A Molecular Model for Poly(oxymethylene) Dimethyl Ethers (OME)

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Poly(oxymethylene) dimethyl ethers (OME*n*) are oligomers with the general structure $H_3C\text{-}O\text{-}(CH_2O)_n\text{-}CH_3$. They are promising novel synthetic fuels and also have other potential applications, e.g. as solvents for CO_2 capture [1, 2]. It is interesting to use molecular simulations for predicting thermodynamic properties of the different OME*n*. However, the available molecular models are not suited for this task. Therefore, in the present work, a set of united-atom models with transferable parameters for OME*n* is developed. The OME*n* are modelled as flexible multi-center Lennard-Jones (LJ) chains with partial charges, where the LJ sites stand either for CH_3, CH_2 or O.

Quantum chemical calculations are carried out to obtain the molecular geometry, the internal degrees of freedom and the charge distribution. The results indicate that depending on their position in the chain, united-atom sites that represent the same chemical group differ in their contribution to the internal degrees of freedom and to the electrostatics.

The LJ parameters are fitted to reproduce the vapour pressure and saturated liquid density of different OME*n*. Reasonable agreement is obtained. For oligomers like OME*n*, the determination of accurate data on the vapour pressure from molecular simulations is particularly challenging. In the present work, Gibbs Ensemble Monte Carlo simulations with configurational bias are employed, and different simulation programs are compared. Additionally, the viscosity of pure OME*n* and the solubility of CO_2 in OME*n* are calculated with the new models. The obtained predictions agree well with the experimental data.

References

[1] N. Schmitz, J. Burger, H. Hasse, Reaction Kinetics of the Formation of Poly(oxymethylene) Dimethyl Ethers from Formaldehyde and Methanol in Aqueous Solutions, Ind. Eng. Chem. Res. 54 (2015) 12553-12560.

[2] N. Schmitz, J. Burger, E. Stroefer, H. Hasse, From methanol to the oxygenated diesel fuel poly(oxymethylene) dimethyl ether: An assessment of the production costs, Fuel 185 (2016) 67-72.