

Orientational and Translational Dynamics of Polyether/Water Solutions

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Optical heterodyne-detected optical Kerr effect (OHD-OKE) experiments and pulsed field-gradient spin-echo NMR (PFGSE-NMR) experiments were performed to measure the rotational and translational diffusion constants of a polyether, tetraethylene glycol dimethyl ether (TEGDE), in binary mixtures with water over concentrations ranging from pure TEGDE to approaching infinite dilution. In addition, hydrodynamic calculations of the rotational and translational diffusion constants for several rigid TEGDE conformations in the neat liquid and in the infinitely dilute solution were performed to supplement the experimental data. The rotational relaxation data follow the Debye–Stokes–Einstein (DSE) equation within experimental error over the entire water concentration range. The agreement with the DSE equation indicates that there is no significant structural change of the polyether as the water content is changed. In contrast to the rotational dynamics, the translational diffusion data show a distinct deviation from Stokes–Einstein (SE) behavior. As the water content of the mixture is reduced, the translational diffusion rate decreases less rapidly than the increase in viscosity alone predicts until the water/TEGDE mole ratio of 7:1 is reached. Upon further reduction of water content, the translational diffusion tracks the viscosity. Comparison of the translational data with the rotational data and the hydrodynamic computations shows that the translational dynamics cannot be explained by a molecular shape change and that the low water fraction solutions are the ones that deviate from hydrodynamic behavior. A conjecture is presented as a possible explanation for the different behaviors of the rotational and translational dynamics.

I. Introduction

Polyethers are a large and chemically important class of compounds, with applications in many fields including biology, medicine, electrochemistry, and environmental chemistry. Particularly interesting is polyethylene oxide, or PEO, which has the molecular formula $\text{H}[\text{O}-\text{CH}_2-\text{CH}_2]_n-\text{OH}$, where n is the number of repeat units. PEO is readily soluble in water and in many organic solvents, while structurally similar polyethers, such as polymethylene oxide and polypropylene oxide, do not show this amphiphilic behavior.¹ As with many water-soluble polymer solutions, PEO exhibits phase separation at high temperatures, and at sufficiently high molecular weights, it shows closed-loop phase behavior.² In addition, PEO-based surfactants are more biodegradable than other alkylphenol-based solvents with similar solvency.³ Applications of PEO include polymer electrolyte membranes and gels,^{4–6} ion chromatography,⁷ macromolecule crystallization,⁸ and fuel cells.^{9,10} The abundance of applications of PEO, its unique physical properties, and its relatively low toxicity have made it the subject of intense study.

Most of the interesting physical properties of PEO solutions to a large extent depend on the polymer's interaction with water. Hydrogen bonding, polymer conformation, and hydrophobic interactions all play a role in the solvation of PEO. For large molecular weight PEO, the effects of the terminal alcohols become negligible, and the polyether's interaction with water

is dominated by the ether oxygens. A common method to model and investigate this interaction is to use glymes, short methyl-terminated oligomers which have the advantage of being infinitely miscible with water. The capping methyl groups remove the interactions of the hydroxyl groups with the solvating water, allowing investigation of the ether oxygen/water interactions. Without the terminal hydroxyl groups, the glymes are hydrogen bond acceptors but not donors. Despite their inability to donate a hydrogen bond, aqueous glyme mixtures display a maximum in their viscosity curve as a function of water composition,¹¹ a trend also seen in other hydrogen-bond-accepting liquids such as acetone¹² and DMSO.¹³

Many of the previous studies of water/polyether mixtures have focused on the molecular structure of the solution as a function of water content. Conformational studies using Raman,^{14–18} FT-IR,¹⁹ and NMR spectroscopies²⁰ and MD simulations^{3,21,22} suggest a peak in the trans-gauche-trans (TGT) population relative to the trans-trans-trans (TTT) population of the O–C–C–O bond sequence as the water fraction is changed. Smith, et al. have done extensive MD simulations on a 530 Da glyme, focusing on hydration, polymer conformation, hydrogen bonding, and water and polyether dynamics.^{21–25} Their results include evidence for significant intramolecular hydrogen bond bridging of the glyme, water clustering at high polymer concentration, and glyme conformational dynamics that depend on water fraction. However, apart from a few quasielastic neutron-scattering experiments,^{26,27} few dynamical measurements of polyether/water systems exist. Recently, the dynamics of the water portion of polyether/water mixtures have been studied using ultrafast IR polarization selective pump–probe experiments over a range of concentrations. The study found

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rapid orientational relaxation (~ 20 ps) of water in contact with the polyether and water pooling at low water content.²⁸

Here, we present a study on binary mixtures of water and tetraethylene glycol dimethyl ether (molecular formula $\text{CH}_3\text{--}[\text{O--CH}_2\text{--CH}_2]_4\text{--O--CH}_3$), also known as tetraglyme or TEGDE, over a range of mole ratios from neat TEGDE to approaching infinite dilution. The goal of this paper is to address the orientational and translational dynamics of the TEGDE molecule as a function of water content. Two experimental methods were employed. Optically heterodyne-detected optical Kerr effect (OHD-OKE) measurements were used to measure the rotational diffusion, and pulsed field-gradient spin-echo (PFGSE) NMR measurements were employed to determine the translational diffusion of the TEGDE molecule. In addition, hydrodynamic calculations of several rigid TEGDE conformations were performed and compared to the experimental results. While there have been many studies of simpler aqueous mixtures with hydrogen bond acceptors, such as DMSO,^{29,30} these studies do not address the issues of this paper, specifically, a hydrodynamic analysis and comparison of the rotational and translational diffusion constants.

TEGDE/water mixtures display a viscosity that is not monotonic with water concentration.¹¹ As TEGDE is added to pure water, the viscosity increases rapidly. The viscosity reaches a maximum when there are about seven water molecules per TEGDE molecule. Further increase in the TEGDE content of the mixtures results in a mild decrease in the viscosity. Despite the concentration dependence of the viscosity, the orientational relaxation appears to obey the Debye-Stokes-Einstein equation; that is, the orientational relaxation time is proportional to the viscosity, within experimental error, over the full range of viscosities. These results indicate that there is no substantial conformation change as water is added to TEGDE. Hydrodynamic calculations based on structures obtained from MD simulations^{31,32} give reasonably good agreement with the values for pure TEGDE and very dilute TEGDE. Therefore, the orientational relaxation is hydrodynamic in the sense that the orientational relaxation diffusion constant is inversely proportional to the friction, which is determined by the viscosity of the solution.

In contrast to the orientational relaxation, the translational diffusion is not hydrodynamic over the full concentration range of TEGDE/water mixtures. At high water content, as the TEGDE concentration is increased (and therefore the viscosity is increased), the translational diffusion constant does not decrease as much as would be consistent with hydrodynamic behavior. Consequently, the Stokes-Einstein equation is not obeyed. However, at sufficiently low water content, the translational diffusion constant becomes linear in the inverse of the viscosity, causing the dynamics to appear hydrodynamic. Despite the linearity of this region, the hydrodynamic calculations clearly identify the infinitely dilute solution as hydrodynamic and the low water content solutions as nonhydrodynamic. This deviation from hydrodynamic behavior cannot be explained by a change in molecular conformation because the magnitude of the change is inconsistent with the orientational data and is outside the bounds of the hydrodynamic calculations. A conjecture on the reason for the difference in the behavior of the orientational diffusion (hydrodynamic) and the translational diffusion (not hydrodynamic) is presented.

II. Experimental Procedures

TEGDE (99+%), D_2O (99.9% atom D), and H_2O (HPLC grade) were purchased from Sigma-Aldrich. Throughout the

course of data collection, several Karl Fisher titrations of TEGDE showed that the residual water content was insignificant for the measurements performed. For the OHD-OKE measurements, mixtures with $\text{H}_2\text{O}/\text{TEGDE}$ mole ratios (referred to as R_w) ranging from 300:1 to pure TEGDE were made. To minimize the effects of scattering due to dust, the mixtures were filtered through $0.1 \mu\text{m}$ filters. The neat TEGDE sample was vacuum distilled to remove impurities. All OHD-OKE samples were placed in 1 cm optical-grade cuvettes that were sealed to prevent evaporation. For the PFGSE-NMR measurements, mixtures with $\text{D}_2\text{O}/\text{TEGDE}$ mole ratios (also referred to as R_w) ranging from 100000:1 to pure TEGDE were made. To determine the dynamic viscosity for the $\text{D}_2\text{O}/\text{TEGDE}$ system, kinematic viscosity and density measurements were performed using a Cannon-Ubbelohde viscometer and volumetric flasks, respectively. The dynamic viscosity, η , can be calculated by the equation $\eta = \nu\rho$, where ν is the kinematic viscosity and ρ is the density of the solution. Since the viscosity measurements were done at 294 K, the results were scaled to 298 K, the temperature at which the OHD-OKE and PFGSE measurements were made. Literature values were available for the $\text{H}_2\text{O}/\text{TEGDE}$ dynamic viscosities.¹¹

The optical Kerr effect experiment is a coherent type of nonresonant pump-probe experiment in which a linearly polarized pump pulse induces a transient birefringence in an initially isotropic sample. A weaker probe pulse linearly polarized at 45° to the pump then interrogates the sample and emerges slightly elliptical due to the pump-induced birefringence. By delaying the time between pump and probe pulses and detecting the probe ellipticity via leakage through crossed polarizers, the decay of the birefringence can be measured as a function of time. To improve the signal-to-noise ratio, the signal is optically heterodyne-detected, and phase cycling is used. The probe is made slightly elliptical before entering the sample by a quarter-wave plate that has its fast axis rotated $\sim 3^\circ$ relative to the probe polarization. The purely homodyne contribution is rigorously removed by flipping the angle of the quarter-wave plate on successive scans (phase cycling) and subtracting the two.³³ The coherent heterodyne signal changes sign, but the homodyne signal and electrical pick-up noise do not. Therefore, subtraction adds the desired heterodyne signal and eliminates the other contributions. To reduce the effects of scattering and to further improve the signal-to-noise ratio, the pump and probe are optically chopped at $f/2$ and $f/4$, respectively, where f is the laser repetition rate, and the signal is detected through a lock-in amplifier.

The laser system used consists of a home-built Ti:Sapphire oscillator that seeds a home-built 5 kHz Ti:Sapphire regenerative amplifier (regen) pumped by a doubled Nd:YAG. The amplified pulses can then be compressed to ~ 55 fs fwhm with the spectrum centered at 800 nm. Because the OHD-OKE is a nonresonant technique, the pulses can be chirped without influencing the measured dynamics. Therefore, by varying the pulse compression, pulses with durations ranging from ~ 55 fs to ~ 125 ps fwhm can be used. For longer time measurements, the signal is increased by increasing the pulse duration and the average power. This makes possible measurements of the dynamics over decades of time, from hundreds of femtoseconds to tens of nanoseconds. For the $\text{H}_2\text{O}/\text{TEGDE}$ system, the dynamics are fast enough to use two ranges, ~ 55 fs pulses from 0 to 20 ps and ~ 2.5 ps pulses from 20 to 600 ps. Data were taken at 298 K and 1 atm over the course of several weeks, and select samples were remade and rerun to ensure reproducibility.

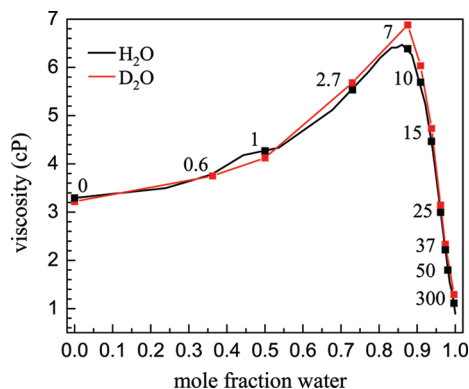


Figure 1. Viscosity of water/TEGDE solutions as a function of the mole fraction for H₂O (black) reproduced from McGee¹¹ and that for D₂O (red) measured in this study.

The scans for different time ranges were overlapped and combined in software to produce the full OHD-OKE decay curve.

PFGSE-NMR is a widely used technique³⁴ that utilizes magnetic three-pulse spin echoes and gradient magnetic field pulses to encode and then read spatial information of molecules. By applying identical magnetic gradient pulses during the dephasing and rephasing periods of the spin-echo sequence, the magnetization density vector is defocused and then refocused. However, due to molecular diffusion during the time between the gradient pulses, the magnetization density vector is not completely refocused by the second gradient pulse. As a result, the amplitude of the echo is reduced. By varying the gradient pulse field strength, the diffusion of the selected nuclide, and therefore the diffusion of the molecule under investigation, is measured. The measured signal is given by the Stejskal-Tanner equation

$$I = I_0 \exp(-\gamma^2 \delta^2 G^2 (\Delta - \delta/3) D) \quad (1)$$

where I_0 is the signal intensity at zero gradient strength, γ is the gyromagnetic ratio of the nuclide, δ is the gradient pulse length, G is the gradient strength, Δ is the delay between gradient pulses, and D is the diffusion coefficient.

Diffusion measurements of the ¹H and ¹³C nuclides were performed on a 600 MHz Varian Inova NMR spectrometer with a Varian triple resonance z -gradient probe and a Highland Technologies L700 pulsed field gradient driver, in a 14.4 T Oxford magnet. D₂O was used as the solvent instead of H₂O to provide a lock signal to correct for magnetic field drift. The strength of the pulsed field gradients was calibrated by measuring the diffusion of a water standard.³⁵ Measurements were made at 298 K and 1 atm over the course of several weeks, and select samples were remade and rerun, monitoring both ¹H and ¹³C nuclides to ensure reproducibility. The self-diffusion coefficient for the neat TEGDE was measured without D₂O lock. Literature values for the self-diffusion of neat TEGDE at 300 and 303 K are 3.1³⁶ and 3.2 × 10⁻⁶ cm²/s,³⁷ respectively. The value measured at 298 K in this study is 3.1 × 10⁻⁶ cm²/s, which is in good agreement with the previous measurements.

III. Results and Discussion

A. Orientational Relaxation. The viscosities of the binary mixtures as a function of water content (H₂O and D₂O) are shown in Figure 1. The points on the curves show the R_w 's at which the time-dependent experiments were conducted. The maximum in the viscosity corresponds to $R_w = \sim 7:1$. The substitution of D₂O for H₂O does not change the shape of

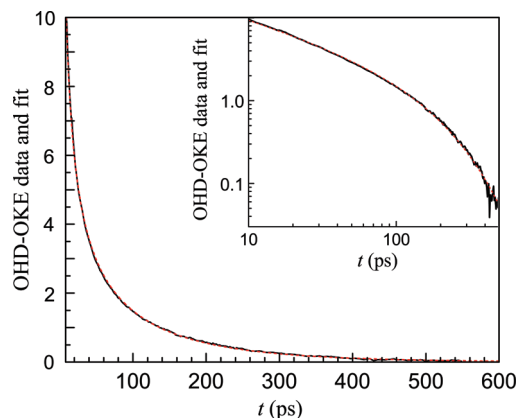


Figure 2. Typical OHD-OKE data (solid black curves) and fit to eq 2 (dashed red curves). The inset shows the same data on a log plot.

the curve but only increases the viscosities slightly. The peak in the viscosity is similar to that seen in other mixtures of liquids capable of forming hydrogen bonds with water, such as methanol/water and ethanol/water mixtures.³⁸

The orientational dynamics of the binary mixtures were measured by OHD-OKE over a range of concentrations, from neat TEGDE to $R_w = 300:1$, as indicated by the points in Figure 1. Figure 2 shows data for the neat TEGDE sample. The data for all of the different samples have the same characteristics. The main part of the figure shows a linear plot. The inset is a log plot. As can be seen from the inset, the data spans almost three decades of amplitude. The decay is nonexponential at short time.

The signal measured by the OHD-OKE experiment is the time derivative of the anisotropic component of the polarizability-polarizability correlation function. Except for times less than a few picoseconds when interaction-induced effects become important,^{39,40} the polarizability-polarizability correlation function is essentially the second Legendre polynomial orientational correlation function.^{39,41} Unlike the dipole-dipole correlation function in which both self- and pair-correlations are important, the long-time portion of the polarizability-polarizability correlation function is dominated by self-correlations.⁴² As has been shown previously, the complex OHD-OKE response of supercooled liquids, liquid crystals, and ionic liquids can display several power laws prior to the long-time exponential relaxation, which corresponds to complete orientational randomization.⁴³⁻⁴⁵ The data on supercooled liquids, liquid crystals, and ionic liquids can be well described using schematic mode coupling theory (MCT).⁴⁵⁻⁴⁷ MCT shows that the lead in to the exponential decay is a power law called the von Schweidler power law.⁴⁸ Here, we are only interested in the exponential portion of the data. However, to obtain an accurate exponential decay constant, it is necessary to account for the preceding power law. It was found previously that the von Schweidler power law and the final exponential decay can be fit with an empirical function

$$F(t) = (dt^{b-1}) \exp(-t/\tau_e) \quad (2)$$

where dt^{b-1} is the von Schweidler power law and $\exp(-t/\tau_e)$ is the complete structural relaxation of the liquid.⁴⁵ As with the other types of liquids that have been studied, there are additional power laws at very short times, but their consideration is not necessary to extract the exponential decay constants for the various water/TEGDE mixtures. Because the derivative of an exponential is, within a scaling factor, the same exponential, the time constant

TABLE 1: Orientational Relaxation Parameters^a

sample	mole fraction H ₂ O	viscosity, ^b η (cP)	τ_r (ps)
0:1	0	3.29	164
1:1	0.50	4.27	197
2.7:1	0.73	5.53	253
7:1	0.88	6.39	304
10:1	0.91	5.69	252
15:1	0.94	4.47	195
25:1	0.96	3.00	141
37:1	0.97	2.22	99
50:1	0.98	1.80	91
300:1	0.997	1.11	49

^a τ_r error bars: see Figure 3; η error bars: ± 0.05 cP. ^b From ref 26.

extracted from the OHD-OKE data using eq 2 is the exponential time constant of the orientational correlation function.

The data were fit with eq 2. As can be seen in Figure 2, the fit (red dashed curve) is very good over almost three decades of decay. The inset is a log plot of the data. The early time portion is the power law. The fits to all of the water/TEGDE mixtures are equally good. We interpret the data as describing the orientational relaxation of TEGDE. The OHD-OKE response of water is very weak, more than an order of magnitude weaker than TEGDE. In addition, the orientational relaxation time of water is 2.6 ps,⁴⁹ and water directly associated with TEGDE has an orientational relaxation time of 20 ps.²⁸ Because of the weak signal and the short decay times, water will make a negligible contribution to the OHD-OKE exponential decay portion of the data in which we are interested.

One of the most common ways to relate the orientational relaxation time τ_r to the shear viscosity and temperature is with the Debye–Stokes–Einstein (DSE) equation, which, for spheres, is given by

$$\tau_r = \frac{1}{6D_r} = \frac{4\pi\eta fr^3}{3kT} \quad (3)$$

where D_r is the rotational diffusion constant, η is the shear viscosity, r is the radius of the sphere, k is Boltzmann's constant, T is the absolute temperature, and f is the hydrodynamic boundary condition (BC) factor (stick, $f = 1$; slip, $f = 0$). Perrin⁵⁰ derived analytical expressions for the rotation of ellipsoids under stick conditions, and Hu and Zwanzig⁵¹ tabulated correction factors for ellipsoids under slip conditions. For ellipsoids, the $(4/3)\pi r^3$ factor in eq 3 is replaced by the molecular volume times a shape factor that is related to the ratio of the major and minor axes of the ellipsoid. For many systems, transient grating OHD-OKE^{39,52} and light scattering^{53–57} experiments have shown that the molecular reorientation time is well described by DSE for the slowest exponential relaxation.

Table 1 lists the viscosities (interpolated from McGee¹¹) and the TEGDE orientational relaxation times from the fits to the OHD-OKE data. The rotation times range from 49 ps for $R_w = 300:1$ to 304 ps for $R_w = 7:1$, which is the peak of the viscosity of the mixture. The neat TEGDE has a rotation time of 164 ps. Figure 3 displays the orientational relaxation decay times, τ_r (filled squares), versus the viscosity as well as a fit to a line. (The open red circles and the open red squares are the results of hydrodynamic calculations discussed in the next section.) The data are linear in the viscosity within experimental error. The results show that the orientational relaxation time depends solely on the viscosity of the mixture and demonstrates that no

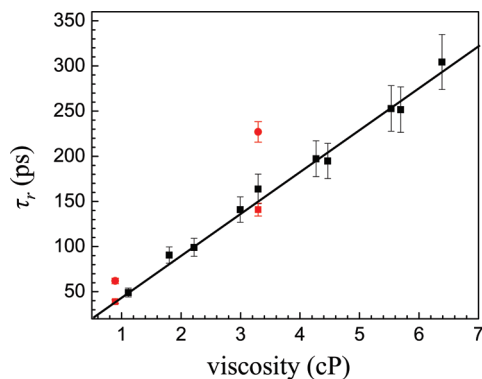


Figure 3. The TEGDE orientation relaxation data (filled squares) versus the viscosity of the water/TEGDE solutions. The line is a fit to the data. The linear behavior of the data shows that it obeys the DSE equation. Therefore, the TEGDE structure does not change with changing water mole fraction. The open red circles are the results of hydrodynamic calculations averaged over 22 typical structures taken from MD simulations of pure TEGDE.^{31,32} The open red squares are hydrodynamic calculations for the bent-TGT structure (see Figure 4).

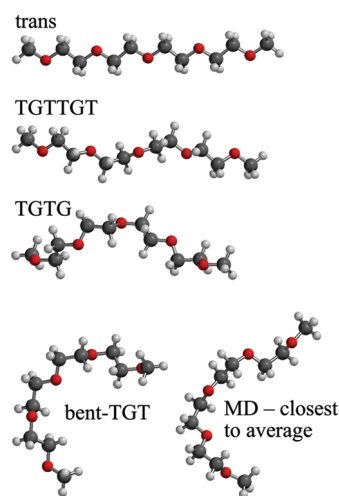


Figure 4. The structures used in the hydrodynamic calculations. The MD-closest to average is one of the MD simulation structures that gave an orientational relaxation time that was closest to the average over 22 structures.

significant structural or shape change occurs as the water content of the mixtures is changed. If the ratio of TTTT/TGT (T, trans; G, gauche) conformer populations changes as a function of water content, as has been suggested in the current literature,^{14–19} the changes cannot be substantial, or the data presented in Figure 3 would not obey the DSE relation. The extent of possible structural changes that might be accommodated by the data is discussed in the next section.

B. Hydrodynamic Calculations. Hydrodynamic calculations were performed on several rigid TEGDE conformations to calculate their orientational relaxation and to gain insights into the relationship between structure and the measured orientational relaxation times. Orientational relaxation measured in an OHD-OKE experiment at long times can be composed of up to five exponential decays whose time constants depend on the three eigenvalues of the rotational diffusion tensor. Wegener⁵⁸ has shown that the amplitudes of the relaxations depend additionally on the components of the polarizability tensor in the frame in which the rotational diffusion tensor is diagonal. These two tensors were computed via precise boundary element methods given for the molecular structures of TEGDE in dilute water

and in the neat liquid. The program POL⁵⁹ was used to compute the classical polarizability tensor for a dielectric constant of 2.054, which corresponds to the optical index of refraction¹¹ of 1.4332. POL solves the surface integral equation formulation of the electrostatic problem as given by Senior⁶⁰ using a surface triangulation of TEGDE produced by Connolly's⁶¹ program MSROLL. The polarizability tensor in the laboratory frame was obtained for a surface representation of TEGDE using 900 triangles for the determination of the relaxation amplitudes. While there are other ways to calculate the polarizability, such as Thole's method,⁶² the POL program takes into account molecular shape in a precise fashion. In addition, it requires the identical input file as the hydrodynamic property computation, allowing us to obtain the transport tensors and the polarizability tensor in the identical frame of reference.

The rotational diffusion tensor of TEGDE was computed with stick boundary conditions with the program BEST⁶³ for each of the structures and with slip boundary conditions⁶⁴ for two structures. BEST solves the surface integral equation formulation of the Stokes hydrodynamics as originally proposed by Youngren and Acrivos.⁶⁵ A series of triangulations of TEGDE structures were produced with MSROLL for the computation of the transport properties. For both the aqueous solution and the neat liquid, the probe size was set to 1.5 Å, the effective radius of a water molecule. The MSROLL radius of the TEGDE molecule is a bit larger, about 1.9 Å, but the hydrodynamic results are not sensitive to this value. In either case, to produce the largest possible value of the diffusion coefficients under stick boundary conditions, no solvation was applied. The diffusion coefficients were extrapolated versus $1/N$, where N is the number of triangles, to produce very accurate values of the rotational diffusion tensor.

The conformations used for the boundary element computations of diffusion and polarizability tensors were generated with the Spartan program (Wavefunction, Inc.). The structures generated were an all trans, a trans-gauche-trans (TGTTGT) of the OCCO bond sequence, an alternating TGTG, and a bent-TGT, in which the local OCCO conformation was TGT almost everywhere but was compacted by suitable bends along the chain. In addition, 22 structures were extracted from the molecular dynamics simulations of Wheeler^{31,32} et al. Hydrodynamic stick boundary condition calculations were run for each of them, and the dynamical properties were averaged over the set. The various structures are displayed in Figure 4, including one of the MD structures that has a reorientation time closest to the average of the 22 MD structures. The hydrodynamic computations assume that the rigid shapes form a suitable representation for the dynamical properties of an ensemble average of flexible molecules in dilute solution and in the neat liquid.

In addition, slip boundary condition calculations were carried out by Stuart Allison for the "average" MD structure and the bent-TGT structure by solving a slightly more general integral equation than BEST solves.⁶⁰ Under slip boundary conditions, the largest rotational diffusion tensor component, the "axial" rotation eigenvalue, is the one that increases the most compared to stick hydrodynamics. Thus, these calculations were used to make reasonable estimates for the stick to slip correction factors to be applied to all of the rest of the structures. The rotational and translational diffusion tensors were computed from the raw 6×6 rotation-translation friction tensor provided to us by Allison and transformed to the center of diffusion with the same general formulas used in BEST.

TABLE 2: Orientational Decay Times of TEGDE from Hydrodynamic Calculations^a

conformation	infinitely dilute τ (ps)		neat TEGDE τ (ps)	
	stick	slip	stick	slip
trans	226	119	829	438
TGTTGT	199	105	731	386
TGTG	155	82	570	301
bent-TGT	82	39	299	141
avg. 22 MD structures	106	62	388	227
experimental		49		164

^a Stick BC error bars: $\pm 1\%$; slip BC error bars: $\pm 5\%$.

As an example, the results of the computation of the polarizability and the slip hydrodynamics for the "average" MD structure shown in Figure 4 in the infinitely dilute case are that the orientational relaxation is described by five decaying exponentials with relative weights of 1.000, 0.4096, 0.003, 0.0564, and 0.0154. The values of the weighting constants show that only two of the five components have significant amplitude. When such a multiexponential decay is fit to a single exponential, the effective relaxation rate is well represented by an amplitude weighted average over the five different relaxation rates. The orientational relaxation rate (inverse of the decay time constant) is

$$g = (1/1.479)[(11.8397) + 0.0506(27.067) + 0.3574(27.047) + 0.0076(16.141) + 0.0633(15.173)] \times 10^9 \text{ s}^{-1} = 16.20 \times 10^9 \text{ s}^{-1}$$

which corresponds to a relaxation time of 62 ps for slip boundary conditions in pure water at 25 °C. The values in parentheses are the relaxation rate values (g_m) given in terms of the eigenvalues of the rotational diffusion tensor by Wegener.⁵⁸ For the most compact structures (bent-TGT, MD), the amplitudes of at least two of the five g_m values have significant contributions to the overall relaxation. For the more extended structures (trans, TGTTGT, TGTG), only one of the g_m values has a significant amplitude, and the structures essentially behave as cylinders with stick BC; this feature is not changed by slip BC. In such cases, the overall relaxation is effectively described by a single exponential. The computed values for all of the structures are given in Table 2 for the infinitely dilute water/TEGDE solution and for neat TEGDE under stick boundary conditions.

To obtain the orientational relaxation times for slip boundary conditions, we apply conversion factors to the results of the stick calculations. Slip hydrodynamic computations have been carried out for spheres,⁶⁶ ellipsoids,^{51,64} and tori.⁶⁴ We apply a conversion factor of 0.53 derived from the average of the two slip calculations that Allison provided for us. The slip results are almost a factor of two times faster than the stick reorientation relaxation rates. The orientational relaxation times for slip boundary conditions are reported in Table 2 beside the corresponding values for stick boundary conditions.

An important question is, What is the proper boundary condition for the solution of the Stokes equations of hydrodynamics for TEGDE systems? Stick boundary conditions, in which the velocity of the fluid matches the velocity of the immersed body at its boundary, are generally applicable for macromolecules in small solvents such as water.⁶⁷ For small molecules in apolar solvents, slip boundary conditions have been found to be appropriate.⁵³ Under slip boundary conditions, the fluid has a zero normal component at the boundary of the immersed body, while the tangential component is free. The

result is less friction than the stick boundary condition and thus larger diffusion coefficients.

In the case of neat TEGDE, one would expect slip boundary conditions since the molecule is small, relatively nonpolar, and cannot form hydrogen bonds. This is confirmed by comparison to the experimental data. The calculated orientational relaxation times for all of the structures under stick BC are too slow. The reasonably good agreement of the hydrodynamic calculated orientational relaxation time for the average of the MD structures under slip BC with the experimental data for the neat TEGDE clearly identifies the boundary condition as slip. The calculations for the infinitely dilute water solution under stick boundary conditions again produce results that are far too slow compared to the experimental result for all of the TEGDE structures including the average of the MD structures. Thus, the boundary condition for the infinitely dilute case is also slip.

The next step is to identify the structure which best reproduces the OHD-OKE data. The experimental values are 164 and 49 ps for the neat and dilute TEGDE, respectively. The trans, TGTTGT, and TGTG structures are all too slow for both concentration ends, indicating that the structures are too elongated. In contrast, the bent-TGT is slightly too fast and compact (141 and 39 ps), while the average of the MD structures is a bit too slow and extended (227 and 62 ps). Had we been able to do slip computations on all 22 MD structures to produce a true average, the result would probably be somewhere between the bent-TGT and average of the MD structures. The computed values for the bent-TGT and the average of the MD structures are shown in Figure 3 as the open red squares and open red circles, respectively. The relaxation times for the other structures (not shown in Figure 3) are far too slow. The important point is that there exists an average structure that reproduces the data for both pure TEGDE and TEGDE in very dilute solution without requiring a significant change in structure. Different structures produce very different orientational relaxation times. In addition, the experimental data are linear in viscosity, demonstrating that there are no significant structural changes in going from pure TEGDE to very dilute water/TEGDE mixtures. In both neat and very dilute TEGDE, the average TEGDE structure is a somewhat folded and bent conformation. If there is any structural variation with changing water content, it must be very minor. Finally, it should be noted that since the calculations can reproduce the OKE data well, the orientational motion is hydrodynamic; that is, the orientational motions are determined by the friction, which is proportional to the viscosity.

C. Translational Diffusion. Translational diffusion measurements were made on D₂O/TEGDE mixtures over the range of water content of $R_w = 0$ –100000:1. For the translational diffusion measurements, the 100000:1 is not infinitely dilute because of the long time scale of the measurement. The field gradient pulse delay is 132 ms, during which time the root-mean-squared distance a TEGDE molecule translates is $\sim 10 \mu\text{m}$. This corresponds roughly to 750 TEGDE–TEGDE collisions during the experiment if the molecules are randomly distributed.

A simple and common way to characterize translational diffusion data is the with Stokes–Einstein (SE) equation,⁶⁸ which, for a sphere, is given by

$$D_t = \frac{kT}{6\pi\eta fr} \quad (4)$$

where D_t is the translational diffusion constant, η is the shear viscosity, r is radius of the sphere, k is Boltzmann's constant,

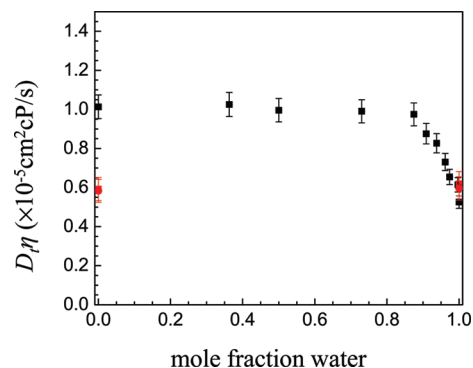


Figure 5. The TEGDE translational diffusion constant, D_t , times the viscosity, η , plotted versus the water mole fraction (filled squares). Hydrodynamic calculations for the average of 22 MD simulation structures of pure TEGDE (red open circles)^{31,32} and the bent-TGT structure (red open squares) (see Figure 4).

TABLE 3: Translational Diffusion Parameters^a

sample	mole fraction D ₂ O	viscosity, η (cP)	$D_t (\times 10^{-6} \text{ cm}^2/\text{s})$
0:1	0	3.22	3.1
0.6:1	0.36	3.75	2.7
1:1	0.50	4.12	2.4
2.7:1	0.73	5.68	1.7
7:1	0.88	6.88	1.4
10:1	0.91	6.04	1.5
15:1	0.94	4.73	1.7
25:1	0.96	3.15	2.3
37:1	0.97	2.34	2.8
300:1	0.997	1.29	4.7
100000:1	~ 1	1.095	4.8

^a D_t error bars: $\pm 6\%$; η error bars: $\pm 1\%$.

T is the absolute temperature, and f is the hydrodynamic boundary condition factor (stick, $f = 1$; slip, $f = 2/3$).⁶⁹

In contrast to the rotation data that are consistent with the DSE equation, the translation does not follow the behavior predicted by the SE equation over the entire concentration range, as can be seen by plotting the product ηD_t versus mole fraction D₂O. This plot is shown in Figure 5. The SE equation predicts that such a plot will yield a horizontal line. At low water content, the line is horizontal within experimental error. However, when the water content becomes substantial ($R_w = 7:1$), the data clearly deviate from the horizontal line. The experimentally determined translational diffusion constants versus the water/TEGDE ratio (R_w), the water mole fraction, and the viscosity are listed in Table 3. The viscosity maximum occurs for $R_w = 7:1$ (see Figure 1). At the viscosity maximum, TEGDE has a diffusion constant of $1.4 \times 10^{-6} \text{ cm}^2/\text{s}$. The neat and dilute liquids have diffusion constants of 3.1 and $4.8 \times 10^{-6} \text{ cm}^2/\text{s}$, respectively.

In physical terms, the sloping tail in the graph of Figure 5 in the water-rich region could mean that the translational dynamics of TEGDE in the water-rich mixtures are slower than what viscosity alone predicts, or, conversely, it could mean that the dynamics in the water-poor mixtures are faster than what the viscosity alone predicts. The first question then becomes, Which of the two concentration ends is the deviation from SE behavior? Looking at the horizontal trend in the dynamics of the water-poor mixtures, it might be tempting to assign the water-poor solutions as those in which SE behavior is seen and the water-rich as those which deviate, but this conclusion is not supported by the calculations, as shown below. The second question is, Is the deviation from SE behavior a deviation from hydrodynamic behavior? The Stokes–Einstein equation is only rigorously true

TABLE 4: Translational Diffusion Constants of TEGDE from Hydrodynamic Calculations^a

conformation	infinitely dilute D_t ($\times 10^{-6}$ cm ² /s, in D ₂ O)		neat TEGDE D_t ($\times 10^{-6}$ cm ² /s)	
	stick	slip	stick	slip
trans	3.94	4.82	1.31	1.60
TGTTGT	4.24	5.19	1.41	1.73
TGTG	4.33	5.30	1.41	1.73
bent-TGT	4.52	5.66	1.50	1.84
MD	4.45	5.44	1.48	1.81
experimental	4.8		3.1	

^a Stick BC error bars: $\pm 1\%$; slip BC error bars: $\pm 5\%$.

for spheres; therefore, it is conceivable that despite the non-SE behavior, the solutions are still behaving hydrodynamically. The final and deeper question is, What is happening in the solutions that causes the TEGDE translational dynamics to so drastically deviate from simply scaling with viscosity, be it a hydrodynamic or nonhydrodynamic effect?

As in the rotational case, to help address these questions, the average translational diffusion coefficient was computed with stick boundary conditions with the program BEST⁶³ for each of the 4 test structures and the 22 MD structures. Stick to slip conversions were estimated using a conversion factor of 1.22 obtained from the average value of the two slip to stick ratios (1.25 and 1.20) from the calculations of Allison for the bent-TGT and the “average” MD structure. For a body whose hydrodynamic surface is not smooth, the ratio should be less than the value of 1.5 for spheres, just as we have found.⁷⁰ The results are presented in Table 4.

For the translation, the agreement between calculation and experiment is not nearly as good as that in the rotational case. The calculations shown in Table 4 tell us that the translational diffusion coefficient is not as sensitive to shape as the rotation, and for the bent-TGT and the average of the MD structures, it is about 10% higher than that from experiments in pure water. This agreement is quite satisfactory even though the calculations have not taken any solvation into account. It is likely that in excess water, there is some solvation at the TEGDE oxygen atoms, and that would bring the calculated values in line with the measured values because the solvation increases the hydrodynamic surface area. Thus, the calculations tell us that the water-rich region follows hydrodynamic behavior. On the other hand, in the neat TEGDE region, the experimental diffusion coefficient is about 42% larger than the calculated slip value for the bent-TGT and average of the MD structures. The slip calculations do not have solvation and have an uncertainty of about 5%; these are the largest values that hydrodynamics can predict. Clearly, the region of low water content is not hydrodynamic. Thus, the translational diffusion in neat TEGDE occurs via dynamics that are not strictly that of friction with a solvent of other TEGDE molecules.

Better agreement for the neat TEGDE translation could be achieved by greatly compacting the structure, but the agreement would still be poor and would give an orientation time that completely disagrees with the rotational data, which is more sensitive to changes in shape. For the water-rich end, the all-trans conformation under slip BC gives the best agreement between experiment and calculation, but again, this structure is entropically unfavorable and produces calculated results that are in complete disagreement with the rotational decays. Alternatively, using stick BC slows down the translation and produces a calculated value for the MD structures or bent-TGT structure that is close to the measurement. However, using a

stick boundary condition is inconsistent with the results for the orientational relaxation. Thus, we conclude that the boundary condition is again slip, that the best structures are the “average” MD and the bent-TGT, and that the pure TEGDE does not behave hydrodynamically. It is important to emphasize that the behavior of the translational diffusion cannot be explained by the structure of TEGDE changing as the water content is reduced. Obtaining agreement with the translational diffusion data by changing the molecular structure produces very large disagreements with the orientational relaxation data. In addition, if one assumes that the translational data can be explained by a change in structure under slip BC, the structures required to reproduce the data are unphysical, ranging from a very compact structure in the neat liquid to an all-trans configuration in the dilute TEGDE solution.

Here, we would like to put forward a conjecture that can explain the deviation from hydrodynamic behavior in the translational data that is not present in the rotational data. Consider the pure TEGDE liquid. According to the MSROLL calculations, the volume of the various TEGDE structures ranges from about 210 to 230 Å³. These values only slightly depend on the probe size used. In contrast, a simple volume calculation of TEGDE based on the liquid density of 1.0047 g/mL corresponds to a volume of 366 Å³ for a TEGDE molecule. Thus, in the neat TEGDE liquid, there is a significant free volume of ~ 150 Å³; that is, $\sim 40\%$ of the volume of the liquid is empty space. This free volume can have different effects on the rotation than on the translation. In the rotational case, a void next to a TEGDE molecule does not necessarily allow a significantly faster molecular rotation because the fastest eigenvalue of the \mathbf{D}_r tensor, the “axial” rotation, needs very little volume to occur, especially under slip BC. This is important because the polarizability calculations used to calculate the hydrodynamic orientational correlation time for the bent-TGT and MD structures show that this axial component has significant amplitude relative to the slower eigenvalues of the \mathbf{D}_r tensor, the “longitudinal” rotation. Thus, an axial rotation will contribute significantly to the OKE signal. In contrast, the translational diffusion could be greatly enhanced by the free volume, especially for anisotropic molecules. In this case, the “transverse” diffusion would behave hydrodynamically since its motion is primarily governed by its frictional interactions with neighboring molecules. Its large cross section would prevent it from moving into adjacent voids easily. However, the longitudinal diffusion would behave less hydrodynamically since its cross section is much smaller, allowing the TEGDE to slip into an adjacent void. Under slip BC, this type of movement is ballistic and does not depend on friction. The diffusion measured in the NMR experiment is an average of the three eigenvalues of the translational diffusion tensor. As a result, the measured translational diffusion will have some of the anomalously fast longitudinal component mixed in and will not be fully hydrodynamic. In addition, coupling between the torsional degrees of freedom and translation can reduce the cross section in the direction of motion, further enhancing the effect of the voids.⁴²

The trend in Figure 5 can also be rationalized in terms of free volume. A water molecule is ~ 12 times smaller than a TEGDE molecule. As water is added to the system, these smaller water molecules should begin to fill in the voids in the liquid and cause the TEGDE translation to become more hydrodynamic. The plateau in Figure 5 from the neat TEGDE to the 7:1 solution might seem to contradict this interpretation, but there is evidence that at low water content, these solutions show significant water pooling or clustering in this range.^{23,28} There-

fore, the local environment of the majority of TEGDE molecules is not changing as water is added until the point is reached where the water clusters are broken up and the solution becomes homogeneous. This breakup point should occur somewhere before the volumes of the water and the TEGDE become equal at the mole ratio of 12:1. Thus, the downward trend from the 7:1 to the 100000:1 in Figure 5 supports this interpretation.

IV. Concluding Remarks

Optical heterodyne-detected optical Kerr effect measurements were performed to determine the rotational diffusion of tetraethylene glycol dimethyl ether in binary mixtures with H₂O over a wide range of concentrations from pure TEGDE to 300 water molecules per TEGDE molecule. Pulsed field-gradient spin-echo NMR measurements were used to determine the translational diffusion in D₂O/TEGDE binary mixtures over the concentration range from neat TEGDE to 100000 water molecules per TEGDE molecule.

Using viscosities from the literature,¹¹ the long-time exponential decays of the OHD-OKE data were evaluated in terms of the Debye–Stokes–Einstein equation. Throughout the entire concentration range, the rotational data show no departure from DSE dynamics within experimental error. This result demonstrates that there is no significant change in the structure of the TEGDE molecule in going from pure TEGDE to very dilute TEGDE. Detailed hydrodynamic calculations of TEGDE orientational relaxation were performed. A variety of structures were studied (see Figure 4). The calculations included the average orientational relaxation of 22 structures obtained from MD simulations of pure TEGDE.^{31,32} The average over the MD structures produced orientational relaxation times that are slightly slower than the experimental data. The bent-TGT structure (see Figure 4) gave calculated orientational relaxation times that are somewhat too fast. More extended structures gave calculated times that are significantly too slow (see Table 2). In all cases, slip boundary conditions were appropriate. The results indicate that the rotational diffusion behaves hydrodynamically and that a structure somewhere between the MD structures and the bent-TGT structure is a good representation of the TEGDE both in pure TEGDE and in very dilute water solutions.

The viscosities of the D₂O/TEGDE mixtures were measured, and the NMR translational diffusion values were evaluated in terms of the Stokes–Einstein equation. Unlike the rotational dynamics, the translation diffusion shows dynamics that deviate from hydrodynamic behavior. From pure TEGDE through a water mole fraction of ~ 0.9 ($R_w = 7:1$), the translational diffusion is linear in the solution viscosity. However, as additional water is added, the translational diffusion constant does not increase as much as it should to be consistent with the decrease in viscosity. Hydrodynamic calculations of the translational diffusion give reasonable agreement with the dilute TEGDE solution data but fail completely to reproduce the neat TEGDE data. The deviation from hydrodynamic behavior as water is removed from the system cannot be accounted for by a TEGDE shape that changes with water content. The change in shape that is required to reproduce the translational data is unphysical and produces orientational relaxation times that are far from the measured orientational data, substantially beyond any possible errors in the data. The anomalous translational diffusion can be qualitatively explained in terms of the free volume of the liquid. While the rotation under slip BC is relatively insensitive to the voids due to the polarizable axial rotation, the translation is much more sensitive, especially for

anisotropic molecules, in which the longitudinal component can move into the voids relatively easily. As water is added to the pure TEGDE, the water forms small clusters and does not uniformly fill the voids. Only around $R_w = 7:1$ does the fractional water volume become too large to cluster anymore, and the waters disperse more homogeneously into the liquid voids, causing the TEGDE translational diffusion to approach hydrodynamic behavior.

Acknowledgment. The authors thank Professor Hans Andersen, Professor Robert Pecora, and Emily Fenn, Stanford University, for very helpful discussions. We would also like to thank Professor Ralph Wheeler, University of Oklahoma, for supplying the MD simulation structural snapshots and Professor Stuart Allison, Georgia State University, for supplying the two sample slip friction tensor calculations. This work was supported by the National Science Foundation (DMR 0652232) and the Air Force Office of Scientific Research (F49620-01-1-0018).

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JP101369E