J. Phys. Chem. A **2005,** *109,* 3009−3014 **3009**

Comparison of and Investigation into the Size Effects on the Rotational Dynamics of Two Spherical Molecules: CCl_4 and C_{60}

Kyle B. Nichols and A. A. Rodriguez*

Department of Chemistry, East Carolina University, Greenville, North Carolina 27858

Received: September 10, 2004; In Final Form: February 9, 2005

^{13}C spin−lattice relaxation measurements were performed on CCl_4 and C_{60}, two spherical molecules, to investigate the role of molecular size on reorientational dynamics. Measurements were taken at common temperatures and in a common environment; deuterated chlorobenzene-d_5. Our data indicate that both CCl_4 and C_{60} reorient in the small-step diffusion limit. Correlation times for CCl_4 were found to be smaller in CBZ than in the neat and much shorter than predicted by viscosity arguments. We have attributed the higher rotational freedom to higher "free volume" or lower solute−solvent contact probability, in CBZ than in the neat. Experimental τ_C values for CCl_4 and C_{60} in CBZ were found to be much different than those predicted by hydrodynamics. Pure inertia differences did not explain the disparities in the correlation times. However, a very reasonable explanation for our experimental findings was found by considering the solvent-to-probe molecular volume ratio and its effect on rotational diffusion. We applied four hydrodynamic-based theories to our data and found that the model by Gierer-Wirtz best duplicated our experimental observations. The success of this model suggests that the relative size of solute and solvent molecules, as well as events at the microscopic level, rather than bulk properties, are excellent descriptors of the factors affecting rotational diffusion.

I. Introduction

For a number of years, the study of molecular rotation in liquids has been a subject of much interest.[1−6] Theoretical characterization of the experimental observations frequently involve Brownian based theories that presume solutes possess spherical geometry which, in a number of cases, is an extreme approximation.[4,7−11] With symmetries of T_d and I_h, carbon tetrachloride (CCl_4) and buckminsterfullerene (C_{60}), respectively, possess molecular shapes which remove any uncertainty of their spheroidal nature. Rarely does one encounter two candidates more suited for probing those factors affecting molecular diffusion. Carbon tetrachloride has been described as the most prominent representative of the pseudospherical tetrahalides, whose individual isotropic polarizability makes them perfect for studies of molecular interactions in liquids.[12] Similarly, C_{60} has been the most thoroughly studied member of the fullerene family. Our interest for several years has been the utilization of dynamic NMR, as well as the employment of various theoretical models, to investigate the intricacies of molecular diffusion in liquids.[13−16] An issue that has persisted for a number of years in these types of studies is how molecular size differences, between solute and solvent, influence solvent structure and diffusional behavior.[4] Because of their size differential, CCl_4 ($V_{CCl_4} = 85$ Å^3) and C_{60} ($V_{C_{60}} = 181$ Å^3) are natural candidates for experimentally addressing these issues.[17,18] In this paper, we present experimental data aimed at improving our understanding of the possible factors affecting molecular reorientation in liquids, in particular, the roles that molecular size differences and/or solvent "free volume" might play in reorientational diffusion. Additionally, we applied four commonly used hydrodynamic-based models in an attempt at explaining our experimental findings as well as to assess their broad applicability.

II. Theory

A. Spin−Lattice Relaxation. ^{13}C spin−lattice relaxation in both CCl_4 and C_{60} is known to proceed via a limited number of pathways: intramolecular dipole−dipole (R_1^{DD}) and spin rotation (R_1^{SR}) in CCl_4 and through the chemical shift anisotropy (R_1^{CSA}) and R_1^{SR} in C_{60}.[19,20] In CCl_4, the overall relaxation rate, R_1, can be expressed as[21,22]

$$R_1 = R_1^{DD} + R_1^{SR} \tag{1}$$

where

$$R_1^{DD} = \frac{20{\gamma_{13}}^2\hbar^2\tau_C}{{r_{C,Cl}}^6}(0.75{\gamma_{35}}^2 + 0.25{\gamma_{37}}^2) \tag{2}$$

and

$$R_1^{SR} = \left(\frac{8\pi^2IkT}{\hbar^2}\right)C^2\tau_J \tag{3}$$

In eq 2, γ_{13}, γ_{35}, and γ_{37} correspond to the gyromagnetic ratios for ^{13}C, ^{35}Cl, and ^{37}Cl, respectively, $r_{C,Cl}$ is the carbon−chlorine bond distance (1.76 Å),[19] and τ_C is the reorientational correlation time. In eq 3, I is the moment of inertia (4.90×10^{-45} kg m^2), C is the spin-rotation coupling constant (0.45 kHz),[19] and τ_J is the angular momentum correlation time. The remaining parameters (i.e. k, T, and $\hbar$) have there usual meaning. The deconvolution of R_1 into its R_1^{DD} and R_1^{SR} contributions readily leads to the dynamical parameters of τ_C and τ_J.

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* Corresponding author. Fax: (252) 328-6210. E-mail: rodriguezar@mail.ecu.edu.

10.1021/jp045899b CCC: $30.25

For C_{60}, the overall relaxation rate is express as

$$R_1 = R_1^{\mathrm{CSA}} + R_1^{\mathrm{SR}} \tag{4}$$

where R_1^{CSA} is the rate due to chemical shift anisotropy interactions given by[22]

$$R_1^{\mathrm{CSA}} = \left(\frac{2}{15}\right)\gamma_{13}{}^2\mathbf{B}_0{}^2S^2\tau_{\mathrm{C}} \tag{5}$$

and R_1^{SR} is again given by eq 3; with the moment of inertia (1.0 $\times$ 10^{-43} kg m^2) and the spin rotation coupling constant (0.258 kHz) values now corresponding to C_{60}. In eq 5, $\mathbf{B}_0$ is the magnetic field strength, whereas S is the shielding anisotropy, 1.78×10^{-4}.[20] The various relaxation contributions in C_{60} are readily isolated by measuring the overall relaxation rate, R_1, at various field strengths, $\mathbf{B}_0$, since R_1^{CSA} is directly dependent on $\mathbf{B}_0$, whereas R_1^{SR} has no such dependence. Once separated, these results lead to the determination of τ_{C} and τ_{J}. The experimental methodology and analysis is explained more thoroughly in our previous communication.[13]

Because of their spherical nature, rotational diffusion for both CCl_4 and C_{60} is characterized by a single diffusion coefficient and related to τ_{C} by[21]

$$D = \frac{1}{6\tau_C} \tag{6}$$

This inherent relationship allows the use of either D or τ_{C} when describing reorientational behavior. Although τ_{C} represents the period of time required by the correlation function for magnetic relaxation to decrease by $1/e$ of its initial value, classically, this parameter is frequently viewed as the amount of time required for a molecule to undergo rotation by 1 rad. Because of their inverse relationship, a small value for τ_{C} indicates rapid diffusion while the reverse is valid for an opposite observation. We chose to describe our experimental observations via our τ_{C} values since these were directly obtained from the various relaxation equations.

B. Theoretical Models. Rotational correlation times are often expressed theoretically as the sum of a hydrodynamic and an inertial contribution[23,24]

$$\tau_{\mathrm{C}} = \left(\frac{V_{\mathrm{P}}\eta}{k_{\mathrm{B}}T}\right)\phi C + \tau_{\mathrm{O}} \tag{7}$$

where V_{P} is the probe volume, η is the bulk viscosity, k_{B} is the Boltzmann constant, T is the temperature, ϕ is a shape parameter (which is unity for a sphere), and τ_{O}, the inertial or "free rotor" correlation time, is an experimentally obtained parameter which is often associated with the rotational motion in the pure "slip" limit. It is common to ignore τ_{O} since inertial effects are usually found to be negligibly small. C is also an experimentally obtained dimensionless fitting coefficient which contains information on a probe's link to its immediate environment. A value of one refers to a condition frequently known as the "stick limit", whereas a value of zero is known as the "slip limit." Under the latter limit, τ_{C} reduces to τ_{O}. The effectiveness of a theoretical model to replicate experimental correlation times lies in its ability to generate acceptable values for C.

The Stokes–Enstein–Debye theory (SED) was one of the early attempts at modeling the behavior of a solute in a viscous environment.[7] In this model, a probe is viewed as being affected primarily by solvent viscosity. The shape parameter ϕ and coefficient C are both set to one, corresponding to a sphere and to the stick condition, and the inertial contribution, τ_{O}, is ignored. Under this approach eq 7 reduces to

$$\tau_{\mathrm{C}}(\mathrm{SED}) = \left(\frac{V_{\mathrm{P}}\eta}{k_{\mathrm{B}}T}\right) \tag{8}$$

A different approach, which has encountered mixed success, and commonly referred as the "free space model", is the theory by Dote–Kevelson–Schwartz.[25] This model incorporates solvent size as well as free volume effects to characterize the rotational diffusion of a solute in solution. In a nut shell, this model suggests that, in the absence of significant intermolecular forces, a perfectly spherical solute should not need any free space to experience "free rotation" as predicted by hydrodynamics. However, it would require increasingly more space as its shape deviates from this ideal geometry. In this theory, C is given by

$$C = \left[1 + \frac{\gamma}{\theta}\right]^{-1} \tag{9}$$

where γ is defined as[25]

$$\gamma = \left(\frac{\Delta V}{V_{\mathrm{P}}}\right)\left[4\left(\frac{V_{\mathrm{P}}}{V_{\mathrm{S}}}\right)^{2/3} + 1\right] \tag{10}$$

and θ is given as[4,25]

$$\theta = \frac{\tau_{\mathrm{slip}}}{\tau(\mathrm{SED})} \tag{11}$$

In eq 10, V_{P} and V_{S} are the probe and solvent molecular volumes, respectively, whereas ΔV is obtained using the isothermal compressibility, k_{T}, viscosity, η, temperature, T, and the Hildebrand–Batschinski parameter, B,[26,27] in eq 12

$$\Delta V = k_{\mathrm{B}}k_{\mathrm{T}}T\eta B \tag{12}$$

The Hildebrand–Batschinski parameter can readily be calculated from a solvent's viscosity, density, ρ, and density at zero fluidity, ρ_0[4]

$$B = \left(\frac{1}{\eta}\right)\left[\frac{\left(\frac{1}{\rho_0}\right)}{\left(\frac{1}{\rho} - \frac{1}{\rho_0}\right)}\right] \tag{13}$$

In eq 11, τ_{slip} is the correlation time calculated under true slip conditions while $\tau(\mathrm{SED})$ is obtained via eq 8.

An alternative approach, proposed by Hynes, Kapral, and Weinberg (HKW),[28,29] introduces the concept of a microscopic boundary layer which surrounds the rotating molecule and proposes that collisional effects within this layer determine the rotational behavior of the molecule. A slip coefficient (β), obtained through the Enskog collision theory,[30–32] is used to measure the velocity coherence (i.e., coupling) of the boundary layer relative to the outer hydrodynamic region. As β approaches zero, the "slip" limit is approached signifying little or no velocity coherence. Molecules in this limit are believed to be experiencing free rotation. The other extreme, the "stick" limit, is approached as β nears infinity. The values of β between these two extremes is referred as the "intermediate" region. In this model, ϕ is still unity (i.e., a sphere) but C is defined as

$$C = \left(1 + \frac{3\eta}{\beta}\right)^{-1} \tag{14}$$

where η is the bulk viscosity and β is given as[33]

$$\beta = \left[\frac{b}{(1+b)}\right]\left(\frac{2k_B\mu_{SP}T}{\pi}\right)^{0.5}\left[1+\left(\frac{V_P}{V_S}\right)^{0.33}\right]^2 \rho_S\sigma_{SP}g(\sigma_{SP}) \qquad (15)$$

In β, k_B is the Boltzmann constant, μ_{SP} is the reduced mass, T is the temperature, V_P and V_S are the probe and solvent molecular volumes, ρ_S is the solvent number density, σ_{SP} is the average solvent-probe contact distance, $g(\sigma_{SP})$ is the pair distribution function at the solvent−solute contact distance,[34] and b, the reduced moment of inertia, is given by[25]

$$b = \mu_{SP}\left(\frac{V_S{}^{0.67}}{I_{SS}} + \frac{V_P{}^{0.67}}{I_{PP}}\right)\left(\frac{3}{4\pi}\right)^{0.67} \qquad (16)$$

where I_{SS} and I_{PP} are the solvent and probe moments of inertia, respectively.

A far more straightforward model that has been used successfully to characterize the reorientational behavior of a number of molecular systems was proposed by Gierer and Wirtz.[35] This theory introduces microviscosity effects, a “sticking factor,” σ_{GW}, and a solvation number, C_0. According to this approach, C is a function of the solvent-to-probe molecular volume ratio (i.e., V_S/V_P) and is defined as

$$C = \sigma_{GW}C_0 \qquad (17)$$

where

$$C_0 = \left[\frac{6(V_S/V_P)^{0.33}}{(1+2(V_S/V_P)^{0.33})^4} + \frac{1}{(1+4(V_S/V_P)^{0.33})^3}\right]^{-1} \qquad (18)$$

and $\sigma_{GW} = (1 + 6(V_S/V_P)^{1/3}C_0)^{-1}$. A σ_{GW} value of unity indicates the “stick” limit, whereas the “slip” limit is reached when σ_{GW} equals zero. Essentially, this approach correlates the frictional changes being experienced by a probe to the varying solvent-probe molecular volume ratios, V_S/V_P.

III. Experimental Section

Carbon tetrachloride was purified by distillation, and a sample, in solution with chlorobenzene-d_5 (CBZ), was prepared in a 5 mm NMR tube. Chlorobenzene-d_5 was purchased from Aldrich Chemical Co. and was used as received. The CCl_4/CBZ solution was prepared with a mole fraction of 3.87×10^{-2} for consistency with the earlier study of C_{60}/CBZ.[13] The sample tube was connected to a vacuum manifold and subjected to at minimum of three freeze−pump−thaw cycles to remove molecular oxygen and then sealed under vacuum.

To test for the presence or absence of the R_1^{CSA} in CCl_4, T_1 measurements on this molecule were performed on two instruments operating at field strengths of 7.05 and 11.75 T. Temperatures were chosen to simultaneously overlap a previous study by Gillen and co-workers and to our study for C_{60} in this same solvent.[13,19] The temperature was regulated and maintained with an accuracy of ±0.5 K. A minimum of three measurements were conducted at each temperature with average values being reported in Table 1.

The dipolar contribution, R_1^{DD}, in CCl_4 was obtained through eq 2 by utilizing values for τ_C generated via the method by Gillen and co-workers, who found τ_C to be in the rotational diffusion limit (i.e., $\tau_J \ll \tau_C$) and obeyed the relation 19

$$\tau_C = (8.67 \times 10^{-14})e^{(1.81\text{kcal/mol})/RT} \qquad (19)$$

TABLE 1: Experimental Relaxation Times and Rates of CCl_4 in Chlorobenzene-d_5 at Different Temperatures and Field Strengths of 11.75 and 7.05 T[a]

	11.75 T		7.05 T	
T (K)	T_1 (s)	$R_1 \times 10^3$ (1/s)	T_1 (s)	$R_1 \times 10^3$ (1/s)
288	204.5 (9)	4.89	210.5 (8)	4.75
303	182.8 (5)	5.47	190.7 (15)	5.24
318	167.8 (11)	5.96	174.2 (14)	5.74
333	153.4 (3)	6.52	153.0 (10)	6.53

[a] Values in parentheses represent standard deviations of at least three measurements at each temperature.

TABLE 2: Experimental Relaxation Rates and Correlation Times of CCl_4 in Chlorobenzene-d_5 at 11.75 T and at Various Temperatures

T (K)	$R_1 \times 10^3$ (1/s)	$R_1^{SR} \times 10^3$ (1/s)	$R_1^{DD} \times 10^4$ (1/s)	τ_J (ps)	τ_C (ps)
288	4.89	4.45	4.41	0.159	1.30
303	5.47	5.09	3.77	0.173	1.13
318	5.96	5.63	3.28	0.182	1.02
333	6.52	6.23	2.88	0.192	0.92

Once values for R_1^{DD} were known, values for R_1^{SR} were deduced from the difference between the experimental R_1 values and R_1^{DD}, as given by eq 1. Angular momentum correlation times, τ_J, were then derived from the extracted R_1^{SR} and eq 3. The correlation times of CCl_4 in the neat were extracted from a fit of the data obtained by Gillen and co-workers on this molecule.[19]

For brevity, the separation of R_1^{CSA} and R_1^{SR}, along with the determination of values for τ_C and τ_J, in C_{60} are thoroughly described in ref 13.

IV. Results and Discussion

A. Experimental Results. Table 1 lists the temperature-dependent ^{13}C relaxation rates of CCl_4 at the two different field strengths, 11.75 and 7.05 T. The relaxation rates at these two field strengths are seen to be within experimental error indicating an independence on frequency (i.e., the chemical shift anisotropy mechanism does not play a significant role in the overall relaxation process). This is expected since the symmetry at the carbon nucleus in this molecule is high. Hence, only intramolecular dipole−dipole, R_1^{DD}, and spin−rotation, R_1^{SR}, rates contribute to the relaxation process, as found by Gillen and associates.[19] Since random experimental error was generally lower at 11.75 T, the data at this field strength were used in the analysis of our measurements.

Table 2 illustrates the relaxation rates and dynamic correlation times, τ_C and τ_J, for CCl_4 at the various temperatures. A comparison of τ_C and τ_J indicates that CCl_4 is indeed experiencing small-step diffusion (i.e., $\tau_J \ll \tau_C$) throughout the temperature range. The reorientational correlation time, τ_C, is observed to decrease slowly with rising temperature indicating a gradual increase in rotational rate.

Table 3 illustrates the correlation times of CCl_4 in the neat and in CBZ. Although the values for τ_C in both the neat and in CBZ span a range of approximately 0.70 ps, the values are appreciably lower in CBZ than in the neat. Although chlorobenzene’s viscosity is roughly 11% lower, the rotational times of CCl_4 in this solvent are an average of 31% lower than in the neat. The larger than expected decrease in τ_C suggests CCl_4 is experiencing higher rotational freedom in chlorobenzene. The presence of weak intermolecular interactions is a possible

TABLE 3: Comparison of the Correlation Times of CCl_4 in the Neat and in Chlorobenzene-d_5 at Different Temperatures[a]

	Neat CCl_4		CCl_4 in CBZ	
T (K)	η (cP)	τ_C (ps)	η (cP)	τ_C (ps)
288	1.05	2.01	0.90	1.30
303	0.85	1.72	0.72	1.13
318	0.70	1.49	0.61	1.02
333	0.59	1.31	0.52	0.92

[a] Correlation times, τ_C, in neat CCl_4 were extracted from a fit of the data found in ref 19.

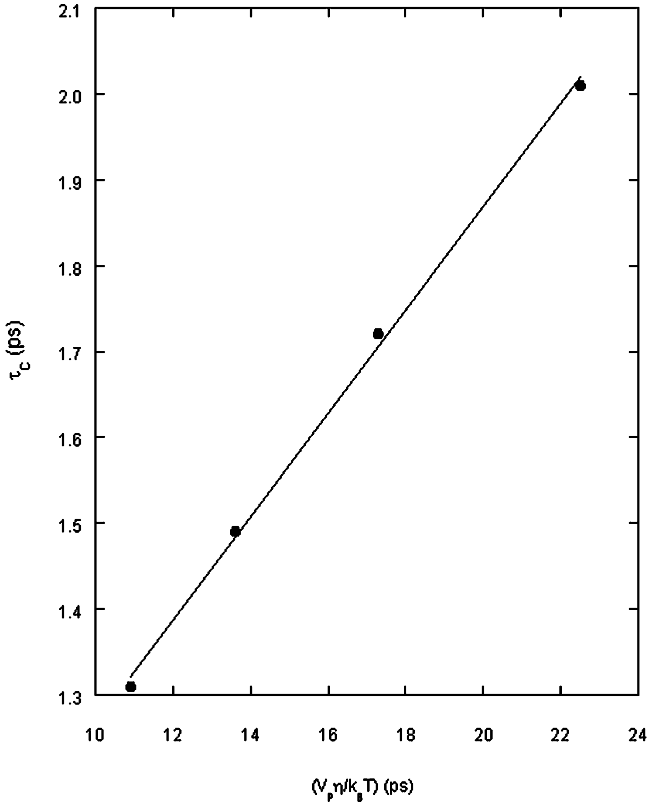

Figure 1. Linear fit of experimental correlation times in neat CCl_4 to obtain values for the friction coefficient, *C*, and "free rotor" contribution, τ_O.

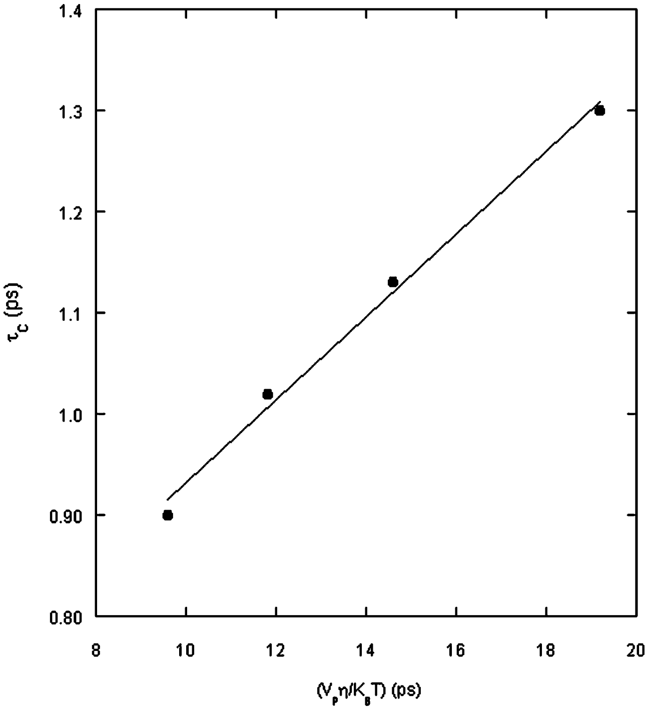

Figure 2. Linear fit of experimental correlation time of CCl_4 in CBZ to obtain values for the friction coefficient, *C*, and "free rotot" contribution, τ_O.

TABLE 4: Comparison of Correlation Times for CCl_4 and C_{60} in Chlorobenzene-d_5 at Various Temperatures[a]

		CCl_4		C_{60}	
T (K)	η (cP)	τ_J (ps)	τ_C (ps)	τ_J (ps)	τ_C (ps)
288	0.90	0.159	1.30	0.008	10.9
303	0.72	0.173	1.13	0.010	8.99
318	0.61	0.182	1.02	0.011	7.40
333	0.52	0.192	0.92	0.019	4.85

[a] Correlation times for C_{60} were obtained from our previous work as given in ref 13. The τ_J values for C_{60} were obtained indirectly and so must be treated as estimates.

explanation for the observed differences, but the polarizabilities of the molecules in question ($\alpha_{CCl_4} = 0.215 < \alpha_{CBZ} = 0.235$),[36] which is a good indicator of possible London dispersive forces, would predict the reverse tendency. A second possibility for the enhanced rotational freedom in CBZ can be due to the lower packing efficiency expected in this solvent. Because of the molecular volume differences, V_{CCl_4} (85 Å^3) < V_{CBZ} (97 Å^3),[17,37] the larger chlorobenzene molecules would be unable to pack as effectively around CCl_4 which would generate more free volume or less solute−solvent contact; more free volume translates to less drag and, hence, freer rotational motion. Moreover, since the size and shape of CCl_4 remains constant, whether in the neat or in CBZ, a linear fit of its experimental τ_Cs versus ($V_P\eta/k_BT$), as given by eq 7, should provide details on the friction coefficient, *C*, for CCl_4 molecules in the neat and in CBZ. The intercept from this fit will also generate information on the free rotor contribution, τ_o. We performed this fit, as shown in Figures 1 and 2 and found values for *C* to be 0.06 and 0.04 for neat CCl_4 and CCl_4 in CBZ, respectively. These values indicate the diffusion of CCl_4, in both cases, to be closer to the "slip" limit and that it is experiencing slightly higher friction (i.e., "stickiness") in the neat than in CBZ. An identical fit of C_{60}'s data in CBZ revealed a friction coefficient of 0.28 suggesting higher interactions between this solute−solvent pair. Similar free rotor contributions were found for neat CCl_4 (0.5 ps) and for CCl_4 in CBZ (0.6 ps), whereas a value of 0.2 ps was found for C_{60} in CBZ. As expected, the free rotor contribution is lower in the larger C_{60} molecule.

Table 4 shows a comparison of τ_C and τ_J for both CCl_4 and C_{60} in chlorobenzene at the same temperatures. As was observed for CCl_4 in CBZ, C_{60}'s rotational dynamics lie in the diffusion limit ($\tau_J \ll \tau_C$).[38] The much longer τ_J values for CCl_4 indicate this molecule is remaining in a rotational state significantly longer than C_{60}. This may arise, once again, from the greater free volume available in the CCl_4−CBZ mixture than in the C_{60}−CBZ case since molecular volume differences, V_{CCl_4} (85 Å^3) < V_{CBZ} (97 Å^3) $\ll$ V_{C60} (181 Å^3),[17,18,37] would predict higher packing efficiencies about C_{60} than about CCl_4. The calculated radial distributions at the van der Waals contact radii for spheres, $g_{12}(CCl_4) = 7$ and $g_{12}(C_{60}) = 9$, support this observation.[34] The rotational correlation times, τ_C, for both CCl_4 and C_{60} are observed to decrease with rising temperature indicating enhanced rotational diffusion with rising temperature. However, the correlation times are very different, with τ_C being significantly longer for C_{60} suggesting this molecule experiences a higher retardation force as it reorients. In fact, an Arrhenius fit of τ_C versus inverse temperature for CCl_4 and C_{60} yielded activation energies of 5.94 and 13.8 kJ/mol, respectively, indicating the

TABLE 5: Solvent Parameters for CCl_4 and the Comparison of Its Experimental Correlation Times to Theoretical Predictions

T (K)	ρ^a (g/mL)	η^a (cP)	$k_T \times 10^{10a}$ (m^2/N)	τ_C (ps)	τ_C(SED)^b (ps)	τ_C(FS)^b (ps)	τ_C(HKW)^b (ps)	τ_C(GW)^b (ps)
288	1.60	1.05	10.01	2.01	22.5	0.34	8.15	3.69
303	1.58	0.85	11.27	1.72	17.3	0.26	6.26	2.84
318	1.55	0.70	12.71	1.49	13.6	0.20	4.92	2.23
333	1.52	0.59	14.32	1.31	10.9	0.16	3.95	1.79

[a] Solvent parameters were either obtain from CRC 71st edition or abstracted from the corresponding temperature relationships. [b] Friction coefficients used or averages generated via the models are $C(\text{SED}) = 1$, $C(\text{FS}) = 0.015$, $C(\text{HKW}) = 0.362$, and $C(\text{GW}) = 0.164$.

TABLE 6: Solvent Parameters for Chlorbenzene-d_5 and the Comparison of the Experimental Correlation Times for CCl_4 to Theoretical Predictions in This Solvent

T (K)	ρ^a (g/mL)	η^a (cP)	$k_T \times 10^{10a}$ (m^2/N)	τ_C (ps)	τ_C(SED)^b (ps)	τ_C(FS)^b (ps)	τ_C(HKW)^b (ps)	τ_C(GW)^b (ps)
288	1.11	0.90	7.21	1.30	19.2	0.38	6.51	3.03
303	1.10	0.72	7.88	1.13	14.6	0.29	4.95	2.31
318	1.08	0.61	8.61	1.02	11.8	0.23	4.00	1.86
333	1.06	0.52	9.43	0.90	9.60	0.19	3.25	1.52

[a] Solvent parameters were either obtain from CRC 71st edition or abstracted from the corresponding temperature relationships. [b] Friction coefficients used or averages generated via the models are $C(\text{SED}) = 1$, $C(\text{FS}) = 0.019$, $C(\text{HKW}) = 0.339$, and $C(\text{GW}) = 0.158$.

TABLE 7: Experimental and Predicted Correlation Times of C_{60} in Chlorbenzene-d_5

T (K)	ρ^a (g/mL)	η^a (cP)	$k_T \times 10^{10a}$ (m^2/N)	τ_C (ps)	τ_C(SED)^b (ps)	τ_C(FS)^c (ps)	τ_C(HKW)^d (ps)	τ_C(GW)^e (ps)
288	1.11	0.90	7.21	10.9	41.1	0.23	9.45	9.85
303	1.10	0.72	7.88	8.99	31.2	0.17	8.88	8.11
318	1.08	0.61	8.61	7.4	25.0	0.14	8.36	7.00
333	1.06	0.52	9.43	4.85	20.5	0.11	7.89	6.17

[a] Solvent parameters were either obtain from CRC 71st edition or abstracted from the corresponding temperature relationships. [b] Friction coefficient used via the SED model, C(SED), was unity. [c] The "free space model" coefficient, C(FS), had a value of 0.0055. [d] The coefficients generated via the HKW model, C(HKW), for C_{60} were found to range from 0.14 to 0.25 and τ_C(HKW) values listed reflect the free rotor contribution as explained in ref 13. [e] The Gierer–Wirtz coeffieciient, C(GW), had a value of 0.2 and τ_C(GW) values listed reflect the free rotor contribution as explained in ref 13.

reorientational barrier is more than twice as high for C_{60} in this solvent. Since the samples were prepared with common mole fractions and share identical solvent environments, it is highly unlikely the differences in the correlation times are due to bulk viscosity. A factor that can contribute to the differing correlation times in these molecules is their relative moments of inertia. In their study, Gillen and co-workers found the correlation times for CCl_4 to be in quantitative agreement with the extended J-difussion theory; a model which depends critically on a molecule's moment of inertia.[39] If we assume the disparity in the rotational times is caused solely by differences in the molecules' moments of inertia (i.e., only inertia effects), one would expect the correlation times to differ by approximately 2 orders of magnitude. However, we only found CCl_4 to be rotating approximately 9 times faster than C_{60}. Therefore, although inertial effects may contribute to the observed differences, it is highly unlikely its influence is the dominating factor. The observed variance is likely due to a balance between various factors. A plausible explanation for the observed diversity in the rotational motions of CCl_4 and C_{60} may be due to the changing solvent-to-probe molecular volume ratio (V_S/V_P) which has been found to affect rotational diffusion.[40] Generally, in the absence of strong solvent–solute interactions, the magnitude of the retarding reorientational force is enhanced with decreasing V_S/V_P ratio. In this scenario, the expected correlation times for CCl_4 in the neat ($V_S/V_P = 1$) would be longer than in CBZ ($V_S/V_P = 1.14$), consistent with our experimental observation. Similarly, in comparing the correlation times for CCl_4 and C_{60} in CBZ, one would expect the rotational times for C_{60} to be longer since the solvent-probe volume ratio here is 0.54.

We applied four commonly employed theories in an attempt at analyzing and supplementing our experimental results. These comparisons are discussed in the following section.

B. Comparisons with Theoretical Models. The first model applied to our data was the theory by Stokes, Einstein, and Debye which treats the rotational motion of a molecule as being similar to the motion of a sphere in a viscous environment. In this approach, as pointed out in the theory section, the shape parameter ϕ and C are set to unity (i.e., stick boundary condition) while τ_O is disregarded. Reorientational times calculated via this model, τ_C(SED), for CCl_4 in the neat and in CBZ are given on the sixth column of Tables 5 and 6. The model predictions for C_{60} are found in the sixth column of Table 7. The reorientational times calculated by this approach are seen to be significantly longer for both molecules, approximately an order of magnitude longer for CCl_4 and 4 times longer for C_{60}, than what is observed experimentally suggesting these molecules are experiencing far greater rotational freedom in this solvent (i.e., slip conditions) than this model predicts. On a positive note, one sees improvement in the predictions as the V_S/V_P ratio decreases.

The predictions via the Dote-Kevelson-Schwartz approach, "free space model", for both CCl_4 and C_{60} are shown on column 7 of Tables 5–7. Since hydrodynamic arguments project zero rotational friction for a sphere in the slip limit, we equated τ_{slip} to the experimentally obtained "free rotor" contribution, τ_O, in the calculation of θ in this model.[25] Probe and solvent volumes ($CCl_4 = 85$ Å^3, $C_{60} = 181$ Å^3, and CBZ = 97 Å^3), along with other solvent parameters given in these tables, were used to calculate the correlation times according to this model, τ_C (FS). As one can see from the tables, all τ_C (FS) values are significantly smaller than what is experimentally observed. The model also predicts that the correlation times for CCl_4 should remain relative constant or experience a very slight increase from the neat to being in CBZ. A more dramatic but opposite trend is however seen. Similarly, the model generates a contradictory trend when comparing the correlation times between CCl_4 and C_{60} in CBZ. Although this model incorporates both solvent and solute molecular volumes, as well as the concept of relative solvent free space, we found that this approach did not adequately duplicate solvent–solute structure and therefore did not generate reasonable predictions of our experimental findings.

Theoretical reorientational times via the HKW model, τ_C (HKW), are shown in column eight of Tables 5−7. The predictions for CCl_4, both in the neat and in CBZ, are all seen to be longer than expected. In C_{60}, the predictions are semiquantitative with experiment at the lower temperatures but gradually degrade with rising temperature. Although this theory generates predictions that are far from quantitative, qualitatively, it does correctly duplicate the observed trend in the reduction of the correlation times in going from neat CCl_4 to being in CBZ. It also successfully duplicates the experimentally observed increase in the correlation times in going from CCl_4 to C_{60} in CBZ. The partial success of this model suggests that collisional effects may indeed play a significant role in determining the rotational behavior of a probe molecule in a given solvent.

The last columns in Tables 5−8 contain the correlation times calculated via the Gierer−Wirtz approach, τ_C (GW). Noticeable improvement in correlation is seen as one compares these predictions to the experimental values. The model generates values that are slightly longer than experiment for CCl_4 but nearly quantitative for C_{60}. The model correctly predicts that correlation times should decrease as CCl_4 is placed in CBZ and that correlation times for C_{60} should be longer than CCl_4 in this same solvent. The calculated “sticking factors”, σ_{GW}, in this theory were found to be 0.013, 0.012, and 0.023 for neat CCl_4, CCl_4 in CBZ, and C_{60} in CBZ, respectively. The σ_{GW} values indicate decreasing solvent-probe “contact” will be found as CCl_4 is introduced into CBZ but should be higher between CBZ and C_{60}. The latter prediction suggesting that CBZ should exhibit strong interactions with C_{60} is congruent with earlier work by Reed and co-workers, who found CBZ had the ability to complex with C_{60} via π-stacking.[41] The improved agreement via this model suggests that the relative size of solute and solvent molecules, as well as events at the microscopic level, rather than bulk properties, are excellent descriptors of the factors affecting molecular rotation. Also of significance, and worth noting, is the model’s versatility and predictive improvement as the solvent-to-probe molecular volume ratio, V_S/V_P, decreases suggesting the model should have very broad applicability.

V. Conclusions

Our data indicate that both CCl_4 and C_{60} reorient in the small-step diffusion limit in chlorobenzene and at the temperature range used here. The correlation times of CCl_4 were found to be smaller in CBZ than in the neat and much shorter than would be expected by viscosity arguments. We believe the higher amount of “free volume”, or lower solute−solvent contact probability, in CBZ is the reason for the enhanced rotational freedom in this solvent. A comparison of the τ_C values for CCl_4 and C_{60} at equivalent temperatures in CBZ showed the motions to be much different than predicted by hydrodynamic arguments. Pure inertia differences did not explain the disparities in the correlation times. However, a very reasonable explanation for our experimental findings was found when we considered the solvent-to-probe molecular volume ratio and its effect on rotational diffusion. Theoretical predictions generated by the Stokes−Enstein−Debye and Dote−Kevelson−Schwartz models were found to be extremely poor. The model by Hynes−Kapral−Weinberg provided improved predictions but were however far from quantitative. The theory by Gierer−Wirtz was found to best duplicate our experimental observations. The success of this model suggests that the relative size of solute and solvent molecules, as well as events at the microscopic level, rather than bulk properties, are excellent descriptors of the factors affecting rotational diffusion.

Acknowledgment. The authors gratefully acknowledge the National Science Foundation for their support of this work.

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