D2H-one in n-tridecane and n-hexadecane solvents with varying temperatures were estimated using the fluorescence steady-state depolarization technique. Anisotropy ( $\langle r \rangle$ ) is expressed by the below equation [1]:

$$\langle r \rangle = \frac{I_{\parallel} - GI_{\perp}}{I_{\parallel} + 2GI_{\perp}} \quad \text{and} \quad G = \frac{I_{HV}}{I_{HH}} \quad (2)$$

Where,  $I_{\parallel}$  and  $I_{\perp}$  are parallel and perpendicular polarized emission intensities w.r.t exciting polarized light.  $G$  -

Instrumental factor,  $I_{HV}$  – emission intensity when excitation and emission polarizers are kept horizontal and vertical respectively. Similarly,  $I_{HH}$  – emission intensity when excitation and emission polarizers are kept horizontal. If fluorescence and anisotropy decay follow single exponential decay, the rotational reorientation time ( $\tau_r$ ) is given by the below equation [20-21]:

$$\tau_r = \frac{\tau_f}{\left(\frac{r_0}{\langle r \rangle} - 1\right)} \quad (3)$$

Where,  $r_0$  – limiting anisotropy,  $\tau_f$  – fluorescence lifetime.

The  $\langle r \rangle$  measurement was performed using Hitachi F-7000 spectrofluorometer. The probe is excited at 450-475 nm and fluorescence spectra are monitored from 490-520 nm. The  $\langle r \rangle$  values were read at every 5-10 nm interval for the selected wavelength range. A TCSPC Edinburgh Instruments, Model: FSP920 was used for fluorescence lifetime measurement of 3BT7D2H-one in selected solvents for varying temperatures. The temperature of the desired sample is maintained within  $\pm 1$  °C using a temperature controller, Eurotherm. The sample 3-(benzo[d]thiazol-2-yl)-7-(diethylamino)-2H-chromen-2-one (3BT7D2H-one) is from Sigma Aldrich Chemicals. The solvents n-tridecane and n-hexadecane are from S.D. Fine Chemicals Ltd, India.

### 3. RESULTS AND DISCUSSION

The rotational reorientation times of 3BT7D2H-one with anisotropies, and fluorescence lifetime in ethyl acetate and acetone with varying temperatures are tabulated in Tables 1a and 1b. Using  $\tau_f$ ,  $r_0 = 0.366$  and  $\langle r \rangle$  in equation 3.  $\tau_r$  values are estimated and tabulated in Table 1a and 1b. The  $\langle r \rangle$  values decrease with increasing temperature in both solvents.  $\langle r \rangle$  shows positive values for different temperatures suggesting that ground and excited state dipole moments are

co-linear [22]. The SED model with limiting boundary conditions has been used to understand the rotational dynamics of 3BT7D2H-one in n-tridecane and n-hexadecane solvents initially. The theoretical SED stick and SED slip values are calculated using  $c = 1$  and  $c = 0.46$  in eqn.1. A plot of experimental and theoretical obtained  $\tau_r$  values using the SED model as a function of  $\eta/T$  are plotted in Fig.1a and 1b for n-tridecane and n-hexadecane solvent respectively. The linear least-square fitting has been performed whose slope and intercept parameters in respective solvents are tabulated in Table 2. In both the solvents negative intercepts and their reasons are yet to be understood [14].

The results from this study provide valuable insights into the rotational reorientation dynamics of 3-(benzo[d]thiazol-2-yl)-7-(diethylamino)-2H-chromen-2-one (3BT7D2H-one) in non-polar solvents (n-tridecane and n-hexadecane) across varying temperatures. This section discusses the experimental findings, theoretical interpretations, and comparison of the observed behavior with different hydrodynamic models, including the Stoke's-Einstein-Debye (SED), Gierer-Wirtz (GW), and Dote-Kivelson-Schwartz (DKS) models.

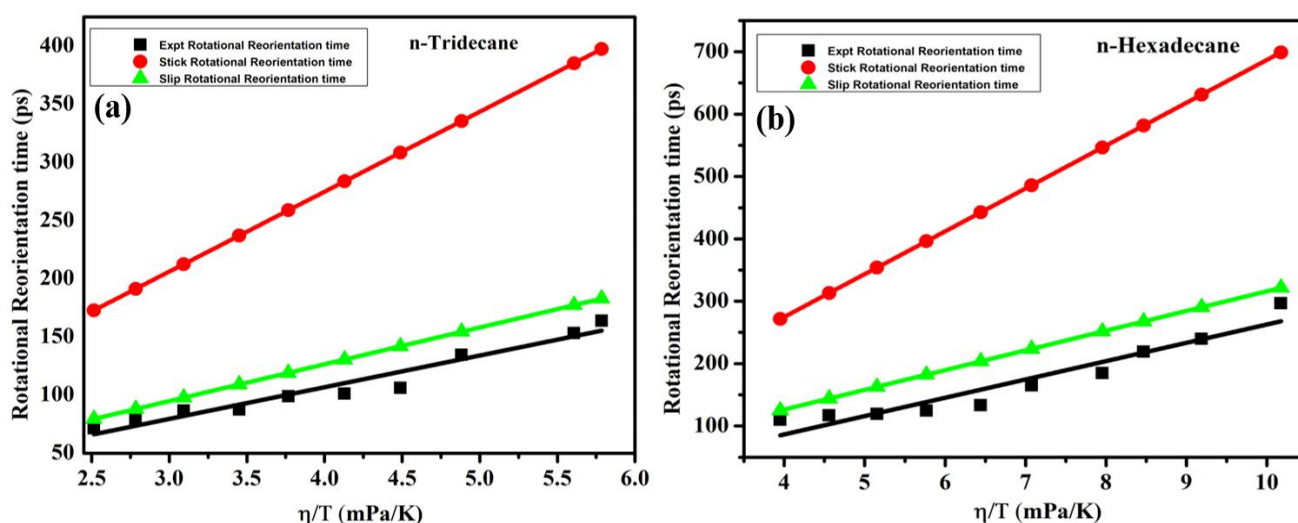
The rotational reorientation times ( $\tau_r$ ) of 3BT7D2H-one were measured at various temperatures using fluorescence anisotropy and lifetime data, as shown in Table 1 and Table 2. The experimental data indicate a clear dependence of the reorientation times on the solvent viscosity and temperature. In both n-tridecane and n-hexadecane,  $\tau_r$  decreases as temperature increases. This trend is consistent with the SED model's prediction that rotational reorientation time inversely correlates with temperature and directly correlates with solvent viscosity. In n-tridecane,  $\tau_r$  decreases from 163.651 ns at 298 K to 71.164 ns at 342 K. A similar trend is observed in n-hexadecane, where  $\tau_r$  decreases from 296.671 ns at 298 K to 109.945 ns at 342 K. The higher values of  $\tau_r$  in n-hexadecane compared to n-tridecane are attributed to its greater viscosity, which introduces more friction, thereby slowing down the rotational motion of the probe molecule.

**Table 1.** Steady-State anisotropy ( $\langle r \rangle$ ), fluorescence lifetime ( $\tau_f$ ), rotational reorientation time ( $\tau_r^{\text{Expt}}$ ), of 3BT7D2H-one in n-tridecane solvent.

T(K)	$\eta/T$ (mPaS/K)	$\langle r \rangle$	$\tau_f$ (ns)	$\tau_r$ (ns)
298	5.785	0.0233	2.407	163.651
303	5.607	0.0219	2.405	153.065
308	4.883	0.0194	2.402	134.445
313	4.489	0.0155	2.399	106.090
318	4.129	0.0148	2.398	101.055
323	3.768	0.0145	2.395	98.798
328	3.451	0.0129	2.393	87.425
333	3.093	0.0128	2.390	86.614
338	2.784	0.0116	2.388	78.163
342	2.515	0.0106	2.386	71.164

**Table 2.** Steady-State anisotropy ( $\langle r \rangle$ ), fluorescence lifetime ( $\tau_f$ ), rotational reorientation time ( $\tau_r^{\text{Expt}}$ ), of 3BT7D2H-one in n-hexadecane solvent.

T(K)	$\eta/T$ (mPaS/K)	$\langle r \rangle$	$\tau_f$ (ns)	$\tau_r$ (ns)
298	10.174	0.0404	2.389	296.671
303	9.188	0.0334	2.387	239.705
308	8.468	0.0308	2.385	219.147
313	7.955	0.0263	2.383	184.495
318	7.075	0.0237	2.381	164.855
323	6.443	0.0194	2.380	133.214
328	5.768	0.0182	2.378	124.438
333	5.153	0.0175	2.377	119.362
338	4.559	0.0172	2.375	117.116
342	3.950	0.0162	2.374	109.945

**Fig. 1.** A plot of  $\tau_r$  vs  $\eta/T$  in (a) n-tridecane, and (b) n-hexadecane solvent with SED boundary conditions.

The SED model with slip and stick boundary conditions was used to predict the theoretical reorientation times. Stick boundary conditions assume complete friction between the solute and solvent molecules, while slip boundary conditions account for partial friction and solute-solvent decoupling. As seen in Figure 1(a) and (b), experimental values of  $\tau_r$  are compared with theoretical SED predictions. The plots show a linear relationship between  $\tau_r$  and  $\eta/T$ , as expected from the SED theory.

However, the experimental  $\tau_r$  values in both solvents show deviations from the theoretical predictions, with sub-slip behavior observed. This suggests that the simple hydrodynamic treatment of solute rotation is insufficient to fully explain the experimental data. The slopes of the linear least-square fittings (Table 3) further highlight this deviation. In n-tridecane, the experimental slope (27.23) is much lower than the theoretical values predicted by the SED slip (68.69) and stick (31.59) models. Similar deviations are observed in n-hexadecane, where the experimental slope (29.36) is lower

than the theoretical slip (68.69) and stick (31.59) values.

The intercepts obtained from the least-square fittings are also negative in both solvents, which remains unexplained. This might be due to the inadequacy of the SED model in capturing complex solute-solvent interactions, particularly at the molecular level where size effects and specific interactions, such as dipole coupling, and play significant roles.

To address the limitations of the SED model, the concept of solute-solvent coupling was introduced. The coupling constant ( $c$ ) was estimated from the slope of the  $\tau_r$  vs.  $\eta/T$  plots for both solvents. In n-tridecane, the coupling constant was found to be 0.396, while in n-hexadecane, it was 0.427. These values suggest partial friction between the solute and solvent, indicating that the probe experiences a combination of slip and stick boundary conditions.

The revised  $\tau_r$  values, accounting for the estimated coupling constants, are in better agreement with the experimental data, especially in n-tridecane (Figure 2(a)).

**Table 3.** Linear regression parameters of  $\tau_r$  v/s  $\eta/T$ .

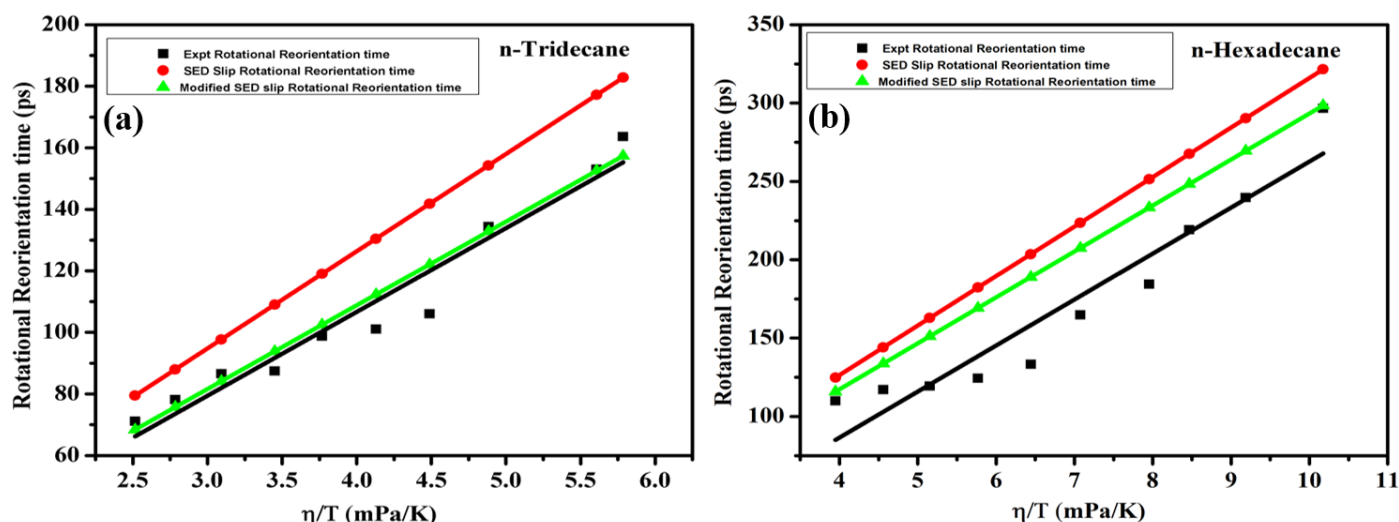
Solvent	Experimental		Theoretical	
	Slope	Intercept	Slope	Intercept
Acetone	27.23	-2.26	68.69 <sup>a</sup>	-2.842 <sup>a</sup>
			31.59 <sup>b</sup>	1.273 <sup>b</sup>
			18.96 <sup>c</sup>	-2.131 <sup>c</sup>
			65.7 <sup>d</sup>	-3.128 <sup>d</sup>
Ethyl acetate	29.36	-30.91	68.69 <sup>e</sup>	-3.979 <sup>e</sup>
			31.59 <sup>f</sup>	-2.842 <sup>f</sup>
			12.23 <sup>g</sup>	-3.696 <sup>g</sup>
			62.78 <sup>h</sup>	-5.115 <sup>h</sup>

<sup>a, c</sup> -SED slip model in n-tridecane and n-hexadecane, respectively.

<sup>b, f</sup> - SED stick model in n-tridecane and n-hexadecane, respectively.

<sup>c, g</sup> - GW model in n-tridecane and n-hexadecane, respectively.

<sup>d, h</sup> - DKS model in n-tridecane and n-hexadecane, respectively.



**Fig. 2.** A plot of  $\tau_r$  v/s  $\eta/T$  in (a) n-tridecane, and (b) n-hexadecane solvent with SED slip and modified slip boundary conditions.

The error margin in n-tridecane is  $\pm 14.3$ , indicating that the modified SED model with an average coupling constant provides a reasonable fit. However, in n-hexadecane, the error margin is significantly higher ( $\pm 43.6$ ), indicating that additional factors, such as solute-solvent size ratio or specific molecular interactions, might be contributing to the observed behavior (Figure 2(b)).

To further understand the deviations from the SED model, two quasi-hydrodynamic models—Gierer-Wirtz (GW) and Dote-Kivelson-Schwartz (DKS)—were considered. These models extend the SED theory by including factors such as solute-solvent size ratio and solvent structure, which can influence rotational dynamics. In particular, the GW model introduces a friction term that depends on the solute's size relative to the solvent molecules, while the DKS model incorporates solvent-induced dielectric friction.

The rotational reorientation times predicted by the GW and DKS models were calculated and compared with the

experimental data. As shown in Table 4, the slopes and intercepts obtained from these models are closer to the experimental values than those predicted by the SED model. In n-tridecane, the GW model gives a slope of 18.96 and an intercept of -2.131, while in n-hexadecane, the DKS model gives a slope of 62.78 and an intercept of -5.115. These values suggest that quasi-hydrodynamic models provide a more accurate representation of the rotational dynamics of 3BT7D2H-one, particularly in accounting for solute-solvent size and interaction effects.

Both n-tridecane and n-hexadecane exhibit sub-slip behavior for 3BT7D2H-one, as evidenced by the deviation of experimental  $\tau_r$  values from the theoretical SED slip predictions. This sub-slip behavior implies that the rotational dynamics of the probe are influenced by factors beyond simple hydrodynamic friction. Specifically, solute-solvent interactions, such as dipole-dipole coupling or specific solvent structuring around the solute, might play a crucial

role in governing the rotational motion.

This finding is consistent with previous studies on non-polar solutes in polar and non-polar solvents, where sub-slip behavior is often observed. In particular, the probe's ground and excited state dipole moments, which are co-linear as indicated by the positive  $\langle r \rangle$  values, might contribute to this deviation. The presence of specific solute-solvent interactions could lead to partial solute immobilization, resulting in slower rotational reorientation times than predicted by simple hydrodynamic models.

**Gierer-Wirtz (GW) Model:** Considering solute and solvent size, the GW [20] model treats solvent to be made of concentric shells with laminar velocity, and solute is placed at the center. The solute angular velocity ( $\omega_0$ ) and solvent first shell ( $\omega_1$ ) are related by  $\omega_1 = \sigma \omega_0$ .  $\sigma$  – is solute ( $V_p$ ) – solvent ( $V_s$ ) size ratio.  $\sigma = 1$  gives stick boundary limiting condition.

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

$$C_0 = \left\{ \frac{6 \left( \frac{V_s}{V_p} \right)^{1/3}}{\left[ 1 + 2 \left( \frac{V_s}{V_p} \right)^{1/3} \right]^4} + \frac{1}{\left[ 1 + 4 \left( \frac{V_s}{V_p} \right)^{1/3} \right]^3} \right\}^{-1} \quad (5)$$

The relationship for  $C_{GW}$  is given by:

$$C_{GW} = \sigma C_0 \quad (6)$$

The obtained  $C_{GW}$  is substituted in eqn.1 for estimating rotational re-orientation times using the GW model.

**Dote-Kivelson-Schwartz (DKS) Model:** Taking into consideration of free space formed between solute-solvent [21]. The solute-solvent coupling ( $C_{DKS}$ ) relation is given by:

$$C_{DKS} = \left[ 1 + \frac{\gamma}{\phi} \right]^{-1} \quad (7)$$

$$\gamma = \frac{\Delta V}{V_p} \left[ 4 \left( \frac{V_s}{V_p} \right)^{2/3} + 1 \right] \quad (8)$$

where  $\gamma/\phi$  – is solvent volume available free to the effective solute size ratio: ( $\phi = \frac{\tau_{slip}}{\tau_{stick}}$ ), and  $\Delta V = V_{sm} - V_s$ ,  $\Delta V$  – Smallest volumes of free space available per solvent molecule,  $V_{sm}$  – the ratio of solvent molar volume to Avogadro number, and  $V_s$  – solute molar volume. The obtained  $C_{DKS}$  is substituted in equation 1 for estimating rotational reorientation times using the DKS model.

The GW and DKS have been applied to the rotation of 3BT7D2H-one in n-tridecane and n-hexadecane solvents. The calculated  $C_{GW}$  are 0.192 and 0.179 and the  $C_{DKS}$  are 0.902 and 0.914 in n-tridecane and n-hexadecane solvents

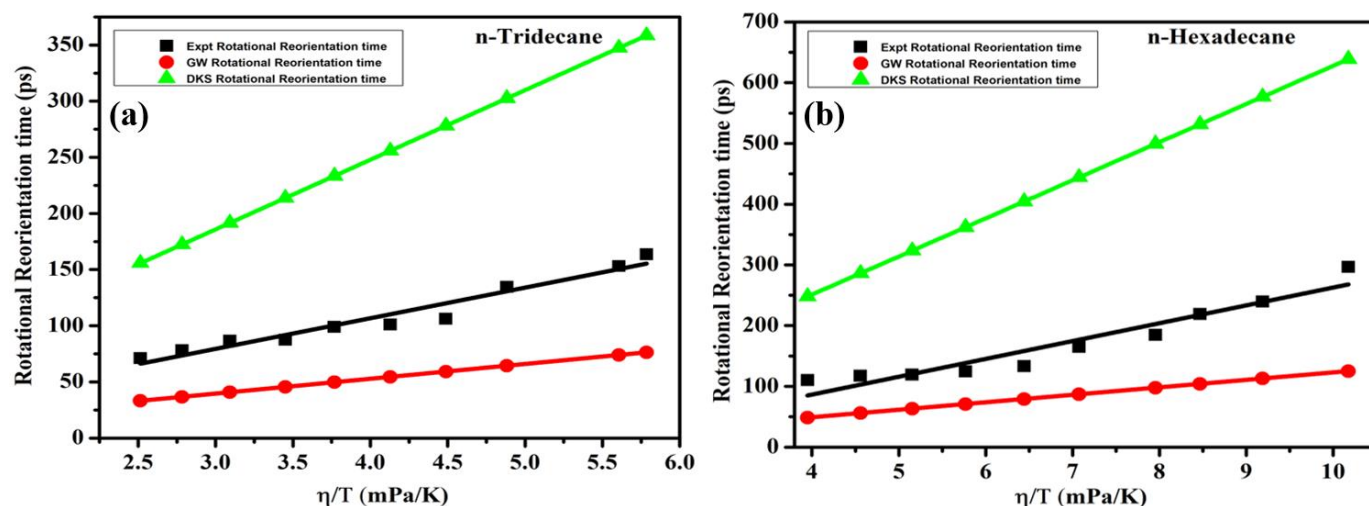
respectively. A plot of  $\tau_r$  v/s  $\eta/T$  using GW and DKS models is plotted in n-tridecane and n-hexadecane solvents along with linear least square fit method as shown in Figure 3.

**Table 4.** Experimental and theoretical values of rotational reorientation times of 3BT7D2H-one in n-tridecane solvent using modified coupling parameter.

$\tau_r$ (ps)	$\tau_r$ (ps) (using $C_{avg}$ )	Ratio
163.651	157.375	1.03988
153.065	152.533	1.00348
134.445	132.835	1.01213
106.090	122.109	0.86882
101.055	112.319	0.89971
98.798	102.495	0.96393
87.425	93.883	0.93121
86.614	84.1409	1.02939
78.163	75.7334	1.03208
71.164	68.4048	1.04033

The rotational reorientation times ( $\tau_r$ ) of 3BT7D2H-one in n-tridecane and n-hexadecane, as depicted in Figure 3 (a) and (b), show a clear deviation from both the Gierer-Wirtz (GW) and Dote-Kivelson-Schwartz (DKS) models. The  $\tau_r$  values of 3BT7D2H-one fall between these two theoretical predictions, reflecting the complexity of its molecular motion in viscous solvents. The experimental  $\tau_r$  values are faster than those predicted by the GW model by a factor of 2.02 in n-tridecane and 2.05 in n-hexadecane. This suggests that 3BT7D2H-one experiences less frictional resistance than anticipated by the GW model, which is primarily designed for spherical molecules in simple solvents. Conversely, when compared to the DKS model, the experimental  $\tau_r$  values are slower by a factor of 2.33 in n-tridecane and 2.45 in n-hexadecane. The DKS model, which accounts for more complex solute-solvent interactions, overestimates the hindrance in molecular reorientation. Neither model provides a quantitatively accurate description of the rotational dynamics of 3BT7D2H-one, indicating that additional factors, such as solute-solvent coupling and molecular shape, may need to be considered for better predictions [23-25].

The experimental results demonstrate that the rotational dynamics of 3BT7D2H-one are significantly influenced by the solvent viscosity, temperature, and solute-solvent interactions. While the SED model provides a basic framework for understanding these dynamics, deviations from the theoretical predictions highlight the importance of considering solute-solvent coupling and size effects. Quasi-hydrodynamic models, such as the GW and DKS models, offer improved agreement with the experimental data, particularly in accounting for sub-slip behavior.



**Fig. 3.** A plot of  $\tau_r$  v/s  $\eta/T$  in (a) n-tridecane, and (b) n-hexadecane solvent with GW and DKS models.

Future studies should explore the molecular-level interactions that contribute to this behavior, potentially using computational techniques or spectroscopic methods to provide further insights into the rotational dynamics of non-polar probes in non-polar solvents.

#### 4. CONCLUSION

The present study provides an in-depth examination of the rotational reorientation times ( $\tau_r$ ) of 3BT7D2H-one in two non-polar solvents, n-tridecane and n-hexadecane, across varying temperatures. The probe's rotational dynamics were analyzed using both experimental techniques—steady-state and time-resolved fluorescence depolarization—and theoretical models. The results reveal that 3BT7D2H-one experiences greater frictional resistance in n-hexadecane than in n-tridecane, as evidenced by its longer  $\tau_r$  in the more viscous solvent. This outcome can be attributed to the higher viscosity of n-hexadecane, leading to more significant hindrance in the rotational movement of the probe molecule. By analyzing the plots of  $\tau_r$  versus  $\eta/T$ , a linear dependence was confirmed, further supporting the close relationship between solvent viscosity and rotational reorientation. The slope of these plots was used to estimate the coupling factor, which in turn provided refined theoretical values for  $\tau_r$ . These revised values showed better alignment with the experimental data, although they still exhibited sub-slip behavior, indicating less rotational friction than would be predicted by a purely hydrodynamic model. The hydrodynamic Stokes-Einstein-Debye (SED) model with sub-slip boundary conditions was found to approximate the experimental data with reasonable accuracy. However, the quasi-hydrodynamic Gierer-Wirtz (GW) and Dote-Kivelson-Schwartz (DKS) models failed to quantitatively match the experimental  $\tau_r$  values. The GW model underestimated the

frictional interactions, while the DKS model overestimated them. This discrepancy highlights the limitations of these models in accurately predicting rotational dynamics, especially in complex solvent systems where solute-solvent size ratio and molecular shape may play crucial roles. This study demonstrates that while traditional models provide a useful framework for understanding molecular rotation, they need refinement to account for more intricate interactions between solutes and solvents in non-polar environments. This work contributes to a more comprehensive understanding of solute-solvent coupling and the limitations of existing models in predicting molecular dynamics.

#### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

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