ADDITIONS AND CORRECTIONS

Jan Fischer, Dietmar Paschek, Alfons Geiger, and Gabriele Sadowski*: Modeling of Aqueous Poly(oxyethylene) Solutions: 1. Atomistic simulations

Pages 2388-2398. The results for the TraPPE-UA [1–4] united atom force field that were reported in ref 5 include an erroneous treatment of 1−4 interactions similar to the OPLS force field[6] and are thus deviating from the definition used in ref 3. In the OPLS-model, the 1−4 Lennard-Jones (LJ), and the 1−4 Coulomb interactions are scaled by a factor 0.5. In TraPPE-UA, however, no 1−4 Lennard-Jones interactions are considered, and 1−4 Coulomb interactions are scaled by 0.5.[3] The different treatment of 1−4 interactions significantly affects the conformer populations of the simulated 1,2-dimethoxyethane (DME) discussed in ref . To complete our study, we provide here additional data for TraPPE-UA with proper 1−4 scaling. All molecular dynamics (MD) simulation details are the same as in ref 5. Particularly, the TraPPE-UA with modified dihedrals still uses an OPLS-like scaling of 1−4 interactions.

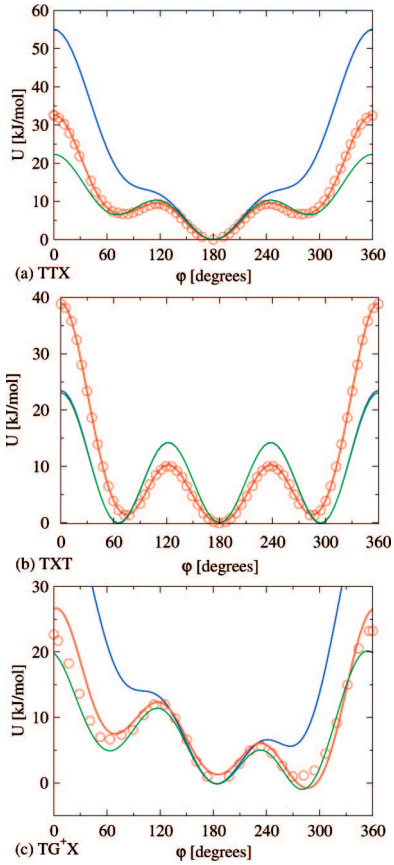

Figure 1. Potential energy of DME depending on the dihedral angle of paths C−C−O-C (a,c) and O−C−C−O (b) for specific conformers. The lines represent data for the different forcefield models: TraPPE-UA (green), TraPPE-UA with erroneous use of OPLS-like 1−4 scaling (blue), and TraPPE-UA with modified dihedral potentials suggested in ref 5 (red). The symbols indicate ab initio data by Anderson and Wilson,[7] given for comparison. All energies are given with respect to the energy of the TTT conformer. (a) TTX: the first two dihedrals were fixed in the "trans" conformation. (b) TXT: The two outer dihedrals were fixed in the "trans" conformation. (c) TG$^+$X: the first two dihedrals were fixed in the "trans" and "gauche (+)" conformation. All other degrees of freedom were optimized. Note that "T" always refers to a dihedral angle of 180°, whereas " G$^+$" refers to an angle corresponding to the position of the first minimum shown in panel b, which is slightly varying with the force field.

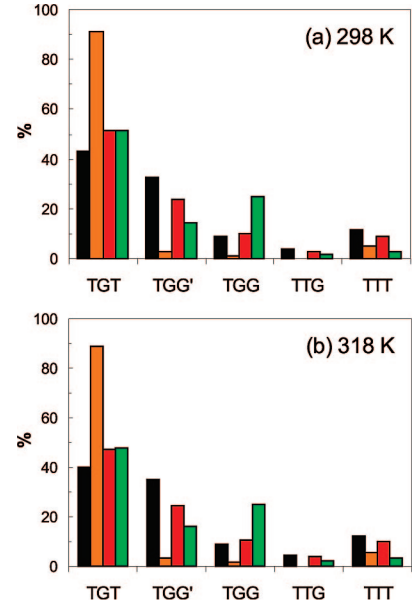

Figure 2. Populations of the five most largely populated conformers of DME in the neat liquid phase at (a) 298K and (b) 318K at 1 bar. We compare data obtained from Raman measurements[8] (black) with data from MD simulation using different force field models: TraPPE-UA[3] (green), TraPPE-UA with modified dihedral potentials[5] (red), and TraPPE-UA with erroneous use of OPLS-like 1−4 scaling (orange). Absolute standard deviations for all simulation results is lower or equal to 2.5%.

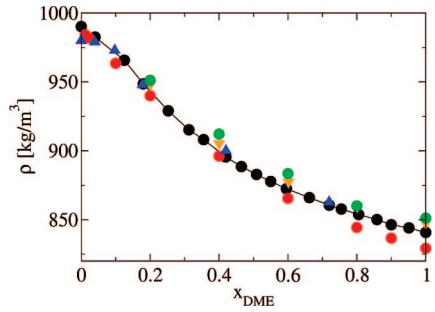

Figure 3. Density of aqueous solutions of DME at 318 K and at 1 bar. We compare experimental data[9] (black) with data from MD simulation using different force field models: TraPPE-UA[3] (green), TraPPE-UA with modified dihedral potentials[5] (red), and TraPPE-UA with erroneous use of OPLS-like 1−4 scaling (orange).

Figure 1 shows torsion-potentials for several important conformers of DME. First of all, it is obvious that the different treatment of the 1−4 interactions significantly affects the calculated torsion potentials. The profiles obtained for TraPPE-UA are much closer to the ab initio data than the torsion potentials obtained for TraPPE-UA with erroneous use of OPLS-like 1−4 scaling. The effect is particularly strong for the C−O−C−C dihedrals (Figure 1a,c) including carbon−carbon

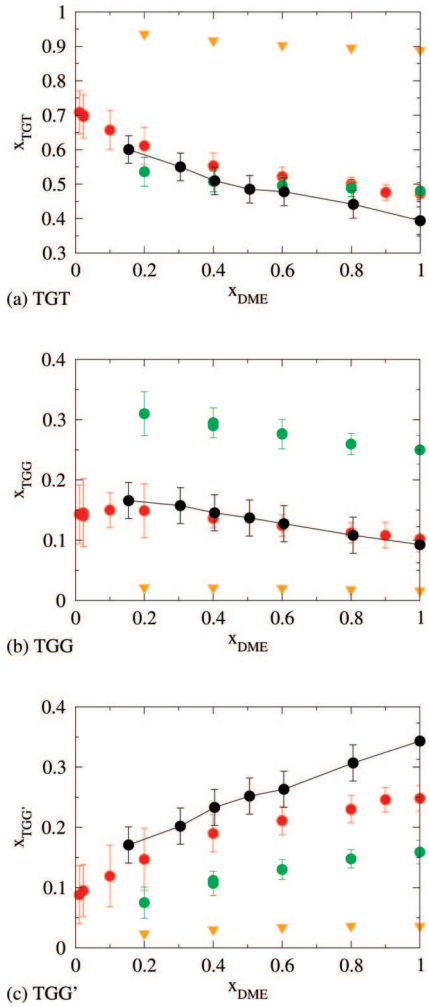

Figure 4. Populations of the three most largely populated conformers of DME in aqueous solution at 318 K and at 1 bar. We compare data obtained from Raman measurements[8] (black) with data from MD simulation using different force field models: TraPPE-UA[3] (green), TraPPE-UA with modified dihedral potentials[5] (red), and TraPPE-UA with erroneous use of OPLS-like 1−4 scaling (orange). Standard deviations for the populations reach from 2 to 6% (absolute) for all force fields (relative standard deviations: 5 to 11% for TGT and TGG, 10 to 20% for TGG′).

1−4 interactions, whereas the data for the O−C−C−O path (Figure 1b) is merely unchanged. The TraPPE-UA with modified dihedral potentials is still lying slightly closer to the ab initio data set, which is not surprising since the dihedral potential was fitted to the ab initio data for "TXT" and "TTX" conformers.

Figure 2 depicts conformer populations for neat liquid DME obtained from MD simulation and from experiment. Contrasting the results for TraPPE-UA with erroneous use of OPLS-like 1−4 scaling reported in ref 5, the populations obtained for TraPPE-UA agree substantially better with the experimental data set.[8] Particularly, the strong overestimation of the stability of the TGT conformer has disappeared. However, compared to the experimental data, the TGG′, TTG and TTT conformations seem to be slightly underrepresented, whereas the population of the TGG conformer is significantly overestimated (TGG′ indicates conformations having two gauche states with opposite sign.). The use of modified dihedral potentials fitted to ab initio data is to some extent able to account for these deficiencies. It turns out that the discussed dihedral potential modifications only slightly influence the obtained neat liquid densities. All force fields reproduce the experimental densities obtained at 318K within 1.5%, expt.[9] 840.76 kgm^{-3}; TraPPE-UA with erroneous use of OPLS-like 1−4 scaling, 847.3 ± 0.5 kgm^{-3}; TraPPE-UA, 851.1 ± 0.5 kgm^{-3}; and TraPPE-UA with modified dihedral potentials, 829.2 ± 0.5 kgm^{-3}.

Simulations of DME-water mixtures using the different force fields show a similar trend as observed for the neat liquid. The DME-water mixture densities obtained by the different force fields do not differ much as can be seen in Figure 3. TraPPE-UA shows a slight overestimation whereas TraPPE-UA with modified dihedrals shows an underestimation of the same extent.

Figure 4 presents the conformer population of the three most abundant conformers of DME in aqueous solution at 318 K and 1 bar. We denote a substantially better agreement of TraPPE-UA with experimental data for all three conformers compared with the previously reported data[5] for TraPPE-UA with erroneous use of OPLS-like 1−4 scaling. The population of the TGT conformer is almost identical for both force fields and rather close to the experimental value.[8] Using TraPPE-UA, the TGG population is overestimated while the TGG′ population is underestimated compared with the modified TraPPE-UA. We conclude that the TraPPE-UA force field with correct 1−4 interactions performs significantly better than the TraPPE-UA model with erroneous use of OPLS-like 1−4 scaling.

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References and Notes

(1) Martin, M. G.; Siepmann, J. I. *J. Phys. Chem. B* **1998**, *102*, 2569.
(2) Wick, C. D.; Martin, M. G.; Siepmann, J. I. *J. Phys. Chem. B* **2000**, *104*, 8008.
(3) Stubbs, J. M.; Potoff, J. J.; Siepmann, J. I. *J. Phys. Chem. B* **2004**, *108*, 17569.
(4) Wick, C. D.; Stubbs, J. M.; Rai, N.; Siepmann, J. I. *J. Phys. Chem. B* **2005**, *109*, 18974.
(5) Fischer, J.; Paschek, D.; Geiger, A.; Sadowski, G. *J. Phys. Chem. B* **2008**, *112*, 2388.
(6) Jorgensen, W. L. *J. Phys. Chem.* **1986**, *90*, 1276.
(7) Anderson, P. M.; Wilson, M. R. *Mol. Phys.* **2005**, *103*, 89.
(8) Goutev, N.; Ohno, K.; Matsuura, H. *J. Phys. Chem. A* **2000**, *104*, 9226.
(9) Das, B.; Roy, M. N.; Hazra, D. K. *Ind. J. Chem. Tech.* **1994**, *1*, 93.

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