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ORIGINAL ARTICLE

Rotational Diffusion of a New Large Non Polar Dye Molecule in Alkanes

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Abstract Rotational reorientation times of a newly synthesized 2,5-bis(phenylethynyl)1,4-bis(dodecyloxy) benzene (DDPE) are experimentally determined in series of n-alkanes by employing steady state and time resolved fluorescence depolarization technique with a view to understand rotational dynamics of large non-polar solute molecule in non-polar solvents and few general solvents of different sizes and varying viscosity. It is observed that rotational reorientation times vary linearly as function of viscosity. The hydrodynamic stick condition describes the experimental results at low viscosities while the results tend to deviate significantly from it at higher viscosities. This is attributed to the possibility of long chains in solvents hosting a variety of chain defects (end-gauche, double-gauche, all-trans, kink, etc.) thereby reducing the effective length of the molecule, leading to a slightly reduced friction. The experimental results are compared with the predictions of Stokes-Einstein-Debye (SED) hydrodynamic theory as well as the quasi-hydrodynamic theories of Gierer-Wirtz (GW) and Dote-Kivelson-Shwartz (DKS). The predictions from these theories underestimate τ_r in the solvents employed in the study.

Introduction

Motion of molecules in liquids occur over nano- to picosecond time scales and play an important role in the chemical and physical properties of solutions. Yet the origin of frictional forces that affect the motion of rotating molecules is not fully understood despite extensive experimental and theoretical studies. In order to visualize a complete picture of how reactions occur in solutions, it is crucial to understand how solvent fluctuations influence chemical dynamics. The generalized Stokes-Einstein-Debye (SED) model of diffusive motion of molecules, derived for large spherical molecules rotating in a continuous liquid, forms the basis for the theoretical description of liquids [1–4]. This model relates the rotational reorientation time to the macroscopic viscosity of the solvent [5–22]. Accordingly, the reorientation time τ_r of a non-spherical solute molecule of volume V is related to the macroscopic viscosity η of the solvent by the expression,

$$\tau_r = \frac{\eta V}{kT} f C \qquad (1)$$

where T is the absolute temperature and k, the Boltzmann constant. The viscosity can be varied by studying probes in different solvents [2, 8, 9, 15, 17], at different temperatures [2, 14], pressures [23, 24], in binary mixtures of solvents [7, 8, 18] and also by examining the salt effect [23]. The shape factor f accounts for the shape of solute molecule approximated as an ellipsoid. The value of the hydrodynamic boundary factor or the coupling parameter depends on the boundary conditions, stick or slip, satisfied at the solute-solvent

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interface. For the stick case, the tangential velocity of the fluid relative to the solute vanishes on the surface of the solute and the hydrodynamic boundary condition $C_{stick} = 1$. For the slip boundary condition, the tangential component of the normal stress on the surface of the molecule is zero. The values of C_{slip} lie between 0 and 1 which are tabulated for spheroids by Hu and Zwanzig [25]. It has been reported in literature that SED model correctly predicts the linear dependence of rotational reorientation times on solvent viscosity for polar and cationic dyes dissolved in polar and non-polar solvents [3–17], whereas the results of neutral and non-polar solutes deviate significantly from the hydrodynamic predictions at higher viscosities [18–24, 26–31]. These probes rotate much faster than predicted by the SED theory and are described either by slip boundary condition or by quasi-hydrodynamic theories. In general, the stick boundary condition appropriately describes rotational reorientation of macromolecules in solutions, while the slip boundary condition adequately describes motion of small molecules [30].

The experimentally measured reorientation times of many probes have been found to lie between the broad limits set by slip and stick hydrodynamic conditions [32]. Nevertheless, experimental evidences of rotational re-orientation times being longer than stick prediction i.e., super-stick behaviour [5, 12, 13] or shorter than slip estimation i.e., sub-slip behaviour [32] are not scarce in literature. The super-stick behaviour is generally attributed to large size of the molecules in that they experience greater friction. The sub-slip behaviour is explained in terms of large interstitial gaps formed in the solvent medium arising from dependence on size and shape of solvent molecules. Probe molecules, considerably smaller than the solvent molecules, can rotate freely in these interstitial gaps and the value of C can be much smaller than C_{slip} suggesting that the relative size of solute and solvent is an important parameter.

The rotational diffusion of non-polar solutes usually follows the SED theory with slip boundary condition, and it has been observed that a transition towards stick hydrodynamics occurs as the size of the solute increases [27, 28]. Reorientation times of non-polar probes in a homogeneous series of solvents show a slight non-linear profile as function of viscosity and also the probes rotate faster in alcohols compared to alkanes [27, 28]. A number of factors are known to cause a failure of SED model to explain the results for some solutes, either in general solvents or in specific class of solvents. These include electrostatic solute solvent interaction causing dielectric friction, solvent attachment by hydrogen bonding and flexible or irregularly shaped solute. Often quasi-hydrodynamic theories that consider sizes of solute as well as solvent molecules are invoked to explain these results. Quasi-hydrodynamic theory proposed by Gierer Wirtz(GW) attempts to explain this by taking into account the relative sizes of both solute and solvent

molecules to calculate the appropriate value for the coupling parameter C, as follows [33]

$$C_{GW} = \sigma_{GW} C_0 \tag{2}$$

with

$$\sigma_{GW} = \frac{1}{1 + 6\left(\frac{V_s}{V_P}\right)^{\frac{1}{3}} C_0} \tag{3}$$

and

$$C_0 = \left[\frac{6\left(\frac{V_S}{V_P}\right)^{\frac{1}{3}}}{\left\{1 + 2\left(\frac{V_S}{V_P}\right)^{\frac{1}{3}}\right\}^4} + \frac{1}{\left\{1 + 4\left(\frac{V_S}{V_P}\right)^{\frac{1}{3}}\right\}^3} \right]^{-1} \tag{4}$$

where V_S and V_P refer to the molecular volumes of the solvent and probe, respectively. In order to correct for the free spaces between the solvent molecules, Dote, Kivelson and Schwartz (DKS) [34] put forth the following equations to calculate the C factor,

$$C_{DKS} = \left(1 + \frac{\gamma}{\varphi}\right)^{-1} \tag{5}$$

where

$$\varphi = \frac{\tau_{slip}}{\tau_{stick}} \tag{6}$$

τ_{slip} corresponds to the rotational correlation time of the solute as predicted by slip hydrodynamic condition and τ_{stick} that predicted by SED relation for a sphere with the same volume as that of solute molecule. The factor γ is defined by

$$\gamma = \left(\frac{B k_B T k_T \eta}{V_P}\right)\left[4(V_S/V_P)^{2/3} + 1\right] \tag{7}$$

where T is the absolute temperature and k_T, the isothermal compressibility of the solvent. B is the Hildebrand–Batchinski parameter relating the viscosity of the solvent to its density [35, 36],

$$B = (1/\eta)/(1/\rho - 1/\rho_0) \tag{8}$$

where ρ_0 is the density of the solvent extrapolated to zero fluidity. For simple solvents such as n-alkanes, B is constant and nearly independent of temperature and pressure. The parameter φ when inserted in Eq. 5 shows that a perfectly spherical solute does not require any free volume in order to rotate freely, while a non-spherical solute requires increasingly more free volume in order to rotate faster than predicted by stick hydrodynamics [27].

In the present paper, rotational reorientation dynamics of a newly synthesized large rigid neutral molecule with flexible side chains, 2,5-bis(phenylethynyl)1,4-bis(dodecyloxy)benzene (DDPE, radius 5.49 Å) (Fig. 1) has been examined in series of alkanes (C=5 to 16) and in some general solvents with a view to understand the photophysical properties such as the effect of solvents of different sizes on the rotational diffusion of such a large non-polar molecule. As the fluorophore is neutral and non-polar, no complication of the anisotropy decay due to dielectric friction is expected, possibly leading to a good correlation with Stokes-Einstein-Debye relation [37]. The study attempts to assess limitations of SED hydrodynamic model in case of larger probes and also the applicability of quasi hydrodynamic models viz., GW and DKS.

Materials and Methods

### Synthesis of 1,4-bis(phenylethynyl)2,5-bis(n-dodecyloxy) benzene

2,5-Dibromo-1,4-bis(n-dodecyloxy)benzene (850 mg, 1.4 mM), bis(triphenyl phosphine) palladium(II)-chloride (41.5 mg, 59 μM), Copper(I) iodide (17 mg, 89 μM),

triphenylphosphine (16 mg, 61 mM), triethylamine (3 ml, 0.0215 mM), THF (10 ml) and phenylacetylene (450 μL, 4.1 mM) were taken in a round bottom flask and proceeded as in general procedure. The solvent was evaporated using vacuum pump, diluted with dichloromethane and extracted with sodium chloride solution. The organic layer was collected, dried over sodium sulphate and concentrated to get yellow crystalline solid. This was washed with acetonitrile several times to remove impurities and recrystallized from petroleum ether. The crystallized compound, DDPE was used directly for rotational diffusion measurements, as a probe.

UV-Visible Absorption and Steady-State Fluorescence

All the solvents of HPCL/spectroscopic grade were obtained from Fluka and used as received for various studies in the solution state. The absorption spectra of the molecules were recorded using UV-vis double beam ratio recording spectrophotometer (Hitachi, Model U1800) and fluorescence spectra by employing spectrofluorometer (JY Horiba, model Fluoromax4). The solution of DDPE was excited at 360 nm and emission was monitored from 300 to 600 nm. The fundamental anisotropy, r_o, when all

Fig. 1 **a** Molecular structure of DDPE. **b** Gaussian optimized structure of DDPE. **c** Gaussian optimized structure of DDPE (*lateral view*)
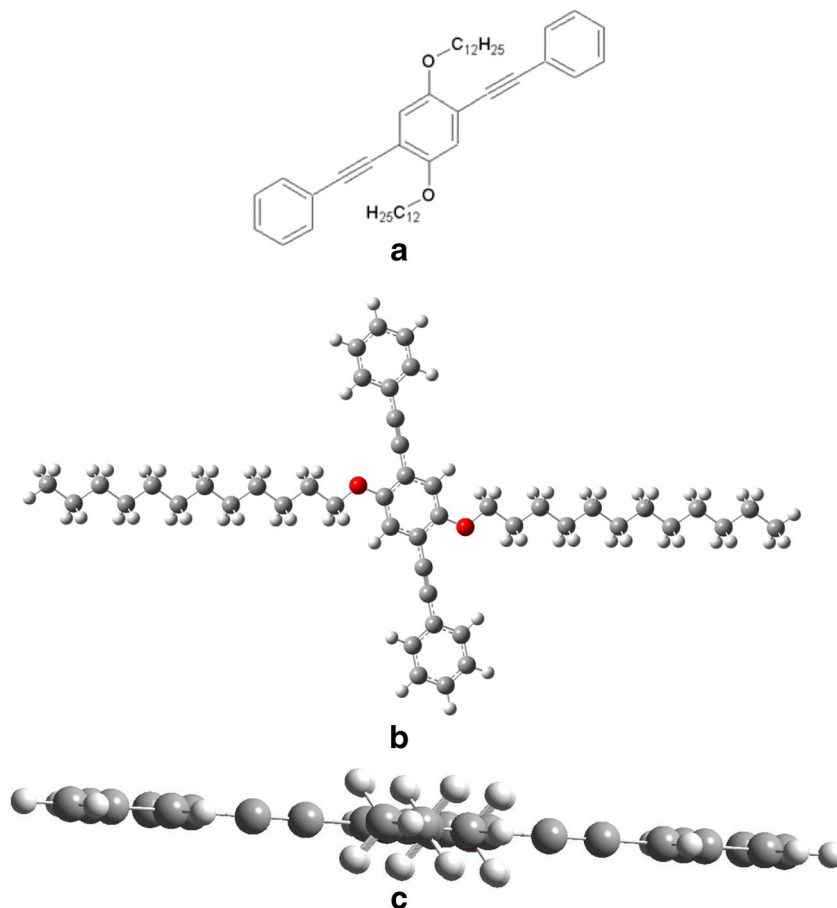
the rotational motions are frozen, was measured by trapping the DDPE molecules in an elastomer poly(dimethyl)-siloxane (PDMS).

Preparation of Poly(dimethyl)siloxane (PDMS) for r_0 Measurement

PDMS was prepared by mixing Sylgard-184 elastomer and curing agent (Dow Corning) in the ratio 10:1. The mixture was sonicated at room temperature to reduce the air bubbles and then degassed under vacuum for one hour. PDMS mixture was poured on a glass slide and cured in the oven at 60 °C for 6 h. The PDMS slabs of ($10 \times 30 \times 5$ mm) were cut and washed in ethanol and air dried. The DDPE molecules were incorporated in the PDMS by dipping it overnight in DDPE solution (15 μM) in toluene, followed by drying at room temperature. PDMS with trapped probe molecules was cooled to 5 °C in refrigerator (Fig. 2). The distribution of DDPE molecules in PDMS matrix was examined by fluorescence microscopy (Carl Zeiss, Axiovision 4.6).

Steady State Fluorescence Measurements

Rotational reorientation times of DDPE in series of alkanes were determined using steady state fluorescence depolarization technique, described elsewhere [38]. For vertical excitation, the steady state fluorescence anisotropy can be expressed as [39]

$$< r > = \frac{I_\parallel - GI_\perp}{I_\parallel + 2GI_\perp} \tag{9}$$

where $I_\parallel$ and $I_\perp$ denote the components of fluorescence intensities parallel and perpendicular with respect to the direction of polarization of exciting beam. G is the instrumentation

factor that corrects for polarization bias in the detection system and is given by,

$$G = \frac{I_{HV}}{I_{HH}} \tag{10}$$

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

## Time Resolved Fluorescence Measurements

The fluorescence life times were determined using time domain fluorescence spectrometer employing time correlated single photon counting (TCSPC) technique described in detail elsewhere [38]. Vertically polarised 375 nm pulses from Ti-Sapphire laser were used to excite the sample. The fluorescence emission at magic angle (54.7°) was counted by a high gain Hamamatsu micro channel plate photomultiplier tube (R3809 U) after being passed through the monochromator and a constant fraction discriminator (CFD), a time to amplitude converter (TAC) and a multichannel analyser (MCA). The instrument response function for this system is ~52 ps. The fluorescence decay obtained was analysed using IBH (UK) software (DAS-6).

The time resolved fluorescence anisotropy was measured by time correlated single photon counting using the same instrument. Decay curves were typically obtained at three different angles (magic angle 54.7^0, parallel and perpendicular to the exciting photons) of an emission polarizer using repeated excitation by a short pulse of a vertically polarized light. The total time resolved anisotropy decay is defined as

$$r(t) = I_V(t) - I_H(t) / I_V(t) + 2I_H(t) \tag{11}$$

where $I_V(t)$ and $I_H(t)$ are the intensity decays when the emission polariser is parallel and perpendicular respectively. Each

Fig. 2 Preparation of PDMS for r_o measurement
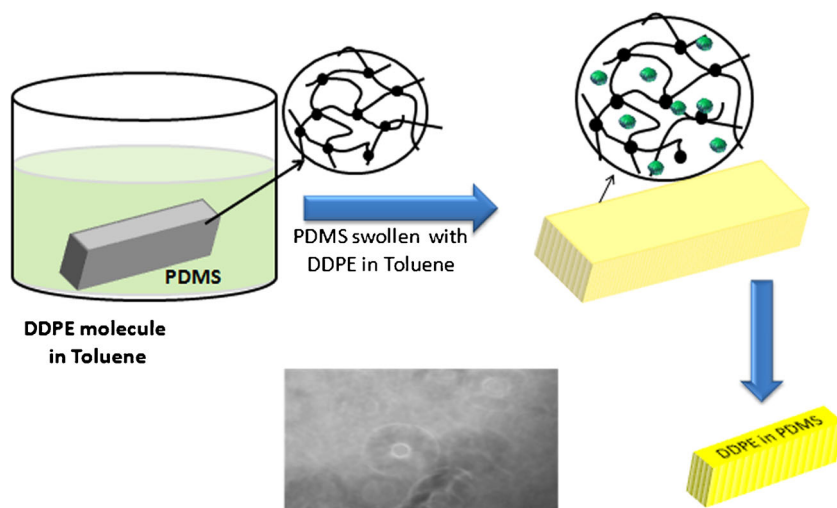
measurement was repeated two to three times and the average values are taken. The data sets consisting of the decays collected at the different polariser positions were analyzed simultaneously by using IBH software [1, 38].

Determination of Rotational Reorientation Times

If both anisotropy and fluorescence decay as single exponential, then the reorientation time τ_r is given by [39],

$$\tau_r = \frac{\tau_f}{\left(\frac{r_0}{<r>}-1\right)} \tag{12}$$

where τ_f is the fluorescence lifetime, r is the steady state anisotropy and r_o the limiting anisotropy when all the rotational motions of the probe are frozen. For a given τ_f the rate of molecular motion governs τ_f/τ_r. In the limit of slow molecular motion, $\tau_r \gg \tau_f$, and $\tau_f/\tau_r \approx 0$ and $r \approx r_o$. In the limit of fast motion, $\tau_r \ll \tau_f$, and $\tau_f/\tau_r \approx \infty$ and $r \approx 0$.

Results and Discussion

Figure 1 gives the molecular structure of DDPE molecule presented in this study. The crystal structure of this compound is previously known in literature and the structure obtained in solution matches closely with that reported [40, 41]. From literature it is also known that the molecule DDPE crystallizes in monoclinic P(2) I/C space group with two half molecules in the asymmetric unit. The molecule, DDPE carries the inversion centre at the geometric centre of the molecule and shows a deviation from planarity with a tilt angle of 0.40°. The C-C triple bond length in this molecule is given by 1.205 Å and the average value of C-C single bond length between the aromatic ring and triple bond is given by 1.437 Å. The average C-C aromatic bonds are in the range of 1.383–1.411 Å and that for the C-O bonds in the molecule are by 1.376 Å (aromatic carbon atom) and 1.435 Å (alkyl carbon atom). The rotational constants of DDPE were calculated by molecular modelling using GAUSSIAN 09 program. The rotational constants obtained for the molecule are A=0.06424 GHz, B=0.01057 GHz and C=0.00909 GHz suggesting that DDPE is a near prolate symmetric top [2]. The lengths of the semi major axis (a) and semi minor axis (b) are 18.78 Å and 8.43 Å, respectively. The short axis perpendicular to these two is c=0.885 Å. The volume of the molecule calculated using these values ($V=4/3\pi abc$) is 587 Å^3. Radius, r is a single length obtained by $r = \left[\frac{3V}{4\pi}\right]^{\frac{1}{3}}$ and is equal to 5.19 Å. The van der Waal's volume of DDPE calculated using Edward's atomic increment method [42] is 694.8 Å^3. The DDPE dye is expected to obey stick boundary condition (C=1), since the ratio of van der Waals volumes for the solvent and the

probe (V_S/V_P) are much smaller than one. The ratio changes from 0.14 for pentane to 0.41 for hexadecane. The value of C_{slip} determined using Hu-Zwanzig table is 0.299.

The typical steady state absorption and fluorescence spectra of DDPE recorded in hexane are shown in Fig. 3. The absorption spectrum of DDPE is quite broad and the emission spectrum shows vibrational structure. Vibrational bands are clearly resolved both in absorption as well as in emission spectrum. Time resolved fluorescence decay of the probe in hexane at 15 μM is shown in Fig. 4. The fluorescence decay measured in all solvents exhibits single exponential. The reorientation times of DDPE in alkanes obtained from the measured value of <r>, r_0 and τ_f using Eq. 10 are summarized in Table 1.

The experimentally measured time resolved fluorescence anisotropy decays were found to be single exponential in all the solvents. The measured time resolved fluorescence anisotropy parameters of the probe along with rotational correlation time (τ_r) are given in Table 2. Typical anisotropy decay of DDPE in decane, dodecane and hexadecane are depicted in Fig. 5. τ_r values obtained from steady state and time resolved anisotropy measurements agree fairly well for lower alkanes and r_0 measured from time resolved anisotropy is noted to be ~16 % smaller than those from steady state measurements (0.301±0.008).

Hydrodynamic Model

The rotational reorientation times with stick and slip boundary conditions were calculated from Eq. 1. The molecular shape factor f was calculated using the relation involving the axial ratio b/a and its value is 1.67. The value of C is 1 for stick and C_{slip} is obtained from the tables of Hu and Zwanzig for near prolate probe molecule [25]. For apolar molecule in apolar solvents, there is no need to correct Eq. 1 for dielectric friction [43]. Variation of τ_r with viscosity η for DDPE in alkanes is shown in Fig. 6(a). It depicts a clear tendency to follow stick behaviour as is normally expected of a molecule of this size ($V=587$ Å^3, $r=5.19$ Å). It may be noted that for the molecules QUI of comparable radius (5.4 Å) and volume (639 Å^3) [28] and exalite 392A ($r=5.3$ Å, $V=609$ Å^3) [32], the experimental
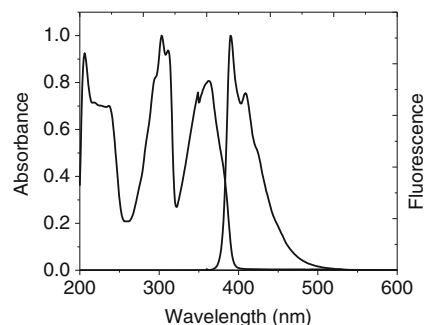
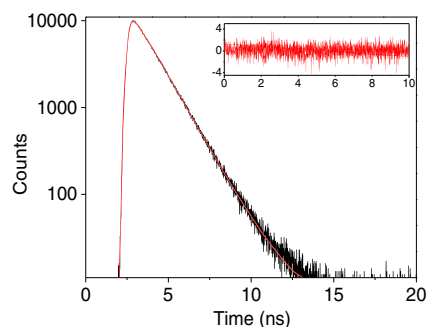**Fig. 3** Steady state fluorescence and absorption spectra of DDPE in hexane at 298 K

Fig. 4 Time resolved fluorescence decay of DDPE in n-hexane

values of τ_r in alkanes showed a tendency to follow stick boundary condition, and these results compare well with the ones obtained for the present molecule. As seen from Fig. 6(a), the τ_r value increases linearly with the increasing viscosity (increasing chain length) from pentane to dodecane due to steric interaction between the alkane chains of the solvent and the flexible side chain of DDPE. The measured τ_r values suggest a slower rotation and are above the stick line at lower viscosities suggesting a specific interaction occurring between the probe and solvent molecules. This is also in agreement with the theoretical stick prediction since the volume of DDPE is considerably larger than that of the solvent alkane molecules.

Ben Amotz and Drake [27], Roy and Doraiswamy [28], Inamdar et al. [32] and Dutt and Ramakrishna [43] have observed rotational reorientation times close to stick limit, respectively, for probes BTBP and QUI in alcohols, E392 in alkanes and DPP in 1-decanol. They have suggested that this

Table 1 Steady state anisotropy (<r>), fluorescence lifetime (τ_f) and rotational reorientation time (τ_r) of DDPE in (A) alkanes and (B) general solvents at 298 K

Solvent	Viscosity (η) mPa. s	Anisotropy <r>	τ_f ns	τ_r ps
(A)				
Pentane	0.23	0.0135±0.004	1.39	66
Hexane	0.29	0.0220±0.007	1.29	102
Heptanes	0.41	0.0245±0.001	1.30	116
Octane	0.52	0.0290±0.005	1.32	141
Nonane	0.66	0.0370±0.007	1.32	186
Decane	0.84	0.0420±0.008	1.35	220
Dodecane	1.35	0.0553±0.002	1.37	310
Pentadecane	2.81	0.0860±0.002	1.42	571
Hexadecane	3.07	0.0932±0.006	1.40	631
(B)				
Isopentane	0.29	0.0165±0.013	1.53	89
Toluene	0.55	0.0326±0.010	1.40	125
Cyclohexane	0.90	0.0366±0.001	1.33	193
1-4 dioxane	1.20	0.0340±0.001	1.58	202

*The maximum error in the fluorescence lifetime is ±50 ps

Table 2 Time resolved fluorescence anisotropy decay parameters of DDPE in alkanes at 298 K

Solvent	Viscosity (mPa s)	r_o	$\tau_{r(exp)}$ (ps)	$\tau_{r(cal)}$ (ps)
Pentane	0.23	–	–	66
Hexane	0.29	0.20	112	102
Heptane	0.41	0.19	139	116
Octane	0.52	0.25	170	141
Nonane	0.66	0.25	282	186
Decane	0.84	0.25	294	219
Dodecane	1.35	0.26	421	310
Pentadecane	2.81	0.35	637	571
Hexadecane	3.07	0.26	792	631

behaviour is due to the large size of the probe molecules. Dutt et al. [44] measured reorientation times for DPP in alcohols at room temperature and observed super-stick behaviour of non-polar molecules for the first time. They attributed this to the strong hydrogen bonding of the two NH groups of DPP with solvent molecules. It may be argued that such super-stick behaviour is also due to the presence of dielectric friction. Nevertheless it can be ruled out in this case, as the non-polar probe DDPE is studied in non-polarsolvents. Numerous reports have compared the rotational diffusion of nonpolar probes in alkanes and alcohols and observed a faster diffusion in alcohols than in alkanes [27, 29, 45]. As the volume of the probe molecules increases, the difference between the τ_r values measured in the two solvent series decreases and the rotational correlation times tend towards the stick limit. Roy et al. [28] studied a series of quarter- and quinquephenyl compounds having radii between 4 and 5 Å and observed a tendency of the probes to follow stick behaviour with increasing solute size. Rotational diffusion of two large non-polar laser dyes exalite 392A (r=5.3 Å) and exalite 398 (r=6.0 Å) in alkanes and alcohols has been reported from our laboratory by Inamdar et al. [32] wherein a faster rotation of both molecules was observed in alcohols than in alkanes. The largest probe
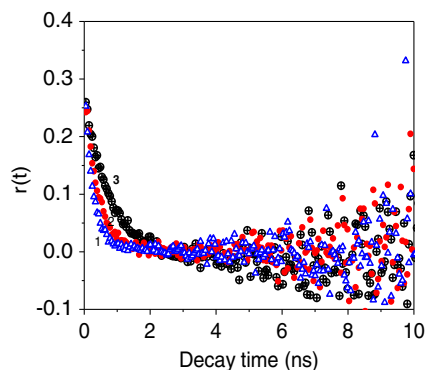

Fig. 5 Time resolved anisotropy decays of DDPE in decane (1), dodecane (2), and hexadecane (3)
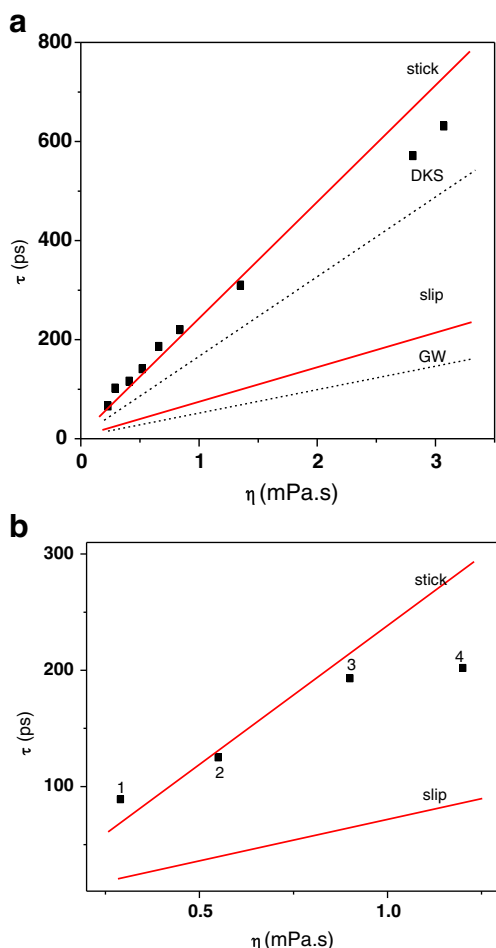
Fig. 6 Plot of experimental rotational reorientation times of DDPE (*black square*) vs. solvent viscosity for (**a**) **n-alkanes** along with hydrodynamic (slip and stick) and GW and DKS predictions; (**b**) **General solvents**, isopentane (1), toluene (2), cyclohexane (3) and 1-4 dioxane (4)

E398 clearly exhibited sub slip behaviour for both the solvent series while E392 showed stick behaviour in alkanes and followed a sub-slip trend in alcohols. The GW model simply failed to predict the results in alkanes. Grummet et al. [46] have studied rotational relaxation of linear π-systems with flexible side chains in liquid butane and found that the classical hydrodynamic theory of Brownian rotational motion is able to predict the rotational relaxation times for irregularly shaped rigid rod like molecules with highly flexible side chains in low molecular weight solvents. The τ_r values obtained experimentally for DDPE in few general solvents are also compared with the SED stick and slip predictions (Fig. 5b). It is interesting to note that it exhibits a stick behaviour in isopentane and toluene while in cyclohexane and 1,4-dioxane, it shows a tendency to deviate from stick line and rotate faster. This is attributed to the possibility of long chains in solvents hosting a variety of chain defects (end-gauche, double-gauche, all-trans, kink, etc.) thereby reducing the effective length of the molecule, leading to a slightly reduced friction.

All chains have defects. For defect and recovery, the time scale is short for smaller molecules. The lifetime of defects becomes significant for longer chains. A small molecule like toluene has similar influence as hydrocarbon chain of similar length. If the conformation is highly twisted like in the case of cyclohexane, the behaviour can be different. The latter deviates from the stick behaviour as long chain alkanes do. Cyclohexane has molecular length ~ 5 Å whereas dodecane has molecular length of 15 Å, which just starts to undergo changes similar to cyclohexane.

Quasi-hydrodynamic Models

The quasi-hydrodynamic theories of GW [33] and DKS [34] account for the friction experienced by the probe molecule considering not only the size of the solute but also that of the solvent. Nevertheless, the GW theory oversees the relatively poor physical contact between the probe and the solvent arising due to the cavities or the free spaces created by the solvent around the probe molecule. The coupling parameter C_{GW} varies from 0.219 to 0.283 for DDPE in alkanes from pentane to hexadecane. The GW theory is unable to account for the average friction experienced by the probe and does not explain the non-linear profile of τ_r vs η. It clearly underestimates the average friction experienced by the probe. It is also noted that DDPE molecules experience reduced friction as the size of the solvent molecule increases. A number of reports [26–28, 47, 48] noted faster rotation of many probes in alcohols when compared to alkanes which has been explained as due to higher free volumes in alcohols compared to alkanes based on DKS theory. In the present study, the solvent size increases by about 3 times from pentane to hexadecane and thus it may be appropriate to invoke DKS quasihydrodynamic theory when size effect is taken into account. C_{DKS} is calculated using Eq. 5 and is found to be 0.77 for heptane and 0.72 for hexadecane. Since DKS theory predicts the friction on the probe molecule, taking into consideration the relative size of the probe and the solvent as well as the free volume of the solvent, the friction estimated from this theory necessarily be included in the calculations though it underestimates the experimentally observed values. The mechanical friction calculated using slip hydrodynamics did not vary considerably from that estimated from GW theory. Hence, the mechanical friction calculated using slip hydrodynamics is considered.

Conclusion

The rotational reorientation times of a newly synthesized large non-polar molecule DDPE are measured in series of alkanes and few general solvents at room temperature by employing steady state and time resolved fluorescence depolarization technique with a view to understand the effect of viscosity

and size of solvent on rotational diffusion. It is observed that the τ_r value increases linearly with the increasing viscosity up to hexadecane (increasing chain length) due to steric interaction between the alkane chains of the solvent and the flexible side chains O-C$_{12}$H$_{25}$of DDPE. The probe experiences higher friction than expected from SED theory and tends to follow stick behaviour. A deviation from stick behaviour is noted in case of longer chain solvents (pentadecane and hexadecane) with τ_r values being lower than the estimated ones. This is attributed to the possibility of long chains in solvents hosting a variety of chain defects (end-gauche, double-gauche, all-trans, kink, etc.) thereby reducing the effective length of the molecule, leading to a slightly reduced friction. The results agree fairly well with those obtained for non-polar molecules of this dimension. Linear dependence of τ_r on η is also seen in case of general solvents.

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