I. INTRODUCTION

Polyethers are an important class of polymers and are used extensively in many industrial, technical, and research applications. Often, the properties of the polyether are modified by the addition of a cosolvent, typically water. One particular polyether, poly(ethylene oxide) (PEO), has been studied over the past few decades with the goal of identifying how the presence of water affects the structure of the polymer in solution and why the mixture exhibits both lower and upper critical solution temperatures at sufficiently high molecular weights. Questions addressed include the following: Is the water/polyether interaction dominated by hydrogen bonding or is there a significant hydrophobic effect? How does the nature of the interaction affect the polyether backbone structure? Is their significant water-mediated polymer “cross-linking” via hydrogen bonds? How do these interactions change as a function of temperature or water content?

In attempts to answer such questions, most studies have focused on the static molecular structure of the polymer and/or water and have attributed certain experimental features to distinct polyether conformations or strong/weak water—polyether hydrogen bonds. For example, many Raman, FT-IR, NMR, and MD simulation studies provide evidence for a favoring of the trans—gauche—trans (TGT) of the $\text{O—C—C—O}$ bond sequence over the trans—trans—trans (TTT) configuration at high water content. Some have gone so far as to suggest that PEO in aqueous solution adopts a helical configuration. Dynamical data on the PEO/water system primarily consist of MD simulations by Smith et al. and some quasielastic neutron scattering, a host of dielectric spectroscopy experiments, and two ultrafast spectroscopic studies. In a recent paper, Sturlaugson et al. presented translational and rotational diffusion data of TEGDE, a methyl-capped PEO oligomer (molecular formula $\text{CH}_3\text{—[O—CH}_2\text{—CH}_2\text{]_4—O—CH}_3$), over the entire water concentration range and showed that there is little conformational change of TEGDE as the water fraction is changed. Instead, the trend in the dynamics can be explained qualitatively by the free volume of solution.

In this paper, we present the temperature-dependent rotational diffusion of dry TEGDE, as measured by optical heterodyne-detected optical Kerr effect (OHD-OKE) spectroscopy. Using the temperature-dependent translational diffusion data of Hayamizu et al., we compare the translational and rotational diffusion of TEGDE as a function of temperature to the dielectric data on the PEO/water system primarily consist of MD simulations by Smith et al., and agree quantitatively with hydrodynamic calculations. Of particular importance is the result that both types of data show nearly identical dependence on the viscosity divided by the temperature ($\eta/T$). We also compare the translational diffusion constants as previously measured by pulsed field gradient spin—echo (PFG-SE) NMR as a function of both temperature and water content. The temperature-dependent data follow the Stokes—Einstein (SE) equation. Similar to the rotation, the low water content mixtures obey the SE equation and show the same proportionality to $\eta/T$ as the temperature-dependent data. At higher water fractions, the data do not obey the SE equation. The principal results are that the influence of temperature on dry TEGDE orientational relaxation is the same as the influence of water content at fixed temperature, and that the influence of temperature on translational diffusion of dry TEGDE is the same as the influence of water content over a range of relatively low water concentrations. The results demonstrate that there are no large TEGDE structural changes or specific, long-lived water—polyether interactions in the solutions over the entire concentration range.
II. EXPERIMENTAL PROCEDURES

TEGDE (99 + %) was purchased from Sigma-Aldrich and vacuum distilled to remove impurities. Water content after distillation was measured by Karl Fisher titration to be 700 ppm. Temperature-dependent optical heterodyne-detected optical Kerr effect (OHD-OKE) data of TEGDE were taken using a custom-built aluminum sample holder with fused silica windows which was housed in a Janis Research cryostat. The temperature ranged from 300 to 350 K in 5 K increments and was stable to within ±0.1 K. Temperature-dependent translational diffusion data were obtained from the pulsed field gradient spin−echo (PFGSE) NMR work of Hayamizu and viscrosities were interpolated from the data of Conesa. The water/TEGDE sample preparation and data collection are described elsewhere.

The temperature-dependent rotational diffusion of TEGDE was measured by OHD-OKE. The optical Kerr experiment is a nonresonant pump−probe experiment in which a linearly polarized pump pulse induces a net birefringence in the sample through two mechanisms. Relatively long pump pulses generate a reorienting torque on the molecules due to their anisotropic polarizability. Short pulses, which have a larger laser bandwidth, excite an anisotropic distribution of librations in the sample through stimulated Raman scattering. In either case, the pump-induced birefringence in the sample decays through the molecular motions of the fluid and can later be probed by another weaker, linearly polarized probe pulse. Optical heterodyne detection is incorporated into the experiment by making the probe slightly elliptically polarized with a quarter wave plate immediately before the sample. In the experiments, the pump and probe pulses (centered at 800 nm) were produced in a 5 kHz Ti:sapphire regen that was seeded by a mode-locked Ti:sapphire oscillator and pumped by an Nd:YAG laser. The details of the OKE experimental setup are described elsewhere. Because the OKE experiment is nonresonant, the laser pulses can be chirped without affecting the measured dynamics. Since in this study we were only interested in the long-time exponential tail of the OKE decay, partially chirped pulses (∼ 2.5 ps full width at half-maximum) were used to measure the dynamics from ∼ 5 to 450 ps.

III. RESULTS

A. Orientational Dynamics. The signal measured in the optical Kerr effect experiment is the time derivative of the anisotropic polarizability−polarizability correlation function. At very short times (less than a few picoseconds), interaction-induced effects contribute to the OKE signal, but at longer times they become negligible and the polarizability−polarizability correlation function is essentially the second Legendre polynomial collective orientational correlation function. Keyes and Kivelson showed that the measured collective correlation time, τc, can be related to the single-particle correlation time, τ, by

\[ \tau_c = \frac{g_2 \tau}{j_2} \]  

where \( g_2 \) is the static orientational correlation factor and \( j_2 \) is the dynamic orientational correlation factor. For liquids with a relatively large reduced free volume (> 0.5), it has been found that \( g_2 \approx 1 \). TEGDE has a reduced free volume of ∼ 0.66. It is also often assumed that \( j_2 \approx 1 \), which is true for acetonitrile, chloroform, carbon disulfide, and benzene. Thus, for the time scale of interest in this paper, we interpret the OKE data as representing the single-particle second Legendre polynomial orientational correlation function.

Figure 1 displays one of the OHD-OKE decays taken at 310 K (red curve) with a fit to the data (dashed black curve). The inset shows the same data set and fit on a log plot so that the full range of the data and fit can be seen more clearly. The data at all temperatures have a similar appearance. The early portion of the data is a power law which merges into an exponential decay. The slope of the power law is, within experimental error, temperature independent while the exponential decay is highly temperature dependent. In many other liquids a second (and sometimes third) power law is seen at very short times. Here such power laws are obscured by the relatively fast dynamics of the liquid (hundreds of picoseconds) and the relatively long (∼ 2.5 ps) laser pulse used to improve the quality of the data at longer times. Overall, these trends for TEGDE are very similar to the dynamics seen in the OHD-OKE response of many other liquids and can be described well in terms of ideal schematic mode coupling theory (MCT). The power law leading into the exponential relaxation is called the von Schweidler power law, and the exponential corresponds to the final structural relaxation of the liquid, i.e., rotational diffusion.

Since we are only interested in the rotational diffusion component, we fit the OKE data to the function

\[ F(t) = (dt) \exp (-t/\tau) \]  

Here, \( dt \) is the von Schweidler power law and \( \exp (-t/\tau) \) is the rotational diffusion decay. The fits using this function are the dashed black curves in Figure 1. The quality of the data and fits at all temperatures is the same as that shown in Figure 1. The inclusion of the power law in the fitting function is essential to extract the correct rotational diffusion time. Since the derivative of an exponential is the same exponential (within a scaling factor), the decay time extracted using the fitting function is the decay time of the single-particle orientational correlation function. As shown in Figure 1, the fits to the data using eq 2 are excellent.

The orientational diffusion time can be related to macroscopic properties via the Debye−Stokes−Einstein equation, which for a sphere in a fluid of viscosity \( \eta \) is

\[ \tau = \frac{1}{6D_0} = \frac{4\pi\eta r^3}{3kT} \]  

Here \( D_0 \) is the rotational diffusion constant, \( f_0 \) is the shape-dependent rotational hydrodynamic boundary condition (BC)
Table 1. Temperature-Dependent DSE Parameters

<table>
<thead>
<tr>
<th>temp, T (K)</th>
<th>τ (ps)</th>
<th>viscosity, η (cP)</th>
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</thead>
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<tr>
<td>300</td>
<td>160</td>
<td>3.16</td>
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<td>305</td>
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<td>1.51</td>
</tr>
<tr>
<td>350</td>
<td>61</td>
<td>1.43</td>
</tr>
</tbody>
</table>

a T error bars, ±0.1 K; τ error bars, ±10%; η error bars, ±1%

Table 2. Temperature-Dependent SE Parameters

<table>
<thead>
<tr>
<th>temp, T (K)</th>
<th>Ds ( \times 10^{-10} ) m²/s</th>
<th>viscosity, η (cP)</th>
</tr>
</thead>
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<tr>
<td>303.14</td>
<td>3.24</td>
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<tr>
<td>353.14</td>
<td>7.90</td>
<td>1.37</td>
</tr>
</tbody>
</table>

a T and \( D_s \) error bars not reported; η error bars, ±1% b Interpolated from ref 29.

The top line in Table 2 is for the average of a large number of structures determined by MD simulations.28 The bottom dashed line is a structure that is similar to the average of the MD simulation structures is small, Figure 2 also demonstrates that the orientational correlation time is very sensitive to the size and shape of the rotating species. Thus, the linearity in the OKE data indicates that there is no significant structural change of TEGDE as water is added or as the temperature is changed. The interesting feature is that both data sets show essentially the same proportionality to \( η/T \) within experimental error. This is rather surprising, considering that adding water to and raising the temperature of TEGDE are very different perturbations. One would expect that if specific water—TEGDE interactions were present and responsible for the change in viscosity (see below), the addition of water to the system would show very different dynamics (as embodied in the DSE equation) compared to a change in temperature.

B. Translational Dynamics. In addition to the rotational data from the OHD-OKE experiments, here we also compare the translational dynamics as measured by PFGSE-NMR. The temperature-dependent data were obtained from Hayamizu and are reproduced in Table 2.28 The hydration-dependent data were measured in this laboratory previously.26 Similar to the DSE equation, the Stokes–Einstein (SE) equation describes the translational diffusion of a sphere in a fluid of viscosity \( η \):

\[
\frac{1}{D_t} = \frac{6πηf_t r}{kT}
\]  (4)

Here \( D_t \) is the translational diffusion constant and \( f_t \) is a shape-dependent translational hydrodynamic boundary condition factor (for spheres, \( f_t = 1 \); for bent-TGT \( f_t = 2/3 \)). The other symbols are the same as above. Again, there are formulas and tables of \( f_t \) for other symmetric shapes under stick and slip boundary conditions.26,52
The numbers correspond to the D$_2$O:TEGDE mole ratio for each point. The black line is a guide to the eye.

Figure 3. Viscosity curve of the D$_2$O/TEGDE solutions measured in ref 26. The numbers correspond to the D$_2$O:TEGDE mole ratio for each point. The black line is a guide to the eye.

Figure 4. Inverse translational diffusion constants as a function of temperature (black squares) and hydration (red circles) for TEGDE plotted vs η/T. The black lines represent hydrodynamic calculations for the MD (top line) and bent-TGT (bottom line) structures from ref 26. The dilute TEGDE point is 100 000 D$_2$O molecules per TEGDE.

The trend in the low-water-content solutions (Figure 4) is strikingly similar to that seen in the rotational data (Figure 2). In this concentration regime, the inverse of the translational diffusion constant is proportional to η/T and both the temperature- and hydration-dependent data have the same linear relationship (dashed line, Figure 4), within experimental error.

IV. DISCUSSION

In the experiments performed here, the viscosity of the TEGDE sample is changed two ways. The temperature of dry TEGDE is changed, or, at fixed temperature, the water concentration is changed. The orientational diffusion (Figure 2) and the translational diffusion (Figure 4) have been measured either here or previously$^{26,28}$ for both the temperature change and the water content change. Over the full range of viscosities, the orientational relaxation times (1/6$D_\square$) track η/T in accord with the Debye−Stokes−Einstein equation. The points fall on the same line within experimental error regardless of whether the temperature or the water content is changed. The translation (1/$D_\parallel$) tracks η/T in accord with the Stokes−Einstein equation over the temperature range that has been measured.$^{26,28}$ The translation also follows SE behavior when water is added to pure TEGDE up to the viscosity maximum (see Figure 3). These temperature- and water-dependent translational values fall on the same line. For water contents greater than that which gives the viscosity maximum, the translational values no longer fall on the SE line. This behavior has been discussed in detail previously.$^{26}$

There are many theories of molecular diffusion, which generally focus on kinetic, collisional effects,$^{53−56}$ collective, hydrodynamic effects,$^{44,51}$ or a combination of both.$^{57,58}$ It has been well documented that, for molecular liquids, hydrodynamic calculations with the slip BC reproduce the experimental diffusion constants well.$^{59}$ The stick BC becomes appropriate for very large solutes, while subslip BC values are generally seen for solutes smaller than the solvent molecules.$^{60−63}$ Thus, for the purposes of this study, the simple slip BC hydrodynamic treatment embodied in the DSE and SE equations is reasonable since the solute (TEGDE) ranges from ~12 times larger than the solvent (for dilute TEGDE) to equal size as the solvent (for pure TEGDE). In addition, the hydrodynamic calculations take into account the average TEGDE shape. Other diffusion theories have only been developed for highly symmetric molecules and are not sufficient to describe the diffusion of the highly asymmetric TEGDE molecule.

It has been suggested that the change in viscosity from that of pure TEGDE upon addition of water arises from specific TEGDE−water
interactions. Water might change the structure of TEGDE by intramolecular hydrogen bonding to ether oxygens giving rise to new structures, such as helices, as the water content increases. Another possibility is that water forms intermolecular hydrogen bonds and effectively forms cross-links between different TEGDE molecules that last for a significant length of time. However, when the temperature of pure TEGDE is changed, these types of structural changes will not occur. Increasing the temperature from 300 to 350 K will very mildly change the thermal equilibrium distribution of structures but not in the same manner as the proposed specific TEGDE—water interactions would. Thus, the results presented here provide strong evidence against a specific TEGDE—water interactions that produce well-defined structural changes as the water content increases.

The question is why does changing the temperature and changing the water content produce the same dynamics for the same viscosity? For pure TEGDE, as the temperature is lowered the density increases, the viscosity increases, and the orientational and the translational dynamics slow down, as is consistent with free volume theories of viscosity. As the temperature is lowered, the free volume decreases. For pure TEGDE at fixed temperature, as water is added, the viscosity increases (see Figure 3). As argued above, the concurrence of the temperature-dependent and water-dependent changes in the rotational and translational dynamics are not in accord with specific TEGDE conformational changes upon water addition. One very qualitative explanation for the increase in viscosity with the addition of water that would give rise to the observed concurrence of the dynamical observables is that water simply changes the free volume. As the small water molecules are added to TEGDE, their primary effect is to reduce the free volume available to the much larger TEGDE molecules. The results indicate that the reduction in free volume caused by the addition of water changes the viscosity in the same manner as the reduction in free volume caused by a decrease in temperature. In this picture, the consistent changes in the rotational and translational dynamics are therefore accounted for. For high water content, the viscosity drops because the system is TEGDE in water rather than water in TEGDE. A TEGDE molecule is more or less surrounded by water, and the primary effect of adding more water is dilution rather than reducing free volume, which would occur at very low water content.

V. CONCLUDING REMARKS

In this study, we measure the optical heterodyne-detected optical Kerr effect signal of tetraethylene glycol dimethyl ether (TEGDE) as a function of temperature from 300 to 350 K and extract the rotational diffusion constant. A comparison with our previous hydration-dependent data using the Debye—Stokes—Einstein relation shows that there is no significant structural change of TEGDE in either system in the range of conditions studied. Also, the trends in the dynamics obtained by changing the viscosity with temperature or water content are the same within experimental error, suggesting that there are no specific water—polyether interactions responsible for the measured dynamics. In addition to the rotational data, we compare Hayamizu’s temperature-dependent translational diffusion constants to previously measured hydration-dependent values via the Stokes—Einstein equation. Similar to the rotational case, the trend in translational dynamics is the same for the temperature-dependent data and the low water fraction solutions. Although the specific mechanism that explains both the rotational and translational data is still not clearly understood, the combined analysis of both temperature- and hydration-dependent data sets shows that the experimental trends in the water/TEGDE solutions cannot be explained by a change in TEGDE structure or by specific, long-lived water—polyether interactions such as water-mediated polyether cross-linking or “folding.” We suggest the qualitative mechanism that addition of water to pure TEGDE reduces the free volume and therefore increases the viscosity, in a manner akin to the reduction of free volume and increase in viscosity that accompanies a decrease in temperature. Having the same free volume mechanism for both methods of changing the viscosity would account for the consistency of the observed trends in orientational and translational dynamics.

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Acknowledgment

The authors thank Professor Kikuko Hayamizu, National Institute of Advanced Industrial Science and Technology, Japan, for providing us with the temperature-dependent translational diffusion values. 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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