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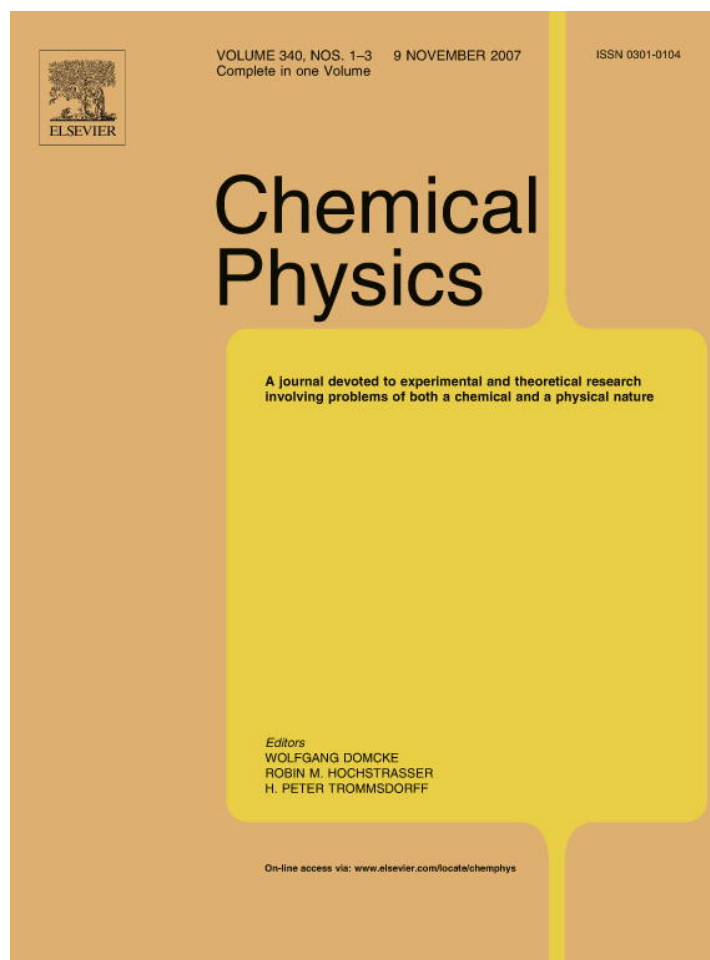


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Rotational dynamics of UVITEX-OB in alkanes, alcohols and binary mixtures

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Abstract

Steady-state and time resolved fluorescence anisotropy measurements were carried out to study the rotational diffusion dynamics of UVITEX-OB (U-OB) in series of alcohols, alkanes and binary mixtures of toluene and butanol at room temperature. The experimentally measured rotational reorientation times were compared with those estimated by the hydrodynamic and molecular models developed for microscopic friction. The experimental results are in good agreement with theoretical slip hydrodynamics and a deviation towards subslip behavior is noted. Also a faster rotation of the probe in binary mixture of toluene and butanol is noted as compared to that in alcohols and alkanes.

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Keywords: UVITEX-OB; SED hydrodynamics; Slip and subslip behavior; GW and DKS theory; Dielectric friction

1. Introduction

It is well known that the rotation on the molecular level in liquids can be monitored by several experimental techniques. An understanding of molecular rotations can be useful in identifying the other molecular processes in liquids. They serve as a rather sensitive probe of molecular dynamics and molecular structure, much more so than translational motion. Stokes–Einstein–Debye (SED) hydrodynamic theory forms the basis of understanding molecular rotations in liquids [1,2] according to which the rotational reorientation time of a solute molecule is proportional to its volume, bulk viscosity of the solvent and inversely related to the temperature. Here the solvent is assumed to be a structureless continuum and the rotational motion of the solute is considered as diffusional.

The SED theory has been found to describe the rotational dynamics of medium sized molecules fairly well

when the coupling between the solute and solvent is purely mechanical or hydrodynamic in nature. It has been reported that the SED model correctly predicts the linear dependence of the rotational reorientation times on the 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 [18–31]. These probes rotate much faster than predicted by the SED theory with stick boundary condition and are described by either slip boundary condition or by quasihydrodynamic theories. Slip boundary condition [32] assumes the solute–solvent coupling parameter to be less than unity, contrary to the stick boundary condition. Quasihydrodynamic theories [33,34] attempt to improve upon SED theory by taking into consideration not only the size of the solute but also that of the solvent molecule, thereby modifying the boundary conditions. It has been argued [22,23] that as the size of the solute molecule becomes much larger than the size of the solvent molecule, the observed reorientation times approach the SED theory with the stick

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boundary condition. The theoretical modeling of molecular reorientation in solution and its correlation with experimental results are far from satisfactory, especially on the short time scales.

While a considerable number of data have been reported on the picosecond reorientational motions of different probes in various liquids with a view to test the predictions of SED formalisms, we focus here on the rotational dynamics of a neutral molecule 2,5-thiophenediylbis[5-*tert*-butyl-1,3-benzoxazole] (UVITEX-OB) to investigate correlations between dynamics and local or continuum liquid structure. Fleming et al. [35] studied the rotational reorientation of BBOT in non-polar and polar solvents viz., cyclohexane and ethanol with viscosities of 1 and 1.2 mPa s, respectively and observed that it followed slip boundary condition in both the solvents. This was attributed to the solvent exchange rates that are comparable with the time scale of the elementary rotations of the molecule. The faster rotation of BBOT might be due to, as argued by others [11], the internal mobility of the dye much as was the case of methyl red, an anionic dye with strong H-bonding acceptor sites. A different picture appears if the experimental results at higher viscosities are included in the discussion as a further check for the influence of the internal mobility on the rotational diffusion. At higher viscosities, it may be of interest to examine, how the experimental relaxation rates deviate from the SED hydrodynamic theory and further, by testing the validity of quasihydrodynamic theories viz., Geirer and Wirtz (GW) [33] and Dote, Kivelson and Schwartz. (DKS) [34] might give a precise microscopic picture of the solvents and solute. It has also been suggested that in considering the motion of the solutes containing hydrogen bonding groups in polar solvents, it is necessary to include friction arising out of the dielectric properties of the solvents [36–38]. Thus, by measuring the reorientation times, one can find out how the magnitude of dielectric friction experienced by the probe depends on its dipole moment, which in turn may give us an idea as to how the coupling between mechanical and dielectric components of the friction influences the overall friction experienced by the probe.

2. Theory

According to SED hydrodynamic theory the rotational reorientation time τ_r is related to the macroscopic viscosity of the solvent η by the equation [1]

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

where k and T are the Boltzmann constant and absolute temperature respectively, and V , the van der Waals volume of the solute. The parameter f is the shape factor introduced to account for the shapes of the solute molecules, which are often non-spherical [39]. The shapes of the solute molecules are usually incorporated into the model by treating them as either symmetric or asymmetric ellipsoids. For

non-spherical molecules, $f > 1$ and the magnitude of deviation from unity in the value of f describes the degree of the non-spherical nature of the solute molecule. C , signifies the extent of coupling between the solute and the solvent and is known as the boundary condition parameter [40]. In the two limiting cases of hydrodynamic stick and slip for a non-spherical molecule, the value of C follows the inequality, $0 < C \leq 1$ and the exact value of C is determined by the axial ratio. The hydrodynamic theories take only the size of the solute molecule into consideration and not that of the solvent. However, it is observed that the magnitude of C also depends on the relative size of the solute compared to the solvent, and the quasihydrodynamic theories of GW [33] and DKS [34] consider this aspect as well while calculating the boundary condition. According to the GW theory, the solvent is visualized to be made up of concentric shells of spherical particles surrounding the spherical probe molecule at the centre. Each shell moves at a constant angular velocity and the velocity of successive shells decreases with the distance from the surface of the probe molecule, as though the flow between the shells is laminar. As the shell number increases, i.e., at large distances, the angular velocity vanishes. The angular velocity ω_1 of the first solvation shell is related to the angular velocity ω_0 of the probe molecule by means of a sticking factor σ by

$$\omega_1 = \sigma \omega_0 \quad (2)$$

At $\sigma = 1$, it gives the stick boundary condition and is related to the ratio of the solute to solvent size, given by

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

where

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

and V_s and V_p are the volumes of the solvent and probe, respectively. The expression for C_{GW} is given by

$$C_{GW} = \sigma C_0 \quad (5)$$

Although the GW theory does consider the size of the solvent molecule, it overlooks the relatively poor physical contact between the probe and the solvent arising due to the cavities or free spaces created by the solvent around the probe molecule. The DKS theory attempts to include these too. If the size of the solute is comparable to the free volumes of the solvents, the coupling between the solute and solvent will become weak, resulting in decreased friction experienced by the rotating probe molecule. Accordingly the solute-solvent coupling parameter, C_{DKS} is given by

$$C_{DKS} = (1 + \gamma/\phi)^{-1}, \quad (6)$$

where γ/ϕ is the ratio of the free volume available for the solvent to the effective size of the solute molecule, with

$$\gamma = \frac{\Delta V}{V_p} \left[4 \left(\frac{V_p}{V_s} \right)^{2/3} + 1 \right], \quad (7)$$

and ϕ is the ratio of the reorientation time predicted by slip hydrodynamics to the stick prediction for the sphere of same volume. ΔV is the smallest volume of free space per solvent molecule and some discretion must be applied while calculating this term [17,26,41]. It is empirically related to the solvent viscosity, the Hilderbrand–Batchinsky parameter B and the isothermal compressibility k_T of the liquid by $\Delta V = Bk_T\eta kT$. (8)

Since the Frenkel hole theory and the Hilderbrand treatment of solvent viscosity were developed for regular solutions [26], Eq. (8) may not be a valid measure of the free space per solvent molecule for associative solvents like alcohols and polyalcohols. Hence, for alcohols ΔV is calculated using

$$\Delta V = V_m - V_s, \quad (9)$$

where V_m is the solvent molar volume.

3. Experimental

U-OB (Ceba Specialty Chemicals, Switzerland) was used as received. All the solvents used in this study were of highest available purity from Fluka and used as such. The absorption and emission spectra of U-OB were obtained from UV–vis ratio recording spectrophotometer (Hitachi, U-2800) and fluorescence spectrophotometer (Hitachi, F-2000), respectively. The samples were excited at 380 nm. Rotational reorientation times of U-OB were measured using steady-state fluorescence depolarization technique, described elsewhere [31]. For vertical excitation, the steady-state fluorescence anisotropy can be expressed as [29,42]

$$\langle r \rangle = \frac{I_{\parallel} - GI_{\perp}}{I_{\parallel} + 2GI_{\perp}}, \quad (10)$$

where I_{\parallel} and I_{\perp} denote the polarized fluorescence intensities parallel and perpendicular to the polarization of the exciting beam. G (=1.14) [31] is an instrumental factor that corrects for the polarization bias in the detection system and is given by

$$G = \frac{I_{HV}}{I_{HH}}, \quad (11)$$

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

The sample solutions in alkanes and alcohols were excited at 380 nm and the emission was monitored from 422 to 433 nm. All the measurements were performed at 298 K. The $\langle r \rangle$ values are in the range of 0.019 ± 0.001 to 0.182 ± 0.003 for various solute-solvent combinations examined. If both anisotropy and fluorescence, decay as

single exponentials then the reorientation time τ_r is given by [42]

$$\tau_r = \frac{\tau_f}{(r_0/\langle r \rangle - 1)}, \quad (12)$$

where r_0 is the limiting anisotropy when all the rotational motions are frozen and τ_f is the fluorescence lifetime. The r_0 value for U-OB was measured at $-60^\circ \pm 2^\circ \text{C}$ by using a solution of U-OB in glycerol (Fluka, Germany). The fluorescence lifetimes were determined using time domain fluorescence spectrometer employing time correlated single photon counting technique, described elsewhere [31]. In brief, the diode pumped second harmonic radiation of a mode-locked Ti-Sapphire laser was used as the excitation light source, producing 750–840 nm light pulses having a repetition rate of 85 MHz. The frequency is decreased to 4 MHz by a pulse picker (Spectra Physics, 3980 2S). The second harmonic output (380 nm) was generated by a flexible harmonic generator (Spectra Physics, GWU 23PS). The fluorescence emission from the sample at magic angle (54.7°) was counted by a micro-channel plate photomultiplier tube (Hamamatsu, R3809U) after being passed through a monochromator and was processed by a constant fraction discriminator (CFD), a time-to-amplitude converter (TAC) and a multichannel analyzer (MCA). The instrument response function of this system is ≈ 52 ps. The fluorescence decay obtained was further analyzed by using IBH (UK) software (DAS-6). The reorientation times (τ_r) of U-OB in alcohols were measured by time resolved fluorescence depolarization method with time correlated single photon counting facility at Indian Association for the Cultivation of Science, Kolkata and the details of the system have been described elsewhere [43]. Here, the samples were excited at 375 nm using a picosecond diode laser (IBH Nanoled-07) in an IBH Fluorocube apparatus. To study the fluorescence anisotropy decay, the analyzer was rotated at regular intervals to get perpendicular [$I_{\perp}(t)$] and parallel [$I_{\parallel}(t)$] components. The G -value (=1.5) of the setup was determined using a probe whose rotational relaxation is very fast [43].

4. Results and discussion

In order to compare the experimentally observed rotational diffusion times with the predictions of stick and slip hydrodynamics a model for the solute's shape must be adopted. Based on the molecular dimensions of U-OB (Fig. 1), major axes, $2a$ (=12.5 Å) and $2b$ (=2.7 Å) [35] it is approximated as prolate ellipsoid. The van der Waals

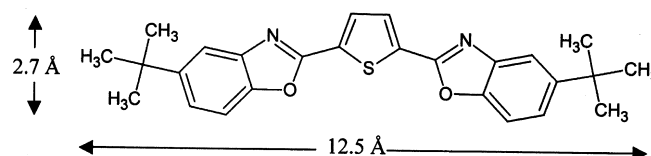


Fig. 1. Molecular structure of U-OB.

volume of U-OB as calculated using Edward's increment method [44] is 383 \AA^3 . The absorption and emission spectra of U-OB are shown in Fig. 2 and a typical fluorescence decay curve is given in Fig. 3. The rotational reorientation times (τ_r) of U-OB in alcohols, alkanes and binary mixture of toluene and butanol determined using the measured values of $\langle r \rangle$, r_0 and τ_f (Eq. (12)) are presented in Table 1. A value of 0.360 ± 0.002 for r_0 indicates that the absorption and emission dipoles form an angle of 15° with respect to each other. As seen from Table 1 the viscosity of the solvents varies from 0.23 to 3.07 mPa s in alkanes, from 0.55 to 11.80 mPa s in alcohols and from 0.90 to 2.01 mPa s in binary mixtures of toluene and butanol. In case of a prolate ellipsoid model, the parameter f_{stick} is given by [26]

$$f_{\text{stick}} = \frac{2(\rho^2 + 1)(\rho^2 - 1)^{3/2}}{3\rho[(2\rho^2 - 1)\ln\{\rho + (\rho^2 - 1)^{1/2}\} - \rho(\rho^2 - 1)^{1/2}]}, \quad (13)$$

where ρ is the ratio of major axis ($2a$) to the minor axis ($2b$) of the ellipsoid. This expression is valid for stick boundary condition. In order to make calculations using SED [Eq. (1)], the volume (V), the axial ratio (ρ), and the boundary condition parameter (C) must be estimated. The value of C is set equal to unity for stick boundary condition, while, for slip boundary condition, it can be evaluated from the tables of Hu and Zwanzig [32] for the same non-spherical solute molecules.

The rotational reorientation times of U-OB in series of n -alcohols, n -alkanes and binary mixture of toluene and butanol (Table 1) were plotted as a function of viscosity (Figs. 4(a) and 4(b)). Linear regression results of these plots are shown in Table 2. Note that a positive intercept at zero viscosity was observed for all the three plots. Such nonzero intercepts have been observed in a number of studies [23,45,46] and their significance or otherwise have not been fully understood. The experimentally measured τ_r values increase linearly with η in all the three solvents systems.

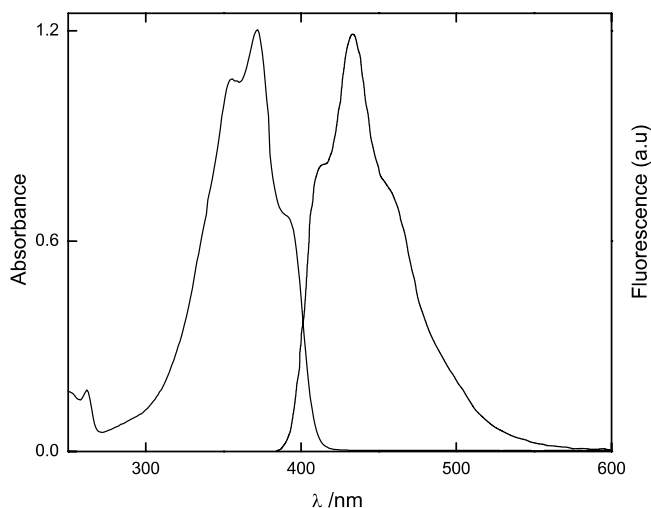


Fig. 2. Absorption and fluorescence spectra of U-OB in methanol.

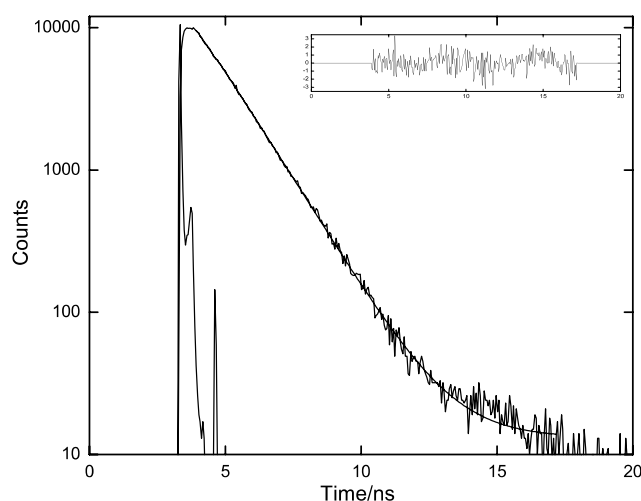


Fig. 3. Fluorescence decay curve of U-OB in methanol.

Table 1
Steady-state anisotropy $\langle r \rangle$, fluorescence lifetime (τ_f) and rotational reorientation times (τ_r) at 298 K

Alkanes	η (mPa s)	$\langle r \rangle$	τ_f (ns)	τ_r (ps)
Pentane	0.23 ^a	0.019 ± 0.001	0.95	53 ± 14
Hexane	0.29 ^a	0.021 ± 0.002	1.00	62 ± 14
Heptane	0.41 ^a	0.029 ± 0.002	1.00	88 ± 18
Octane	0.52 ^b	0.036 ± 0.002	1.01	112 ± 17
Nonane	0.66 ^a	0.044 ± 0.002	1.04	145 ± 19
Decane	0.84 ^b	0.052 ± 0.002	1.07	181 ± 17
Dodecane	1.35 ^b	0.067 ± 0.002	1.23	281 ± 28
Tridecane	1.55 ^a	0.078 ± 0.002	1.26	349 ± 34
Pentadecane	2.81 ^a	0.106 ± 0.003	1.28	465 ± 51
Hexadecane	3.07 ^a	0.118 ± 0.003	1.33	649 ± 71
Methanol	0.55 ^b	0.021 ± 0.002	1.33	82 ± 21
Ethanol	1.08 ^a	0.049 ± 0.002	1.34	211 ± 46
Propanol	1.96 ^a	0.061 ± 0.002	1.35	275 ± 58
Butanol	2.59 ^a	0.085 ± 0.002	1.36	420 ± 59
Pentanol	3.55 ^a	0.094 ± 0.002	1.37	484 ± 63
Hexanol	4.59 ^b	0.112 ± 0.003	1.38	623 ± 81
Heptanol	5.87 ^a	0.122 ± 0.003	1.40	718 ± 72
Octanol	7.63 ^a	0.151 ± 0.003	1.41	1019 ± 102
Nonanol	9.59 ^a	0.166 ± 0.003	1.41	1206 ± 121
Decanol	11.80 ^a	0.182 ± 0.003	1.41	1442 ± 130
Bu/Tol 9.2%	2.01 ^c	0.044 ± 0.002	1.36	189 ± 25
Bu/Tol 19.87%	1.59 ^c	0.041 ± 0.002	1.35	174 ± 17
Bu/Tol 29.83%	1.28 ^c	0.037 ± 0.002	1.33	152 ± 15
Bu/Tol 39.30%	1.08 ^c	0.036 ± 0.002	1.31	146 ± 13
Bu/Tol 50.91%	0.90 ^c	0.035 ± 0.002	1.29	139 ± 14

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

^a From Ref. [31].

^b From Ref. [23].

^c From Ref. [59].

The calculated stick and slip lines are also shown in the figure. The ratio of the calculated, using slip boundary condition, to the observed reorientation times is in the range of 1.27–2.03 for alcohols, 1.07–1.5 for alkanes and 1.12–3.00 for binary mixtures indicating much faster rotation compared to SED hydrodynamics. It has been shown that the rotational diffusion times of BBOT are nearly the same (≈ 180 ps/mPa s) both in cyclohexane and ethanol

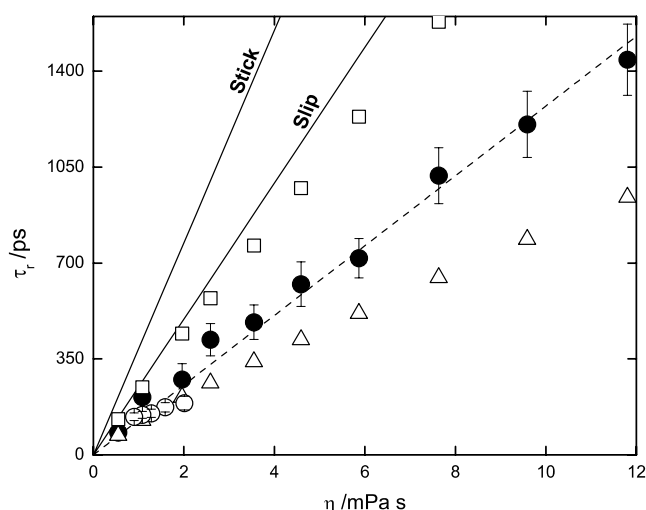


Fig. 4(a). Plot of rotational reorientation times of U-OB as a function of solvent viscosity in *n*-alcohols and binary mixture of butanol and toluene at 298 K. The symbols (●) and (○) represent experimentally measured reorientation times in alcohols and binary mixtures, respectively. The dashed line represents a linear best fit through the experimental points in alcohols. The solid lines are the theoretical plots of hydrodynamic models with stick and slip boundary conditions. Reorientation times calculated using GW and DKS theories are given by (Δ) and (□), respectively.

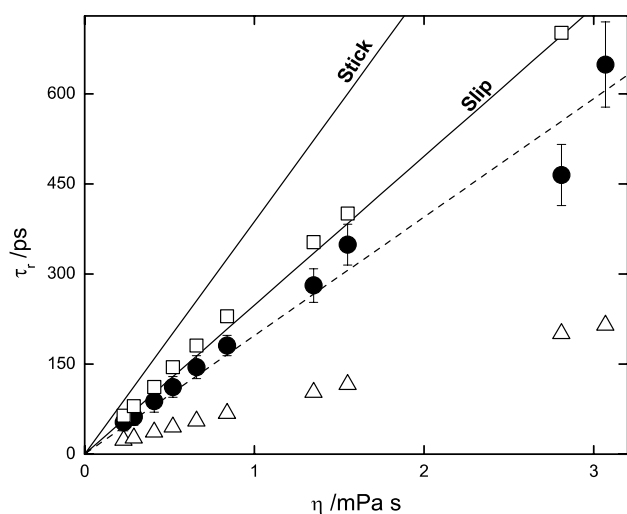


Fig. 4(b). Plot of rotational reorientation times of U-OB as a function of solvent viscosity in *n*-alkanes at 298 K. The symbol (●) represents experimentally measured reorientation times. The dashed line represents a linear best fit through the experimental points. The solid lines are the theoretical plots of hydrodynamic models with stick and slip boundary conditions. Reorientation times calculated using GW and DKS theories are given by (Δ) and (□), respectively.

[35] following slip behavior, which also holds good for the present situation for U-OB in ethanol and dodecane (≈ 200 ps/mPa s) having almost similar viscosity. This is due to rapid solvent exchange (weak hydrogen bonds) in which the directional properties of the hydrogen bonds are smeared out. Further, fluorescence lifetime of 1.34 ns obtained for U-OB in ethanol ($\eta = 1.08$ mPa s) at 298 K seems reasonable as compared with the previous literature

Table 2

Linear regression results of rotational reorientation of U-OB in series of alcohols, alkanes and binary mixture

Alcohols		Alkanes		Binary mixture (toluene + butanol)	
Slope (ps/mPa s)	Intercept (ps)	Slope (ps/mPa s)	Intercept (ps)	Slope (ps/mPa s)	Intercept (ps)
119	62	189	17	46	97
122 ^a	0 ^a	180 ^a	0 ^a	85 ^a	0 ^a

^a The second entry for solute is a slope of the best fit line made to pass through the origin.

data ($\tau_r = 1.17$ ns at $\eta = 1.2$ mPa s in ethanol) [35]. However, the situation is different for the solvents of higher viscosity. We notice a considerable change in reorientation times of U-OB on increasing the solvent viscosity. For the solvents of lower viscosity till ethanol in alcohols and octane in alkanes U-OB exhibits a slip behavior. In higher alcohols, alkanes and in binary mixture of toluene and butanol it is interesting to note a much faster rotation than predicted by slip boundary condition, clearly following subslip trend.

The subslip behavior was first noted experimentally by Canonica et al. [19] for non-polar molecules *p*-terphenyl ($V = 224$ Å³) and *p*-quaterphenyl ($V = 296$ Å³) which incidentally possess no hydrogen bonding groups and are normally expected to rotate faster in any solvents system. The viscosity of the solvents was varied over a wide range of temperature from 288 to 323 K. The authors argued that the subslip behavior suggested that the macroscopic viscosity is greater than microviscosity, i.e., the actual viscosity experienced by the rotating molecule. Later, Benzler and Luther [28] studied the rotational dynamics of same molecules in alkanes at room temperature and observed a marked deviation from the SED slip hydrodynamics at the higher viscosity. They observed that the viscosity of the solvent at which the standard hydrodynamic SED description breaks down is related to the size of the rotating molecule: in *n*-alkanes with solvent molecules larger than the probe molecule, simple hydrodynamics fails to explain the experimental results. Unlike *p*-terphenyl and *p*-quaterphenyl, the present probe U-OB has electronegative groups such as –O and –N and is most likely to form hydrogen bonds with the adjacent solvent molecules. In addition, the size of the probe molecule is larger by a factor of 2–11 in alcohols, 1–4 in alkanes and almost four in binary solvents which should clearly explain the SED description at least by slip behavior as suggested by these authors [28]. The estimated hydrogen bond strength for U-OB is less than 3 kcal/mol, which is classified as weak hydrogen bond and therefore the time scale of the solvent exchange must vary with the charge and polarizability of the solute molecule [35]. Further, a faster rotation of the probe in alcohols compared to alkanes of comparable viscosity indicates the importance of nonhydrodynamic effects in one or both the solvents series. In such case the microscopic friction of the solvent is reduced well below the

macroscopic value, which may be resulting from either dynamic or structural features of the macroscopic solvation environment. Table 3 presents an overview of rotational diffusion times of neutral molecules dissolved in series of alkanes and alcohols reported in literature. The solutes listed in Table 3 are in the order of increasing size. The diffusion time ratios clearly indicate a strong deviation from the slip hydrodynamics. For example, stilbene whose rotational time is about 38 ps/mPa s in *n*-alkanes, rotates more than twice as fast in *n*-alcohols. While the largest probes, QUI and BTBP take nearly the same time of about 420 ps/mPa s and 430 ps/mPa s in both *n*-alkanes and *n*-alcohols, respectively. For the intermediate solute sizes the trend, although not perfect, is towards a smaller difference between the rotation times in alcohols and alkanes. It is seen that the solvent fluctuations in *n*-alcohols occur roughly on the 100 ps/mPa s time scale i.e., precisely the time scale of the Debye absorption in these solvents [47]. Smaller solutes, which diffuse in times shorter than or comparable to these fluctuations would experience reduced friction

compared to *n*-alkane solvents and so the diffusion time ratio approaches unity. From Table 3, as this ratio becomes ≥ 1 , the observed rotational reorientation times approach stick behavior. Interestingly, the results of U-OB whose diffusion time ratio >1 follow subslip behavior, and the probe rotates faster in alcohols than in alkanes.

The pronounced subslip behavior found in alcohols may represent the additional influence of the local solvation environment offered by *n*-alcohols. The hydrophobic solvation environment around non-polar solutes appears to offer a weaker coupling to the bulk solvent motion than the hydrophilic solvation environment around charged molecules in *n*-alcohols. However, the results of the previous studies indicate that macroscopic hydrodynamic theories are good to within a factor of 2 in many cases [47]. The rotation factor of 3.0 in case of U-OB, below the slip line also explains that the probe is rotating much faster compared to *p*-terphenyl and *p*-quaterphenyl in binary mixtures. Binary solvent mixtures are commonly used to customize solvent properties in chemical reactions and

Table 3
Rotational diffusion of some neutral solute molecules in alkanes and alcohols

Solute	Volume (\AA^3)	Solvent	Diffusion time (ps/mPa s)	Ratio	Reference
Stilbene	180	<i>n</i> -Alcohols	13	0.34	[21]
		<i>n</i> -Alkanes	38		
<i>p</i> -Terphenyl	224	<i>n</i> -Alcohols	39	0.68	[9]
		<i>n</i> -Alkanes	57		
9,10-Diphenyl	312	<i>n</i> -Alcohols	50	0.64	[47]
		<i>n</i> -Alkanes	78		
BMQ ^a	325	<i>n</i> -Alcohols	78	0.73	[23]
		<i>n</i> -Alkanes	107		
TMQ ^b	359	<i>n</i> -Alcohols	110	0.81	[23]
		<i>n</i> -Alkanes	136		
DMQ ^c	376	<i>n</i> -alcohols	130	0.75	[23]
		<i>n</i> -Alkanes	174		
U-OB	383	<i>n</i> -Alcohols	119	0.63	Present work
		<i>n</i> -Alkanes	189		
TMI ^d	429	<i>n</i> -Alcohols	179	0.65	[23]
		<i>n</i> -Alkanes	277		
TP ^e	496	<i>n</i> -Alcohols	104	0.67	[60]
		<i>n</i> -Alkanes	155		
TT ^f	601	<i>n</i> -Alcohols	222	0.86	[60]
		<i>n</i> -Alkanes	259		
QUI ^g	639	<i>n</i> -Alcohols	418	0.98	[23]
		<i>n</i> -Alkanes	426		
BTBP ^h	733	<i>n</i> -Alcohols	430	1.00	[22]
		<i>n</i> -Alkanes	430		

^a 2,2'''-dimethyl-*p*-quaterphenyl.

^b 3,3',2'',3'''-tetramethyl-*p*-quaterphenyl.

^c 2-methyl-5-*t*-butyl-*p*-quaterphenyl.

^d 2,5,2''',5'''-tetramethyl-*p*-quinquephenyl.

^e 2,5,8,11-tetra-*tert*-butylperylene.

^f 2,5,10,13-tetra-*tert*-butylterylene.

^g 3, 5, 3''',5'''-tetra-*t*-butyl-*p*-quinquephenyl.

^h *N,N'*-bis(2,5-di-*tert*-butylphenyl)-3,4,9,10-perylene dicarboxamide.

chromatography. Upon mixing, solvent interaction often creates new solvent properties that were not present in the pure solvents. Numerous studies [48–50] have indicated that alcohols are associated through hydrogen bonded linear chains (with restricted rotation about hydrogen bonds) into variable degrees of polymerization. When toluene is mixed with butanol the presence of π -electrons in toluene result in the formation of weak intermolecular complexes, which inturn leads to faster rotation of the solute due to poor interaction with solvents. This could also be one of the possible reasons for faster rotation of U-OB in binary mixture than in alcohols and alkanes series.

The steady-state anisotropy measurements agree well with the time resolved anisotropy measurements wherein the rotational correlation times deviate remarkably from SED slip hydrodynamics and follow a subslip behavior in higher alcohols. The fluorescence anisotropy decay parameters of U-OB in higher alcohols are summarized in Table 4 and anisotropy decay curves are shown in Fig. 5 in hexanol and decanol. The rotational correlation function decays as a single exponential as is usually expected for a prolate ellipsoid with transition moment along the symmetry axis [30,35], which is of the form

$$r(t) = r_0 \exp(-t/\tau_R), \quad (14)$$

where τ_R is the rotational reorientation time about the symmetry axis. The initial anisotropy (at zero time) r_0 for U-OB measured in alcohols are in the range of 0.349–0.375, and are comparable to the steady-state r_0 value of 0.360 (in glycerol at a temperature of -60°C where the rotational motions of U-OB are frozen). Justus et al. [51] have studied fluorescence anisotropy kinetics for the probe $\text{Cl}_2-\phi_2\text{-TPD}$ containing two electronegative groups O and N which has similar structure and volume ($V = 397 \text{ \AA}^3$) to U-OB in chloroform. They noticed the stick-limit prolate models overestimating and slip-limit model underestimating the experimental results. They concluded this as a result of internal rotations within the molecules, which shortened the fluorescence anisotropy decay times. This may also account for somewhat much shorter fluorescence anisotropy decay that we observe for U-OB as compared to $\text{Cl}_2-\phi_2\text{-TPD}$ falling in subslip-limit with increasing solvent viscosity. Theoretical justification for this approach is provided by the microfriction theories of Geirer-Wirtz and Dote-Kivelson-Schwartz to calculate the reorientation

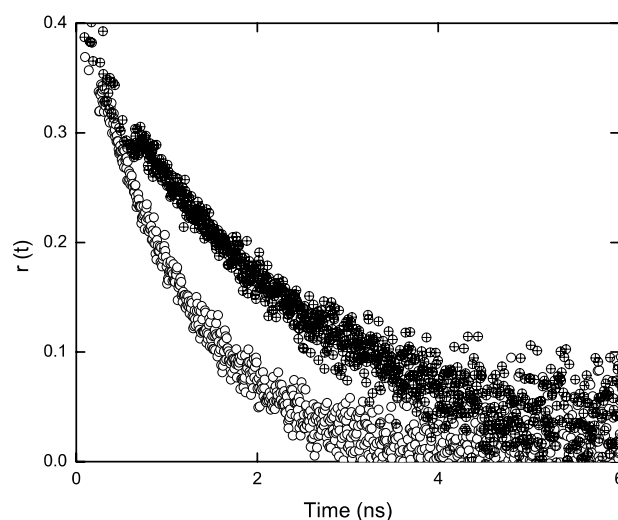


Fig. 5. Anisotropy decay of U-OB in hexanol (O) and decanol (⊕) at 298 K.

times in which the solvent sizes as well as free spaces are taken into account.

5. Applicability of quasihydrodynamic theories to rotational reorientation of U-OB

In the first place, the GW theory is used to calculate the parameters σ and C_0 using Eqs. (3) and (4), respectively, and the van der Waals volume of the solvent V_s in different alcohols, alkanes and in binary mixture were used. The coupling parameter C_{GW} , obtained from Eq. (5) varies from 0.21 to 0.34 in alcohols, 0.18 to 0.25 in alkanes and 0.25 to 0.26 in binary mixture of toluene and butanol. The reorientation times calculated using C_{GW} values were plotted as a function of η in Figs. 4(a) and 4(b). Though the GW theory is able to reproduce the nonlinear profile of τ_r vs. η , it underestimates the friction experienced by the probe by a factor of 1.1–1.7 in alcohols, 2.3–3.0 in alkanes and 0.9–2.3 in binary mixture. In view of the large deviation between the experimentally measured reorientation times and those calculated theoretically, we also employed DKS theory. C_{DKS} and γ were calculated using Eqs. (6) and (7) in alcohols, alkanes and binary solvents. ΔV is calculated using Eq. (8) in alkanes and Eq. (9) is used for alcohols and binary mixtures. Figs. 4(a) and 4(b) also incorporate the τ_r values calculated using DKS method in all the three solvent systems. Clearly, the DKS theory overestimates the friction experienced by the probe by a factor of 1.4–1.7 in alcohols, 1.2–1.3 in alkanes and 1.1–2.3 in binary mixtures. An interesting finding of the present investigation is that, as noted from Figs. 4(a) and 4(b), there is an almost perfect coincidence between the predictions of the slip hydrodynamic model and DKS model which has been observed for the first time. Also the experimental results are in good agreement with both slip and DKS theory up to nonane in alkanes. We may confidently say that the DKS description of microscopic friction properly

Table 4
Fluorescence anisotropy decay parameters in alcohols at 298 K ($\lambda_{\text{ex}} = 370 \text{ nm}$)

Solvents	η (mPa s)	r_0^a	τ_{R1} (ps)
Pentanol	3.55	0.355	510 ± 50
Hexanol	4.59	0.365	655 ± 55
Heptanol	5.87	0.349	780 ± 84
Octanol	7.63	0.375	1195 ± 67
Nonanol	9.59	0.362	1306 ± 75
Decanol	11.80	0.356	1495 ± 77

^a $\pm 10\%$.

accounts for non-polar solvents up to nonane and polar solvents up to ethanol both qualitatively as well as quantitatively. However, in higher alcohols, alkanes and binary mixtures the experimentally obtained reorientation times lie in between the theoretical models of DKS and GW. The DKS quasihydrodynamic theory has been applied to analyze the observed results and a good agreement between the experiment and theory has been found [22,23,28,29, 52,53], though in few cases it could not predict the experimental results quantitatively. For example, in the study of few quarter and quinquephenyl molecules with radii in the range from 4 to 5 Å, Roy and Doraiswamy [23] noted a good correlation between the DKS theory and the experiment up to a solute radius of 4.5 Å. Dutt et al. [29] studied the rotational dynamics of 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo [3,4-c]pyrrole (DMDPP) in a series of alcohols and observed a poor agreement between the experiment and the DKS theory, though, DMDPP has radius of 4.1 Å. It was argued that the reason for the poor correlation between the theory and experiment could be due to the shape of molecule. When noticed with U-OB, the magnitude of reduction in the microscopic friction coefficient in case of GW is very small compared to DKS theory in all the solvent systems studied, perhaps due to the fact that the GW theory does not take into account the cavities or free spaces created by the solvent molecules around the probe molecule. Also the DKS theory accounts for the degree of contact between the probe in a cavity and the surrounding solvent, whereas the GW theory accounts for a stepwise decrease of angular velocity due to the finite size of the solvent molecules [34].

When the rotational motion of solutes containing –O and –N in polar solvents needs to be described, the simple hydrodynamic friction arising out of the viscosity of the solvent alone is inadequate. An additional contribution due to dielectric friction has to be included [14]. We have calculated dielectric friction with an intention to check the contribution of dielectric friction, if any, to the rotational motion of U-OB. Within a dielectric continuum model for the solvent, the contribution due to dielectric friction to rotational reorientation time is given by [54]

$$\tau_{\text{DF}} = \frac{4\pi\mu^2}{3VkT} \frac{\varepsilon - 1}{(2\varepsilon + 1)^2} \tau_{\text{D}}, \quad (15)$$

where μ is the dipole moment of the probe in the excited state, ε and τ_{D} are the dielectric constant and Debye dielectric relaxation time of the solvent, respectively. The equations that are necessary to calculate the experimentally measured ground and excited state dipole moments using solvatochromic and Guggenheim method are taken from the references [55,56], respectively. The ground state geometry of U-OB was fully optimized using DFT with popular hybrid B3LYP functional with 6–31 g^* basis set [57] and is shown in Fig. 6. The calculated dipole moments are tabulated in Table 5. The values of dipole moments in the ground and excited states using all the three methods are

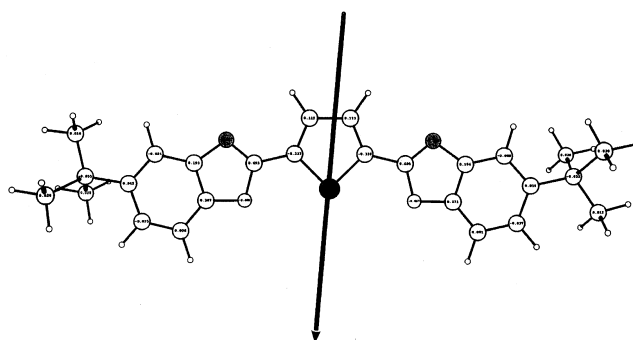


Fig. 6. Optimized structure of U-OB obtained using B3LYP level theory with the 6–31 G^* basis set. The direction of the transition dipole is also indicated in the figure.

Table 5
Dipole moment values of U-OB using different methods

	μ_g/D	μ_e/D
Solvatochromic shift method	1.20	2.94
Guggenheim method	1.61	3.29
DFT method	1.39	2.41

in good agreement. The excited state dipole moment ($\mu_e = 2.94 \pm 0.1D$) calculated using solvatochromic method was used to calculate the τ_{DF} . The values of ε and τ_{D} were taken from Ref. [14] for alcohol solvents at 298 K. The calculated τ_{DF} values are in the range of 9–913 ps from methanol to decanol. Thus, τ_{DF} calculated using Eq. (3) is added to the theoretically calculated reorientation times (τ_{SED}) which perhaps increases the τ_r ($=\tau_{\text{SED}} + \tau_{\text{DF}}$) to a large extent. This suggests that the microscopic friction of the solvent is reduced well below the macroscopic value, which may be resulting from either dynamic or structural features of the macroscopic solvation environment [58]. Also the strong overlap between the slip hydrodynamics and the DKS theory is an indication of the fact that the solute U-OB rotating unhindered in free spaces created in solvents thus exhibiting the faster rotations in alcohols. The faster rotation of U-OB in alkanes is normal for a molecule of this size.

In conclusion, the τ_r values were examined as a function of viscosity in a series of alcohols, alkanes and binary mixture of toluene and butanol using steady-state and time resolved fluorescence depolarization techniques. From the plots it is clear that the experimental results follow slip hydrodynamics and DKS quasihydrodynamic theories, which go together in alkanes completely and to some extent in alcohols. A larger deviation will break down the continuum model to cause faster rotational reorientation time than that predicted by the modified SED equation at higher viscosities with subslip behavior. The quasihydrodynamic models of GW and DKS were used to correct for the solute and solvent size effect on the molecular scale. In spite of these corrections, only the DKS theory is able to predict experimental trend both qualitatively and quantitatively in alkanes and alcohols. Further study to check the contri-

bution of dielectric friction, if any, would not help the theoretical models, when included with the mechanical friction. This indicates that, in spite of the presence of electronegative groups, which have the ability to form hydrogen bonds with any solvents has negligible interaction, even with the highly polar solvents like alcohols. A faster rotation of the probe is noted in binary mixtures than in series of alcohols and alkanes. Perhaps this needs an extensive study in some other binary mixtures of different polarities with a view to check the possibility of faster rotations of probes such as U-OB.

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