

# Simulation and QENS Studies of Molecular Dynamics in Aqueous Solutions of 1,2-Dimethoxyethane

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We compare the composition dependence of the self-diffusion coefficient of water in aqueous solutions of 1,2-dimethoxyethane (DME) as obtained from incoherent quasielastic neutron scattering measurements and molecular dynamics simulations. Simulations were performed using the TIP4P water model and a quantum chemistry based potential for DME and DME/water interactions. Excellent agreement is seen between experiment and simulation, including the minimum in the water self-diffusion coefficient at  $X_{\text{DME}} \approx 0.2$  predicted by our earlier simulations. Further, we investigated the influence of the water potential on molecular dynamics in DME aqueous solutions by performing simulations using the SPC, SPC/E, and MCY water models. The SPC and MCY models yielded a water self-diffusion coefficient as a function of composition in qualitative agreement with experiment, including the before mentioned minimum. Quantitative agreement with experiment is poorer for these potentials than for the TIP4P model. Surprisingly, simulations employing the SPC/E model, known to provide the best description of self-diffusion in pure water, showed a qualitatively incorrect dependence of water self-diffusion on composition. The failure of the SPC/E water model was attributed to overestimation of the strength of water–water interactions.

## I. Introduction

In previous work,<sup>1</sup> molecular dynamics (MD) simulations were used to probe the structural, conformational, and dynamic properties of aqueous solutions of 1,2-dimethoxyethane (DME). The composition dependence of the solution properties was compared for TIP4P,<sup>2</sup> SPC,<sup>3</sup> SPC/E,<sup>4</sup> and MCY<sup>5</sup> water models. With the exception of the MCY model, the conformations of DME were found to be nearly independent of the water model for dilute (water-rich) solutions, and only weakly dependent upon the water model for more concentrated solutions. Structural and dynamic properties were found to be more dependent on the water model, particularly the self-diffusion coefficient of water. For three of the investigated models (TIP4P, SPC, and MCY), the self-diffusion coefficient of water was found to have a minimum at a mole fraction  $X_{\text{DME}} \approx 0.2$ , although the values for the self-diffusion coefficient of water varied widely. In contrast, simulations employing the SPC/E water model did not show a minimum in this concentration range. It is known that the SPC/E model is in closest agreement with the experimental self-diffusion coefficient of pure water for nonpolarizable potentials.<sup>6</sup>

In this work we report results of incoherent quasi-elastic neutron scattering (IQNS) measurements performed on aqueous solutions of DME. We compare the dynamics of water molecules obtained from IQNS with values obtained from MD simulations. These comparisons allow us to (1) investigate the ability of classical MD simulations using a quantum chemistry based

potential to reproduce molecular dynamics in these solutions and (2) differentiate between the various water potentials.

## II. Experimental Measurements

Scattering experiments were carried out at the intense pulsed neutron source (IPNS) located at the Argonne National Laboratory, using the QENS (quasi-elastic neutron scattering) spectrometer.<sup>7</sup> As the focus of the experiment was the determination of the translational self-diffusion coefficient of water, a fully deuterated sample of DME was used ( $\text{C}_4\text{D}_{10}\text{O}_2$ , Cambridge Isotopes, 98% deuteration) in conjunction with  $\text{H}_2\text{O}$ . As the scattering cross-section of hydrogen is approximately 16 times greater than that of deuterium, water scattering dominated the signal. Nevertheless, the scattering from a pure DME- $\text{d}_{10}$  sample was measured and subtracted from the aqueous solutions in proportion to the amount of DME present. This is not an exact correction for the DME scattering, as it does vary with the concentration of the solution, but it is an adequate approximation as a consequence of the reduced scattering from deuterated DME.

The samples were loaded into a container consisting of two concentric thin aluminum cylinders approximately 12 cm long and 0.7 cm in diameter. The sample was located between the cylinders with a typical gap of approximately 0.05–0.1 cm, and the sample was kept in the container using an indium gasket seal. For the samples with a high fraction of deuterated DME ( $X_{\text{DME}} = 1.0, 0.63, 0.39$ ) approximately 2 g of sample was used

in the 10 cm high neutron beam, while this was reduced to 0.6–0.9 g for the samples with more water ( $X_{\text{DME}} = 0.17, 0.09, 0.04$ , and bulk water). This was done to reduce the effects of multiple scattering, as no corrections were made for this in the analysis.

The water scattering data were analyzed using the Singwi and Sjolander model for translational jump diffusion,<sup>8</sup> in conjunction with isotropic rotational motion on the surface of a sphere, as employed by Teixeira et al.<sup>9</sup> to analyze the scattering from ambient and supercooled water. Nine spectra measured over the momentum transfer range of 0.5–2.5 Å<sup>-1</sup> were simultaneously fitted using this model, yielding a Debye–Waller factor, a self-diffusion coefficient (translational motion), a translational residence time, and a rotational diffusion coefficient for each composition. As the scattering from the water is incoherent, the self-diffusion and rotational diffusion coefficients obtained in this manner can be directly compared with the values obtained from the time dependence of the mean-square displacement of the water center-of-mass and the autocorrelation function for the O–H vector, respectively, obtained from the MD simulations.

### III. Force Field Parametrization and MD Methodology

The quantum chemistry based intramolecular potentials for DME and the DME/DME nonbonded potential are described in previous work.<sup>10</sup> The TIP4P, SPC, SPC/E, and MCY potentials were used for the water/water interactions. The DME/water potential was derived in previous work,<sup>1,11</sup> where the MP2 level quantum chemistry binding energies of a DME/water complex, consisting of the *tgt* conformer of DME and a single water molecule, was calculated as a function of the separation along the DME C<sub>2</sub> axis. Polar interactions were included using partial charges for DME and water. As the set of charges differs between water models, polar interactions are dependent upon the choice of water model. The Lennard-Jones parameters for the description of repulsion/dispersion interactions between DME and water were fitted in order to reproduce the quantum chemistry binding energies. The details of the fitting procedure are described in refs 1 and 11.

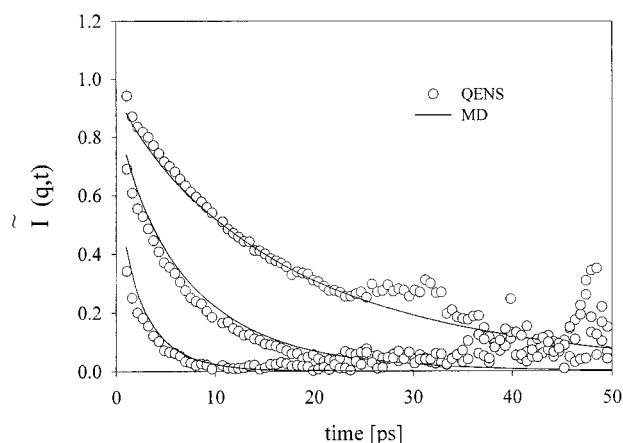
After parametrization of the DME/water potentials, molecular dynamics (MD) simulations were carried out for five DME/water compositions (mole fraction  $X_{\text{DME}} = 0.04, 0.10, 0.18, 0.42$ , and 0.72) at 318 K.<sup>1</sup> All systems were initially equilibrated for 1.0 ns. Constant pressure-constant temperature (NPT) simulations were performed over 0.4 ns in order to establish the equilibrium density at atmospheric pressure. The statistical runs lasting over 1.5–2.5 ns (depends on solution composition) with a 1.0 fs time step were performed in the constant volume-constant temperature (NVT) ensemble. Periodic boundary conditions were employed. The standard Shake algorithm<sup>12</sup> was used to constrain the bond lengths, while all other degrees of freedom remained flexible. The Ewald summation method<sup>13</sup> was employed to handle long-range electrostatic interactions.

### IV. Results and Discussion

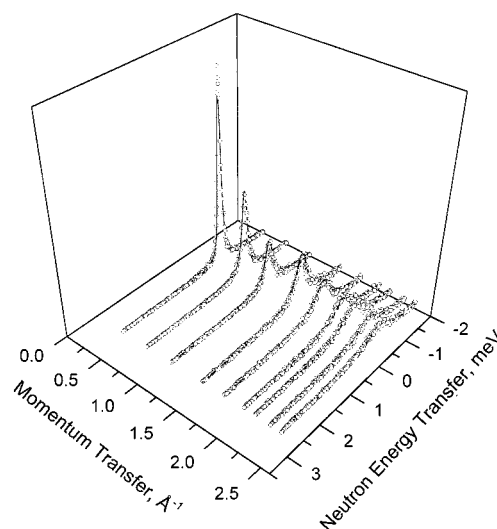
**Comparison of Experiments and Simulations.** In Figure 1 the normalized intermediate incoherent dynamic structure factor  $\tilde{I}(q,t)$  obtained from both experiment and MD simulations is shown for  $X_{\text{DME}} = 0.17$  for various momentum transfers.  $\tilde{I}(q,t)$  was obtained directly from simulation using eq 1

$$\tilde{I}(q,t) = \left\langle \frac{\sin(q\Delta r(t))}{q\Delta r(t)} \right\rangle \quad (1)$$

where  $\Delta r(t)$  is hydrogen atom displacement over time  $t$ , and



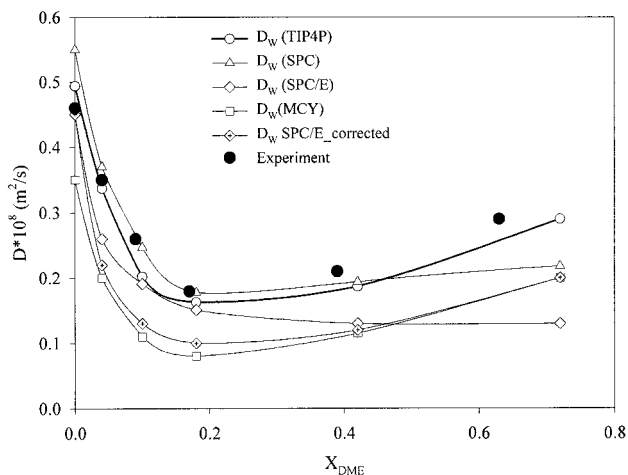
**Figure 1.** Intermediate incoherent dynamic structure factor  $\tilde{I}(q,t)$  for various momentum transfers obtained from experiment and MD simulations for  $X_{\text{DME}} = 0.17$ .



**Figure 2.** Incoherent dynamic structure factor  $S(q,\omega)$  for nine  $q$  values for  $X_{\text{DME}} = 0.17$  as obtained from experiment (symbols) and fitted using the jump-diffusion model with the same set of parameters for all  $q$  (lines).

$\langle \dots \rangle$  denotes averaging over all hydrogen atoms in the system and all time origins. Fourier transform of the incoherent dynamic structure factor  $S(q,\omega)$  to the time domain yields the experimental  $\tilde{I}(q,t)$ .<sup>14</sup> Agreement between experiment and simulation is excellent for all  $q$  values. A similar agreement was seen for all compositions investigated. Therefore, we conclude that the dynamics of water in the DME/water solutions are accurately reproduced in the simulations.

To extract from experimental measurements translational and rotational diffusion coefficients, the measured incoherent dynamic structure factor  $S(q,\omega)$  for various momentum transfers has been fitted using the jump-diffusion model described above. The experimental  $S(q,\omega)$  and the fits are shown in Figure 2 for nine  $q$  values for solution  $X_{\text{DME}} = 0.17$ . It can be seen that the same set of parameters of the jump-diffusion model adequately describes the experimental dynamic structure factors for all  $q$  values. The water self-diffusion coefficient as a function of solution composition obtained from fitting QENS measurements by the jump-diffusion model and MD simulations is shown in Figure 3. Simulations are in excellent agreement with experiment. This agreement clearly demonstrates the ability of our quantum chemistry based potential function, in conjunction with the TIP4P water model, to reproduce the translational dynamics of water in these solutions, and supports our analysis of the



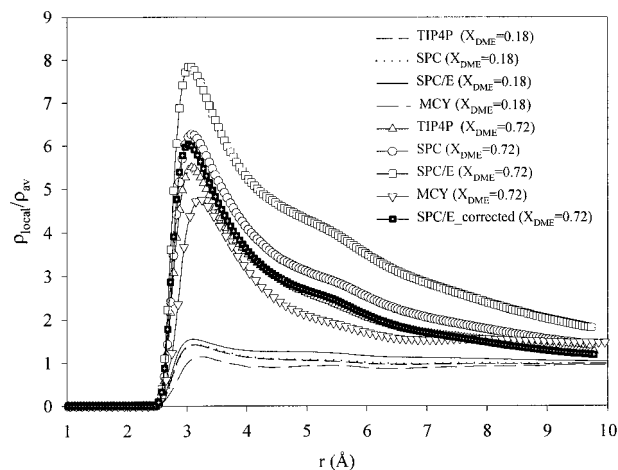
**Figure 3.** Composition dependence of the water self-diffusion coefficient as obtained from experiment and MD simulations using different water models.

composition dependence of molecular dynamics in these solutions elucidated from MD simulations.<sup>16</sup> The agreement in Figure 3 also indicates that the jump-diffusion model is capable of reflecting the translational motion of water molecules.

We have found that the quality of the fits of the incoherent dynamic structure factor  $S(q, \omega)$  was very insensitive to the value of the water rotational diffusion coefficient. We therefore conclude that the rotational diffusion coefficients obtained by fitting the  $S(q, \omega)$  using the jump diffusion model are not sufficiently accurate to allow quantitative comparison with MD results. Nevertheless, it is worth mentioning that the composition dependence of the water rotational diffusion coefficient as obtained from experiment is in qualitative agreement with that seen in the simulations, showing a minimum around  $X_{\text{DME}} \approx 0.20$ .

**Influence of the Water Potential.** The composition dependence of the self-diffusion coefficient of water in DME solutions obtained from simulations employing different water models is shown in Figure 3. The SPC and TIP4P models yield a self-diffusion coefficient for pure water higher than that obtained from experiment, while the MCY model underestimates this value. Deficiencies of these water models in predicting pure water self-diffusion have been discussed previously.<sup>6,15</sup> The SPC/E water model yields the best agreement with experiment for the self-diffusion coefficient of pure water. With increasing DME concentration the SPC/E model no longer provides the most accurate prediction of the self-diffusion coefficient of water. In particular, unlike the other models, which demonstrate, to a greater or lesser degree, a minimum in the water self-diffusion coefficient as function of composition, the SPC/E water model shows a monotonic decrease in the water self-diffusion coefficient with increasing DME content. The IQNS measurements reveal that the minimum in the water self-diffusion coefficient  $X_{\text{DME}} \approx 0.2$ , first observed in our simulations,<sup>1,16</sup> is a real characteristic of DME/water solutions. A detailed explanation of such extremum behavior was given in our early work.<sup>1,16</sup> Despite the largest systematic variance from experiment, the MCY model yields a qualitatively correct composition dependence of the water self-diffusion coefficient. The TIP4P water model yields the best overall agreement with experiment.

In Figure 4 the ratio of local water density (water coordination number per unit volume in a sphere of radius  $r$  from a given water molecule) to the bulk solution density of water is shown for  $X_{\text{DME}} = 0.72$  and  $X_{\text{DME}} = 0.18$ . This ratio allows us to compare the tendency of water molecules to form clusters in DME/water solutions as a function of the water model. It is

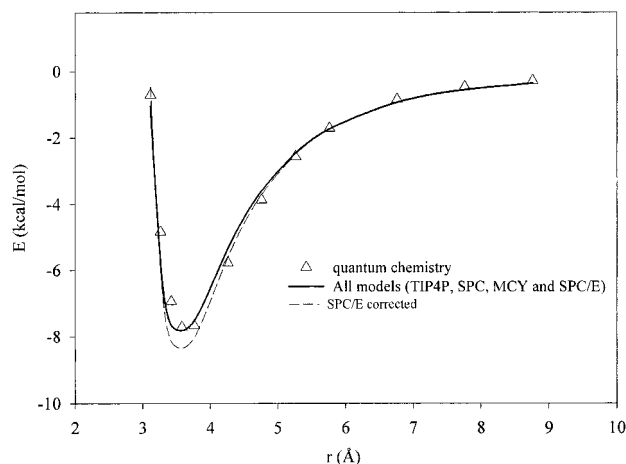


**Figure 4.** Ratio of the local density of water to the bulk solution density of water for various water models for  $X_{\text{DME}} = 0.18$  and  $X_{\text{DME}} = 0.72$  as obtained from MD simulations.

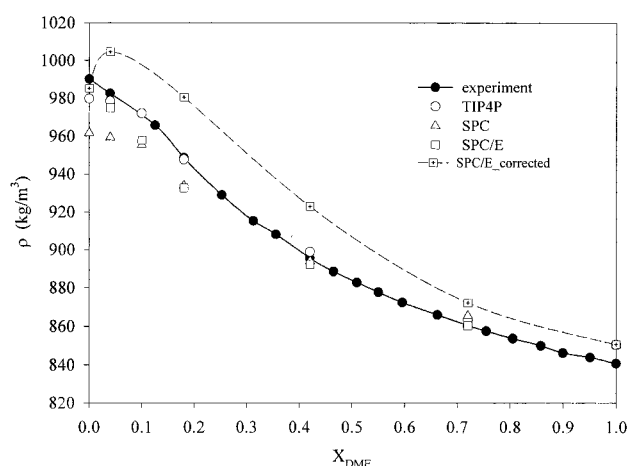
clear that SPC/E water molecules have a much stronger tendency, in comparison with other water models, to form clusters in solutions with high DME content.

Since the interactions between DME and water for the different water models are almost identical,<sup>1</sup> it is reasonable to suspect that the SPC/E water model overestimates water–water attraction in DME/water solutions. This shortcoming of the SPC/E water is consistent with recent MD simulations of van der Spoel et al.<sup>17</sup> where it was found that simulations with the SPC/E model predict about 10% larger (negative) potential energy per water molecule than other models and experiment. On the other hand, we do not have unambiguous evidence that the DME/water interactions employed in the simulations are precise. One can argue that the quantum chemistry energies used in the DME/water force field parametrization are not accurate enough or the particular path along which the quantum chemistry calculations were performed does not provide an adequate representation of the potential energy surface. Our general strategy in force field parametrization<sup>11</sup> includes three major steps: (1) performing quantum chemistry calculations, (2) fitting the force field parameters in order to reproduce the quantum chemistry potential energy surface, and (3) empirical adjustment of the force field, if necessary, to reproduce available experimental data. Empirical adjustment of the quantum chemistry based force field for DME/water (TIP4P) solutions was found to be unnecessary.<sup>11</sup>

Following the strategy described above, we decided to make empirical adjustments to the DME/water (SPC/E) potential in order to improve the description of the water self-diffusion coefficient. The largest discrepancy between the experimental and simulation self-diffusion of water is observed for the solution with the highest DME concentration (Figure 3) for the DME/water (SPC/E) system. Based on the analysis of Figure 4 this inaccuracy can be attributed to the stronger tendency of water molecules to form clusters compared to other models, indicating that DME/water (SPC/E) attraction is not strong enough in comparison with the water–water attraction in this system. Therefore, we increased DME/water (SPC/E) attraction by making the minimum in the DME–water interaction along the  $C_2$  path deeper, as illustrated in Figure 5. The DME–water (SPC/E) interaction strength was increased by 0.1, 0.25, 0.5, 0.75, 1.0, and 1.5 kcal/mol. None of the modified force fields gave the desired description of the self-diffusion coefficient at  $X_{\text{DME}} = 0.72$ . The best description was obtained when the depth of the minimum was increased by 0.75 kcal/mol. A further



**Figure 5.** Binding energy of DME (*tgt*) and water as a function of separation along the DME  $C_2$  axis.



**Figure 6.** Density of DME/water solutions as a function of composition for various water models.

increase in the strength of the DME/water (SPC/E) attraction resulted in a strong coupling of DME and water motion and self-diffusion of water became equal to the self-diffusion of DME molecules.

We performed simulations of DME/water (SPC/E) solutions at other concentrations using the modified potential shown in Figure 5. The self-diffusion coefficient of water obtained from the simulations using modified DME/water (SPC/E) potential is also shown in Figure 3. The composition dependence of the diffusion coefficient is more consistent with experiment, while the absolute values are systematically lower than experimental data. From Figure 4 it is clear that the stronger DME/water interaction in the modified force field reduces the extent of water clustering for the SPC/E model. The empirical adjustment of the force field also influenced the description of the PVT data of the solution. In Figure 6, the composition dependence of solution density as obtained from MD simulations using the various water potentials is compared with experiment.<sup>18</sup> It is obvious that the modified DME/water (SPC/E) force field provides a very poor description of solution density despite some improvement in the water self-diffusion coefficient.

In the above discussion we make an assumption that DME/DME interactions are adequately described. To investigate this supposition, we have performed proton NMR pulsed-field gradient measurements of neat hydrogenous DME liquid at 298 K and compared results with MD simulations. A value of  $D = 0.32 \times 10^{-8} \text{ m}^2/\text{sec}$  was obtained, in good agreement with the

value of  $D = 0.23 \times 10^{-8} \text{ m}^2/\text{sec}$  obtained from the simulation. We therefore conclude that the translational dynamics of DME are reproduced accurately in the simulations. Consequently, discrepancies observed for water dynamics in DME/water solutions for the various water models in comparison with experiment, particularly with the SPC/E model, are not due to an inadequate description of DME molecular dynamics in our simulations.

## V. Conclusions

Excellent agreement for the molecular dynamics of water in DME solutions was seen between QENS studies and MD simulations using a quantum chemistry based potential in conjunction with the TIP4P water model. This agreement validates the predictions of molecular dynamics in DME solutions obtained from our MD simulations, and lends important support to our interpretation of their concentration dependence gleaned from these simulations.

While the SPC/E model appears to provide the best description of the self-diffusion of pure water, the overestimation of the strength of water/water interactions in the SPC/E model results in qualitatively incorrect dependence of the self-diffusion of water on composition in DME/water solutions. It appears that mixture properties, which are determined by a balancing of interactions between molecules of the same species and molecules of different species, are more subtly dependent upon the description of intermolecular interactions than the properties of pure liquids. Attempts to compensate for the over(under)estimation of one interaction (e.g., water/water) by corresponding over(under)estimation of another interaction (e.g., water/DME) may improve the description of some properties, but at the same time result in unsatisfactory description of other properties.

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