Molecular Dynamics Simulation of 1,2-Dimethoxyethane/Water Solutions. 2. Dynamical Properties

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We have performed molecular dynamics simulations of 1,2-dimethoxyethane (DME)/water solutions at 318 K in order to examine conformational, translational, and rotational dynamics of the solutions as a function of composition. The rate of conformational transitions for the C−O—C−C and the O−C—C−O dihedrals in DME decreases with increasing water content for mole fraction $X_{DME} \geq 0.18$. For more dilute solutions, the conformational transition rate is independent of composition. Self-diffusion coefficients of DME and water for $X_{DME} \geq 0.18$ indicate that the dynamics of DME and water comprising the first coordination shell of DME are highly correlated. We found that the average residence time of water in the first coordination shell was only about 2 ps and was not significantly longer for water that is hydrogen bound to the DME. For more dilute solutions, the additional water manifests the dynamical characteristics of bulk water. The rotational diffusion coefficient for DME shows qualitatively similar dependence on solution composition to that seen for the DME center-of-mass diffusion. We found that water comprising the first coordination shell of DME showed significantly reduced rotational dynamics compared to those of free water, which closely resembles bulk water.

I. Introduction

To gain a better understanding of the important role played by hydration, including hydrogen bonding, in determining the dynamical properties of both water and solutes in aqueous solution, we have investigated the dynamical properties of solutions of 1,2-dimethoxyethane (DME) via molecular dynamics simulations. In our previous work[1] we developed an atomistic description of DME/water interactions. This atomistic force field was parametrized to reproduce the geometries and energies of DME/water clusters determined from high-level ab initio calculations, while employing an earlier quantum chemistry based force field for DME[2] and the TIP4P (four-point transferable intermolecular potential) model for water.[3] Using this force field, we performed molecular dynamics simulations of DME in aqueous solution as a function of solution composition. Thermodynamic properties of the solutions were found to be in excellent agreement with experiment.[1] The conformational and structural properties of DME/water solutions as a function of concentration and temperature from molecular dynamics simulations were also investigated.[4]

In this paper we discuss the conformational, translational and rotational dynamics of DME/water solutions as a function of composition obtained from molecular dynamic simulation. We also briefly review previous experimental and simulation studies of the dynamics of related systems. Solution viscosity as a function of composition from simulations was reported earlier[1] and compared with experiment, and hence will not be further considered in this work.

II. Previous Studies and Simulation Methodology

Experiments. There is a paucity of reported experimental data on dynamical properties of DME/water solutions. Two studies[5,6] of the viscosity of DME/water systems give consistent data in the whole range of compositions for a temperature range of 298−318 K. It was observed that a maximum in the viscosity occurred at about $X_{DME} \approx 0.20$. The appearance of a well-defined maximum in the viscosity was explained by the supposition that some clusters or aggregates form in the system. Our simulations[1] yielded a maximum in viscosity at approximately the same composition. An ultrasonic study of DME aqueous solutions[7] also showed a maximum in ultrasonic absorption at $X_{DME} \approx 0.2$. An ^{17}O NMR study has been performed on dilute DME/water solutions.[8] The authors found that the rotational dynamics of water slowed with increasing DME content. They assigned four "bound" waters to each DME molecule, and assuming that unbound water maintained bulk dynamics, found a decrease in the rotational diffusion coefficient of bound water by a factor of 4.

Three other works report on the dynamic properties of similar systems relevant to our investigation of DME/water. Pulsed gradient spin−echo NMR measurements[9] of self-diffusion coefficients for binary systems containing water and oligomers of ethylene glycol were reported for the whole range of compositions at temperature $T = 298$ K. The discussion of these results and comparison with our simulations are given below. The dielectric relaxation behavior of aqueous solutions of ethylene glycol oligomers has also been investigated.[10] The authors found that the dependence of the dielectric relaxation time as a function of composition is consistent with the presence of bulklike water up to a concentration of $X_{monomer} = 0.35$ (equivalent to $X_{DME} = 0.21$). Poly(ethylene oxide) (PEO)/water dynamics were investigated in a quasielastic neutron-scattering study (QENS)[11] of long PEO chains in aqueous solution. The measurements were interpreted in terms of at least two kinds of water molecules from dynamic point of view: "perturbed" and "unperturbed". Fitting the experimental QENS spectra by various models resulted in semiquantitative values of the
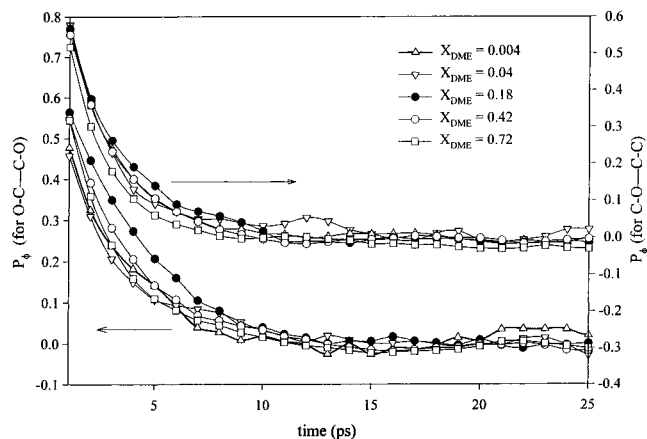
Figure 1. Torsional angle autocorrelation functions for the O−C⎯C−O (left *Y*-axis) and the C−O⎯C−C (right *Y*-axis) dihedrals as a function of solution composition.

diffusion coefficients for the proposed kinds of water molecules and the rate of intermediate exchange.

Previous Simulations. Two simulation studies, which discuss the dynamics of PEO/water system, were recently reported. A molecular dynamics study[12] of a single PEO chain with 15 ethylene oxide units in aqueous solution found that the average residence time of water molecules in the first coordination shell of ether oxygen atoms (closer than 3.5 Å) is about 25 ps. This time is about 3 times greater than the residence time estimated from QENS measurements[11] and reflects overestimation of PEO/water interactions. A Langevin dynamics simulation[13] of a PEO/water solution with different friction coefficients allowed the authors to calculate the torsional angle autocorrelation functions and estimate the transition rates between trans and gauche conformations.

Molecular Dynamics Simulation Force Field and Methodology. A detailed description of the atomistic force field for the DME (PEO)/water systems is given in ref 1. In this work we perform simulations using the constant temperature/pressure methods[14] implemented as described elsewhere.[15] Seven DME/water systems with mole fraction of DME X_{DME} = 0.004, 0.040, 0.100, 0.180, 0.420, 0.720, and 0.900 were investigated. Simulations were performed at T = 318 K and an average pressure about 1 atm. Periodic boundary conditions were employed. The standard Shake algorithm[16] was used to constrain the bond length, while all other degrees of freedom remained flexible. The Ewald summation method[17] was employed to handle long-range electrostatic interactions. The initial systems, consisting of DME and water molecules in a regular array with a greatly reduced density, were equilibrated for 0.1 ns. The density was increased over 0.5 ns until the pressure reached 1 atm. Each system was then equilibrated over 2 ns. Sampling for each system occurred over 0.8−to 3.0 ns (depending on composition) with a time step of 1.0 fs. Each system contained about 1300 atoms and all systems, except X_{DME} = 0.004, contained at least 10 DME molecules.

III. Conformational Transitions Rates

Figure 1 shows the torsional angle autocorrelation function $P_\phi(t)$ given by

$$P_\phi(t) = \frac{\langle \cos \phi(t) \cos \phi(0) \rangle - \langle \cos \phi(0) \rangle^2}{\langle \cos^2 \phi(0) \rangle - \langle \cos \phi(0) \rangle^2} \quad (1)$$

where ϕ is the dihedral angle of either a C−O⎯C−C bond or

a O−C⎯C−O bond at time *t* or time 0. We found that $P_\phi(t)$ could be well represented by the Kohlraush−Williams−Watts (KWW) equation[18]

$$P_\phi(t) = \exp[-(t/\tau)^\beta] \quad (2)$$

The KWW parameters and the torsional correlation times τ_c for each composition are given in Table 1. The latter were determined from the integral of $P_\phi(t)$, given by eq 2, with respect to time. The correlation times show a maximum at X_{DME} = 0.18, behavior consistent with that seen experimentally in dynamical properties of DME/water solutions.[5,6,7,10]

Included in Table 1 is the concentration dependence of the torsional residence time, which is a measure of how long a dihedral remains in a given conformational state before undergoing a transition to another state. Also shown are the average transition rates (N_{trans}) for the C−O⎯C−C and O−C⎯C−O bonds. Here, we determined the state of the dihedral every picosecond, and if the state differed from that of the previous sampling, the dihedral was considered to have undergone a transition. For the C−O⎯C−C bond the average time in the *t* state is much greater than that for the *g* state and is strongly composition dependent. In contrast, the *g* residence time for the C−O⎯C−C bond is nearly independent of composition. For the O−C⎯C−O bond we can see that the *g* state residence time is much greater than that for the *t* state, and shows strong composition dependence, while the *t* state residence time is nearly independent of composition. The relatively large and increasing (with increasing dilution) *t* residence time for the C−O⎯C−C bond and *g* residence time for the O−C⎯C−O bond are consistent with the large DME tgt population, which increases with dilution. The fact that the C−O⎯C−C bond *g* state and O−C⎯C−O bond *t* state residence times are independent of composition implies that water has little influence on the difference in energy between these states and their barriers for g_t and t_g transitions, respectively. The increase in the C−O⎯C−C *t* state and O−C⎯C−O *g* state populations with increasing water content indicate a stabilization of these states by water.[4] This stabilization results in an increase in the t_g rotational energy barrier for the C−O⎯C−C bond and the g_t barrier for the O−C⎯C−O bond, consistent with the decrease in average transition rates for these bonds with increasing water content.

IV. Translational Dynamics

Self-Diffusion. The self-diffusion coefficients of DME and water were calculated using Einstein relation[17]

$$D = \frac{\langle |r_i(t) - r_i(0)|^2 \rangle}{6t} \quad (3)$$

where r_i is the position of molecule center of mass at time 0 and *t*. The concentration dependence of the self-diffusion coefficients is shown in Figure 2. It can be observed that the self-diffusion of water dramatically drops with increasing DME concentration, reaching a minimum at $X_{DME} \approx 0.20$. The water self-diffusion coefficient then increases monotonically with increasing DME concentration, showing only weak concentration dependence. The changes in the DME self-diffusion coefficient with composition are less dramatic but qualitatively demonstrate the same features. There is a shallow minimum in the DME self-diffusion coefficient in the range X_{DME} = 0.1−0.2 and an almost linear increase for compositions X_{DME} > 0.2. It is worth noting that for X_{DME} > 0.2 the composition

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TABLE 1: Torsional Dynamics Characteristics for C−O―C−C and O−C―C−O Dihedrals as a Function of Composition

| X_{DME}	τ^a	β	$\tau_c{}^a$	$N_{trans}{}^b$	time^c in t	time^c in g	τ^a	β	$\tau_c{}^a$	$N_{trans}{}^b$	time^c in t	time^c in g
			C−O―C−C						O−C―C−O			
0.004	1.93	0.85	2.10	107	16.3	2.5	1.67	0.72	2.07	41	2.9	44.7
0.04	1.94	0.88	2.07	110	14.8	2.6	1.52	0.65	2.06	39	3.3	42.5
0.18	2.07	0.84	2.27	119	13.7	2.6	2.55	0.78	2.94	48	3.4	34.3
0.42	1.90	0.88	2.02	142	11.1	2.7	2.11	0.80	2.40	75	3.5	21.4
0.72	1.61	0.92	1.70	166	9.3	2.6	1.91	0.83	2.11	110	3.3	14

^{a} Torsional correlation times τ (eq 2) and τ_c in picoseconds. ^{b} Number of dihedral transitions per 1 ns. ^{c} Average time in the dihedral state in picoseconds.
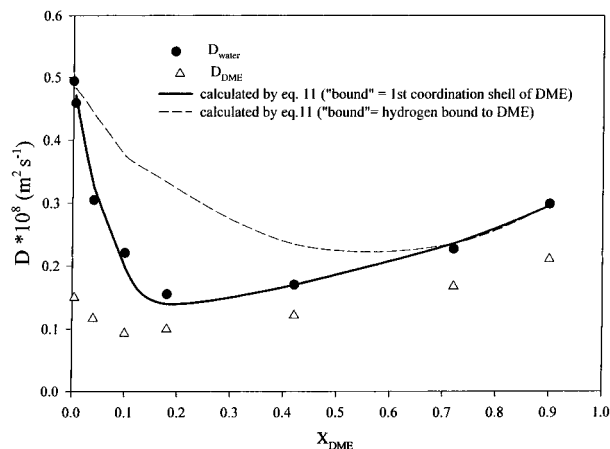
Figure 2. Self-diffusion coefficients of DME and water molecules as a function of solution composition.

Figure 3. Probability distributions of the water molecule residence time near C_{DME} and O_{DME} and for hydrogen bound water at X_{DME} = 0.04.

Figure 4. Probability distribution of the water molecule residence time in the first coordination shell of a DME molecule as a function of solution composition.

dependence of water and DME self-diffusion coefficients appear to be nearly identical, indicative of strong correlations between the motions of DME and water molecules. These correlations are considered further in the discussion section.

No experimental measurements of self-diffusion in DME/water solutions are available. We can, however, compare our simulations with recent NMR measurements[9] of the self-diffusion of ethylene glycol oligomers in aqueous solutions. Unfortunately, direct quantitative comparison is not possible because the measurements and simulations were performed at different temperatures. Additionally, the −OH termination of ethylene glycol can be expected to influence the dynamics of the system. Nevertheless, a qualitative comparison is instructive. As in DME/water solutions, the ethylene glycol oligomer/water solutions show a significant drop in water self-diffusion with increasing mole fraction of oligomer for dilute solutions, and then only a weak dependence on composition for more concentrated solutions. As was seen in DME/water, the water self-diffusion coefficient is somewhat greater than the oligomer self-diffusion coefficient in more concentrated solutions, and both water and oligomer show the same, nearly linear dependence on concentration. However, neither the self-diffusion coefficient of water molecules nor ethylene glycol oligomers show a minimum with increasing of oligomer concentration. We believe that absence of minima in the self-diffusion coefficients in ethylene glycol oligomers/water solutions is simply a consequence of the much lower self-diffusion coefficient of the ethylene glycol oligomers compared to DME, due to hydrogen bonding between the ethylene glycol oligomers.

Residence Time of Water near DME. To understand better the mechanisms and factors influencing translation dynamics in DME/water solutions, we have determined the residence time of water molecules near DME. We define the water residence times as the length of time that a water molecule remains in the first coordination shell of the entire DME molecule
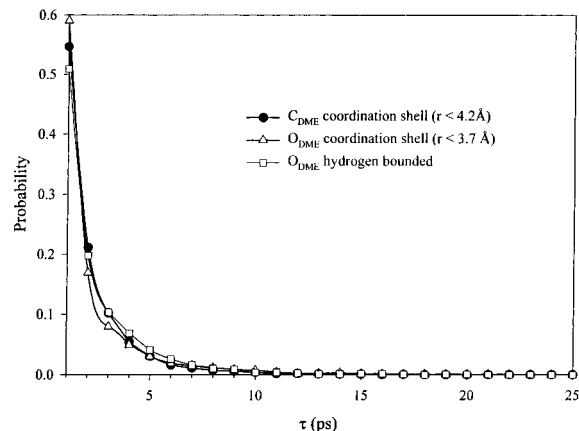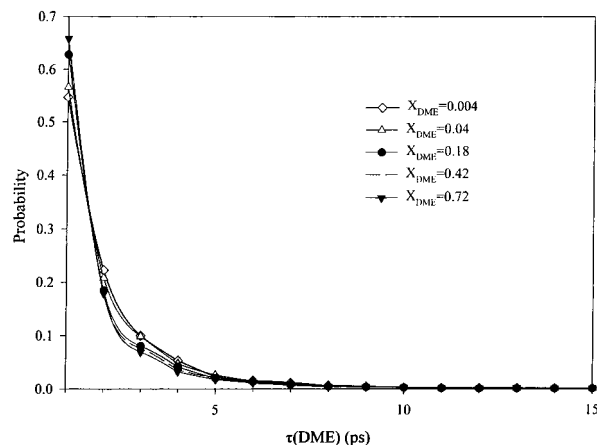
$[\tau(DME)]$, of the DME carbon atoms $[\tau(C)]$, of the DME oxygen atoms $[\tau(O)]$, and remains hydrogen bound to the DME molecule $[\tau(O_{HB})]$. The first coordination shell consists of water molecules within 3.7 Å of a DME oxygen atom or 4.2 Å of a DME carbon atom. On average, this shell consists of around 16 water molecules in dilute solutions, only 2 of which are actually hydrogen bound to the DME molecule.

Figure 3 shows the distribution of $\tau(C)$, $\tau(O)$, and $\tau(O_{HB})$ for composition X_{DME} = 0.04. The distributions are very similar, indicating that the residence time of hydrogen bound water is nearly identical to that of the other water molecules comprising the first coordination shell. Figure 4 illustrates the composition dependence of the distribution of $\tau(DME)$. The residence time distribution shows only a weak dependence on composition. For the more concentrated solutions, the residence time decreases slightly due to sharing of water between DME
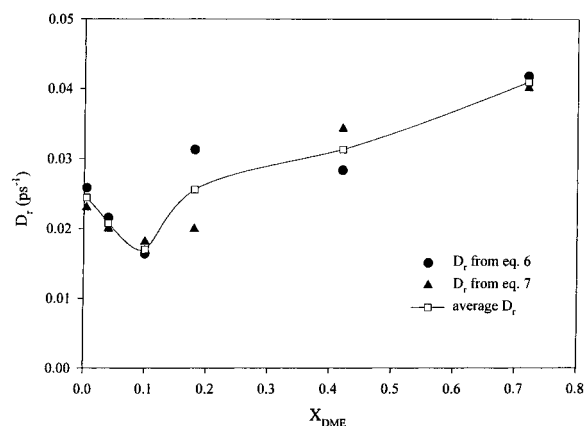
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Figure 5. Rotational diffusion coefficient of DME as function of solution composition.

molecules. Integration of the probability distributions from Figures 3 and 4 yields average residence times. In all cases, these were around 2 ps. This value is an order of magnitude less than the 25 ps found in previous simulations of PEO (DP = 15)/water solution.[12]

V. Rotational Dynamics

DME Rotation. We investigated the rotational dynamics of DME by analyzing the $P_1(t)$ and $P_2(t)$ end-to-end vector orientation autocorrelation functions as a function of concentration. $P_1(t)$ and $P_2(t)$ are given by the first and second Legendre polynomials

$$P_1(t) = \langle \cos \theta(t) \rangle \qquad (4)$$

$$P_2(t) = \langle 0.5[3\cos^2 \theta(t) - 1] \rangle \qquad (5)$$

where $\theta(t)$ is the angle between the end-to-end vector of DME molecule at times 0 and t. Assuming that the Debye theory of rotational relaxation[19] is applicable, the autocorrelation functions can be represented as

$$P_1(t) = \exp(-2D_r t) \qquad (6)$$

$$P_2(t) = \exp(-6D_r t) \qquad (7)$$

where D_r is the rotational diffusion coefficient. All correlation functions could be well represented by a single-exponential function except for $X_{DME} = 0.18$. Figure 5 shows D_r as a function of composition as obtained from eqs 6 and 7. As in translational diffusion, the rotational diffusion of DME manifests a minimum at low DME concentrations and increases linearly within increasing DME concentration.

Water Rotation. In Figure 6 we show the $P_2(t)$ orientational autocorrelation function for the vector along the C_2 rotation axis of water. We show separately the autocorrelation function for bound (first coordination shell of DME) and free water for two dilute solutions where the majority of water is free. The autocorrelation function for free water is nearly independent of composition and closely resembles that for pure water. The autocorrelation function for bound water is also nearly independent of composition in the dilute region. The rotational correlation time for bound water is approximately 1.5 times that of free water, indicating significantly slower rotational dynamics for those waters involved in the hydration of DME molecules. The rotational diffusion rate of hydrogen bound water does not differ from that for other water molecules comprising the
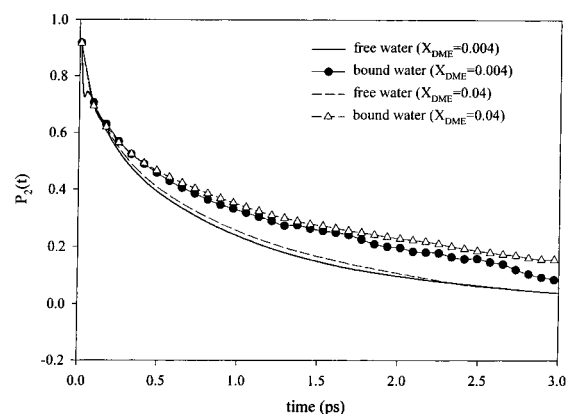

Figure 6. Rotational autocorrelation functions for free and bound water.

hydration shell of DME. The bound water in the dilute solutions was found to form approximately as many water−water hydrogen bounds as free water, despite having fewer neighboring water molecules due to the presence of the DME molecule.[4] It is therefore likely that the reduced rotational diffusion rate of the bound water molecules is due to their increased correlation with neighboring water molecules. In the high DME concentration regime the rotation rate of bound water molecules increases in comparison with bound water in the dilute solutions. At higher DME concentrations the bound water molecules are not fully hydrogen bound due to the lack of neighboring water molecules,[4] and hence their rate of rotational diffusion increases.

In the NMR relaxation studies of water dynamics[8] discussed in the Experimental Section above, a DME molecule was considered to perturb only four water molecules, slowing their rotational dynamics by a factor of 4. The excess rotational correlation time for water in very dilute solutions can be described by the relation

$$\tau_R^{ex} = N_p X_{DME} [\tau_R^p - \tau_R] \qquad (8)$$

where τ_R^p is the rotational correlation time for perturbed water, N_p is the number of perturbed water per DME molecule, and τ_R is the rotational correlation time for pure water. Using $N_p = 4$, a value of $\tau_R^p = 4\tau_R$ was obtained from the NMR relaxation data.[8] Using these values in eq 8, one finds that the experimental data are well represented by $\tau_R^{ex} = 12X_{DME}\tau_R$. From simulations, we obtain $N_p = 16$ and $\tau_R^p = 1.54\tau_R$, yielding $\tau_R^{ex} \approx 9X_{DME}\tau_R$, in good agreement with experiment.

VI. Discussion

The dynamical and structural properties of water in aqueous solutions are frequently discussed in terms of perturbed or "bound" and unperturbed or "free" water molecules.[8,9,11,20,21] Usually, these classifications are invoked without clear definitions or ability to directly determine the amount of bound or free water. One advantage of molecular dynamics simulations is that once we define "bound", we can simply count the number of bound and free water molecules in the system and determine if the properties of the system as a function of composition are consistent with our definition.

We constructed a model for the self-diffusion of water in DME/water solutions by considering two kinds of water molecules: bound and free. We made two definitions of bound water. In the first, we consider only those water molecules hydrogen bound to a DME molecule. In the second, we consider all water molecules comprising the first coordination shell of DME molecule. The fraction of bound water was
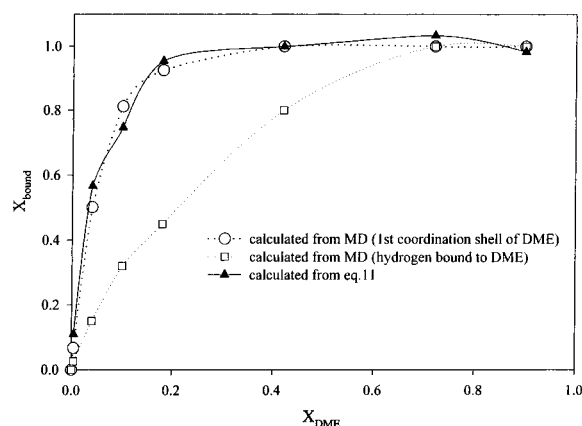
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Figure 7. Fraction of bound water molecules as a function of solution composition.

determined by *counting* the bound water during simulations of solutions for the various compositions and is shown in Figure 7.

Figure 2 shows that, for concentrated solutions (where all water is bound by either definition), the self-diffusion coefficient of water is strongly correlated with that of DME. We therefore assume the following relationship

$$D_{bound} = qD_{DME} \tag{9}$$

where D_{bound} is the self-diffusion coefficient of bound water. In their modeling of QENS measurements on PEO/water solutions, Barnes et al.[11] notice that bound water molecules may very well experience translation mobility greater than that of the polymer due to the short residence time of bound water molecules. Hence, we can expect q to be somewhat greater than unity.

We also assume that the dynamics of free water are not perturbed by DME and, hence, the self-diffusion coefficient of free water was set equal to that of pure water. This assumption is supported by our observations about the interaction of water and DME in relatively dilute solutions. It is observed that additional dilution of solutions beyond $X_{DME} = 0.18$ results in little change in the conformations of DME,[4] the local structure of hydrating water,[4] or the conformational or rotational dynamic of DME (see above). The tendency of water in DME/water solutions to assume bulk-water like behavior is seen even in concentrated solutions, where water molecules try to manifest bulk water structure by forming small clusters.[4] Therefore we assume that

$$D_{free} = D_0 \tag{10}$$

where D_0 is the self-diffusion of bulk water at the same temperature and pressure. Hence the total water self-diffusion coefficient can be represented as

$$D_{cal} = (1 - X_{bound})D_0 + X_{bound} qD_{DME} \tag{11}$$

Since we have determined X_{bound} from simulation, the only unknown parameter in eq 11 is q. We obtained $q = 1.4$ by fitting the self-diffusion coefficient of water in the high concentration regime. Assuming that bound water corresponds only to those water molecules hydrogen bound to DME, we obtain from eq 11 the dashed curve shown in Figure 2. Using the first coordination shell definition yields the solid curve. The solid curve accurately represents the self-diffusion coefficient of water, supporting our conclusion based upon the water residence times and the rotational dynamics of water (see above)

that DME perturbs the dynamics of all water in the first hydration shell. In Figure 7 we also show X_{bound} calculated from eq 11 as a function of composition. The perfect agreement with X_{bound} calculated from MD simulation using the first coordination shell of the DME definition can be observed.

VII. Conclusions

A molecular dynamics study of the dynamic properties of 1,2-dimethoxyethane in aqueous solution as a function of composition was performed. Conformational transition rates for both the C−O─C−C and O−C─C−O bonds decrease with increasing of water content and reflect an increase in the average residence time in t and *g* states, respectively. Self-diffusion coefficients of water and DME molecules show a minimum near $X_{DME} = 0.20$. Further increasing the DME content results in strong correlation between the motions of DME and water molecules. The analysis of water in the first coordination shell of DME shows that the average residence is nearly 2 ps for all hydrating water, including those hydrogen bound to the DME molecule, and does not depend strongly on solution composition. Rotational dynamics of DME molecules show a near linear dependence on composition at high DME concentrations as is seen in the self-diffusion coefficients and manifest a minimum in the regime $X_{DME} = 0.1-0.2$. The results of rotating free and bound (first coordination shell) water molecules were found to differ significantly. A simple model incorporating two kinds of water molecules (free and bound) was constructed and found to accurately represent both translational and rotational diffusion of water.

Taking into account the simulation results summarized above and in our previous manuscript,[4] the following picture of the composition dependence of the dynamical properties of DME/water solution emerges. In dilute solutions two kinds of water molecules, bound and free, exhibit quite different rotational and translational dynamics, with the bound water being dynamically slower than the free water. The dynamics of bound and free water appear to be independent of concentration in the range $X_{DME} = 0.00$ up to $X_{DME} = 0.20$. The dramatic increase in the fraction of bound water with increasing DME concentration is responsible for the sharp decrease in the rotational and translation dynamics of water in this regime.

In concentrated (high DME content) solutions, the water molecules prefer to form small clusters. Due to the ability of water to form hydrogen bonds with DME, these clusters are strongly correlated with DME oxygen atoms.[4] Because of this correlation, and the fact that the majority of the volume is occupied by DME, the motion of water is highly correlated with that of DME. DME with its hydrating water is larger than a DME molecule alone, resulting in reduced mobility. With increasing dilution, the DME molecules are more completely hydrated, forming more extended clusters. This further reduces the mobility of DME, and also results in a reduction of the rotational mobility of the water as it forms more hydrogen bonds with neighboring water.

The concentration $X_{DME} = 0.20$ corresponds to a dynamic crossover regime. All dynamical properties of the solution (viscosity, self-diffusion coefficients, and conformational correlation times) exhibit an extremum at this composition. At this concentration there is no free water in the system, but additional dilution results in the formation of free water. (Note, however, that only a fraction of the additional water is free: some of the additional water participates in formation of the hydration shells around DME). The dynamical characteristics of the bound water at this concentration are very close to those

in the very dilute solutions due to the fact that at $X_{DME} = 0.20$ each water molecule still forms approximately the same number of hydrogen bonds with neighboring water molecules as a bulk water. This tendency results in significant local reorientation or structuring of the hydrating water.

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