
Molecular Modeling of Hydrogen Bonding Fluids: Transport Properties and Vapor-Liquid Coexistence

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Summary. Predictions of the transport properties self-diffusion coefficient and shear viscosity are presented for a recently developed molecular ammonia model. These data show mean unsigned deviations to the experiment over a temperature range from 200 to 500 K of 8 % for the self-diffusion coefficient and 12% for the shear viscosity. Furthermore, the vapor-liquid equilibria of the ternary system carbon dioxide+cyclohexanol+cyclohexane and its binary subsystems are investigated. The modified Lorentz-Berthelot combination rule with one state-independent binary interaction parameter was used for the pairwise unlike dispersive interactions. Per binary subsystem, the parameter was adjusted to a single experimental vapor pressure. The binary subsystems are in good agreement with experimental data throughout the entire composition range. For the ternary system, the vapor pressure is under-predicted by about 12 %.

1 Introduction

In this project on molecular modeling and simulation of thermodynamic properties of hydrogen bonding fluids, numerous molecular models have been developed in recent years. In order to set up a new molecular model for a given substance, a methodology is now at hand. Starting from quantum mechanical calculations of a single molecule in the vacuum, the geometry is determined via the Hartree-Fock approach. On top of this geometry optimization, also the electrostatics of the molecule can reasonably be determined by quantum mechanics. By following the COSMO idea to a single molecule is embedded into a dielectric cavity that mimics the electrostatics of a liquid, a Moller-Plesset 2 calculation yields the electron density distribution of the molecule.

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On the basis of this data, polar moments are derived. To finalize a molecular model, the Lennard-Jones parameters have to be determined which can be done by optimization to vapor-liquid equilibrium (VLE) data. Particularly experimental data on the vapor pressure and the saturated liquid density of the pure fluid from the triple point to the critical point should be considered.

It was shown for numerous substances that hydrogen bonding itself may also reasonably be modeled by electrostatic interaction sites, i.e. partial charges that are located eccentrically within Lennard-Jones sites. Examples for fluids which were described in this way are water, methanol, methylamine, ammonia and cyclohexanol. The achieved quality of optimization to experimental VLE data gives valuable information whether the model structure, e.g. the chosen number and type of interaction sites, was reasonable. If a chosen structure is oversimplified, an accurate adjustment to the experimental VLE data is not feasible.

Nonetheless, the most attractive capability of molecular models is their transferability. This allows obtaining information on other types of properties or how the molecules behave in other environments like in mixtures. In the present report, the two hydrogen bonding molecules ammonia and cyclohexanol, which were modeled in preceding periods, are investigated in this sense. The following section, discusses a fully predictive application of the ammonia model to obtain the transport properties self-diffusion coefficient and shear viscosity over a range of temperature and up to very high pressures, being 2000fold of the ambient pressure. Thereafter, an application of three molecular models for carbon dioxide, cyclohexane and cyclohexanol is given, to describe and predict the phase behavior of the mixtures that can be formed out of these components.

2 Transport Properties of Ammonia

Transport properties play an important role in many fields of science and engineering. They are generally obtained from experiments, however, at high temperatures and pressures, usually sophisticated and expensive equipment is required. Moreover, traditional phenomenological equations of state are often unable to even reproduce the static thermodynamic behavior of hydrogen bonding fluids under these conditions. In cases when direct measurements are difficult, molecular simulation offers an attractive alternative route to predict these properties [1].

Different methods for calculating transport properties using molecular dynamics simulations are available. The equilibrium methods (EMD) using the using either the Green-Kubo formalism or the Einstein relations, analyze the time dependent response of a fluid system to spontaneous fluctuations. In this work, EMD and the Green-Kubo formalism were used to predict the self-diffusion coefficient and the shear viscosity of liquid ammonia. For details on these approaches, see [2].

Ammonia is a well-known chemical intermediate, mostly used in fertilizer industries but also as refrigerant. It is a strongly hydrogen-bonding molecule that possesses a simple symmetric structure, which makes it attractive for experimental and theoretical studies.

Numerous potential models for the intermolecular interactions of ammonia have been proposed in the literature, e.g. [3–5]. These models have mostly been used to study hydrogen bonding in liquid ammonia. Just a few of them have been tested with respect to their ability to predict transport properties. E.g., Impey and Klein [3] predicted the self-diffusion coefficient of liquid ammonia at 260 K, underestimating it by around 45%. Sagarik et al. [4] also tested their model with respect to the self-diffusion coefficient obtaining slightly better results than [3]. Only Mansour and Murad [5] predicted the self-diffusion coefficient and the shear viscosity along the coexistence curve achieving a good agreement to experimental data.

The present work assesses the predictive power of the rigid, non-polarizable molecular model for ammonia developed in preceding work of our group [6] with respect to transport properties over a wide range of thermodynamic conditions. It was also reported in the present book series in 2005 [7] on the development of this ammonia model. The ammonia model was optimized on the basis of quantum mechanical data as well as experimental data on vapor pressure and saturated liquid density. No experimental transport property data was thus taken into account.

Two types of transport properties, i.e. self-diffusion coefficient and shear viscosity, were studied here using EMD and the Green-Kubo formalism. Both properties were predicted for ammonia at 10, 50, 75, 100, 150 and 200 MPa in the temperature range from 203 to 473 K. Exemplarily, Fig. 1 shows the temperature dependence of the predicted self-diffusion coefficient at a pressure of 50 MPa in comparison with experimental data from the literature. The predicted temperature dependence of the shear viscosity is shown in Fig. 2 at 50 MPa together with data taken from the literature.

As can be seen, the predicted transport properties show a good agreement with the data from the literature. This is the case throughout the regarded wide range of temperature and pressure with a similar accuracy. Molecular modeling and simulation correctly reproduces the temperature dependence for both properties. The predicted self-diffusion coefficient deviates from the literature data by 8% on average and the shear viscosity by 12%. Higher deviations are observed for the shear viscosity at low temperatures, where the molecular approach tends to overestimations. This can be explained as an effect of the long-time behavior of the shear viscosity autocorrelation function, cf. [2]. In case of the self-diffusion coefficient, the molecular model exhibits at high temperatures a slightly lower molecular mobility than indicated by the experiment. Nonetheless, it was confirmed that molecular modeling is a robust approach to predict transport properties also for strongly hydrogen bonding fluids like ammonia.

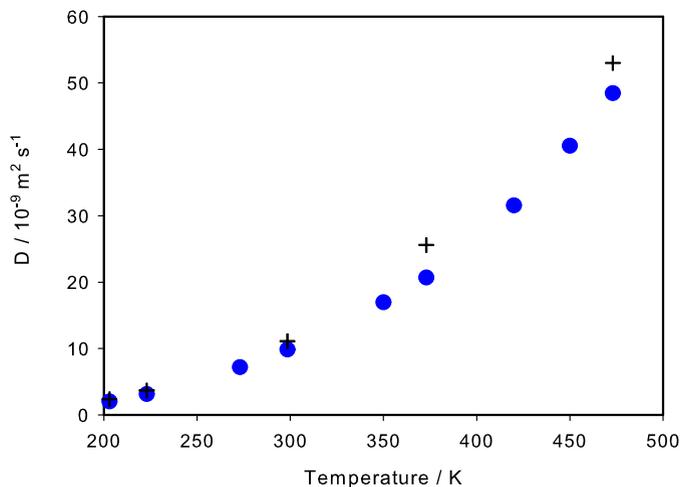


Fig. 1. Temperature dependence of the self-diffusion coefficient of ammonia at 50 MPa. Present simulation results (●) are compared to literature data (+) from [8]

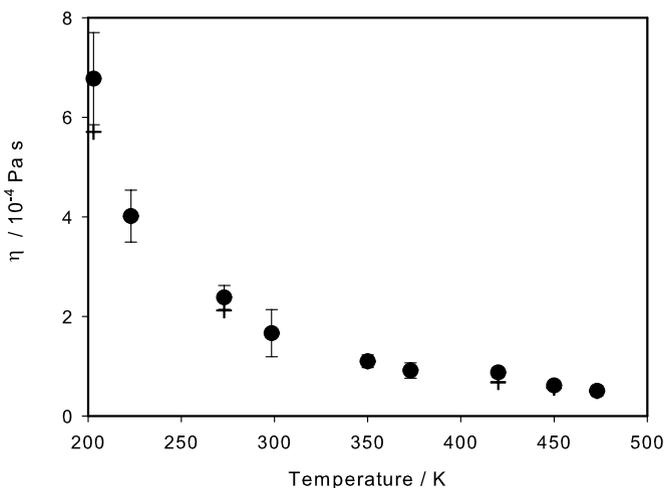


Fig. 2. Temperature dependence of the shear viscosity of pure ammonia at 50 MPa. Present simulation results (●) are compared to literature data (+) from [9]

3 Vapor-Liquid Equilibria of Carbon Dioxide + Cyclohexane + Cyclohexanol and Its Subsystems

In the Collaborative Research Centre 706 (SFB 706) at the University of Stuttgart, novel octahedral molecular sieves for the heterogeneously catalyzed selective oxidation of cyclohexane are investigated. There, supercritical fluids and carbon dioxide-expanded liquids are used as innovative reaction media.

For a rational planning of catalytic experiments and process design, especially at higher pressures, reliable thermodynamic data are needed. Due to the fact that systems containing both oxygen and cyclohexane are highly reactive, they can hardly be investigated with respect to the phase behavior. Most groups used nitrogen as a substitute for oxygen to predict the phase behavior of the reacting system. Alternatively, for predictive applications, e.g. the Peng-Robinson equation of state has been used. Molecular modeling and simulation is an approach to generate data on a physically more sound basis.

Using the molecular model for cyclohexanol that was reported in the present book series in 2008 [10], predictions of VLE of the ternary mixture carbon dioxide + cyclohexane + cyclohexanol were carried out. The molecular models for carbon dioxide [11] and cyclohexane [12] were taken from prior work of our group as well. For an accurate modeling of mixtures, the pairwise unlike interactions have to be determined. While the unlike polar interactions are fully specified by the laws of electrostatics, the unlike dispersive interaction is not straightforward. In order to specify this often weak cross-interaction, combining rules are applied. Here, the modified Lorentz-Berthelot combining rule with one state-independent binary interaction parameter ξ was used

$$\sigma_{ab} = \frac{\sigma_a + \sigma_b}{2}, \quad (1)$$

$$\epsilon_{ab} = \xi \sqrt{\epsilon_a \epsilon_b}. \quad (2)$$

For VLE, ξ should be adjusted to a single experimental binary vapor pressure, as shown in [13]. In the following, the adjustment and predictions for the three binary subsystems and the ternary system are presented.

3.1 Carbon Dioxide + Cyclohexane

The binary interaction parameter ξ was adjusted for this binary mixture at 410.9 K to the vapor pressure, yielding a value of $\xi = 0.978$. Figure 3 presents the simulation results together with experimental data [14–16] and the Peng-Robinson equation of state [17] over a range of temperature from 344.4 to 473.15 K. For 410.9 K the agreement between simulation and experiment is excellent, however, at 473.15 K simulation overpredicts the vapor pressure and at 344.4 K simulation somewhat underpredicts the vapor pressure. Interestingly, the Peng-Robinson equation of state shows the same trend.

3.2 Carbon Dioxide + Cyclohexanol

For the binary mixture carbon dioxide + cyclohexanol the binary interaction parameter was adjusted to the vapor pressure at 393 K, yielding $\xi = 0.938$. Of these components, cyclohexanol is hydrogen bonding. For mixtures with hydrogen bonds, classical equations of state, like the one by Peng and Robinson

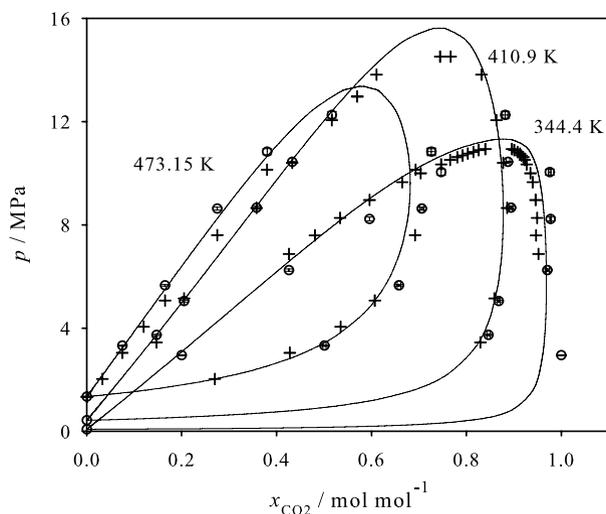


Fig. 3. Vapor-liquid equilibria of carbon dioxide + cyclohexane at 344.4, 410.9 and 473.15 K: (●) present simulation data; (+) experimental data [14–16]; (—) Peng-Robinson equation of state with $k_{ij} = 0.123$.

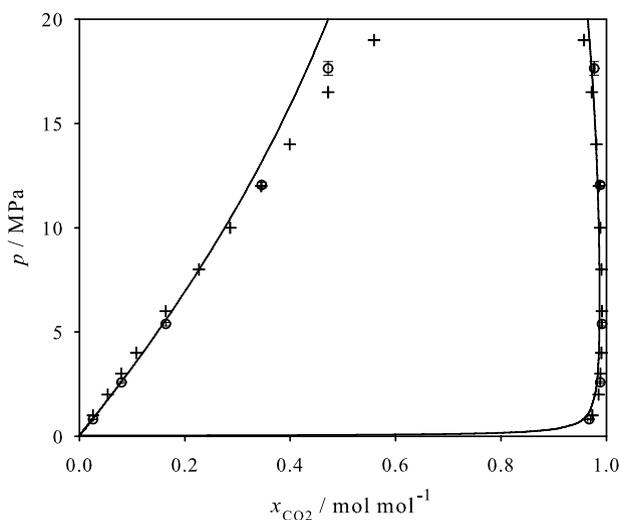


Fig. 4. Vapor-liquid equilibria of carbon dioxide + dicyclohexanol at 393 K: (●) present simulation data; (+) experimental data [18]; (—) Peng-Robinson equation of state with $k_{ij} = 0.15$.

[17], are often inaccurate in predicting the VLE. In Fig. 4 the simulation results are compared to experimental data [18] and the Peng-Robinson equation of state. The simulation results are in a very good agreement with the exper-

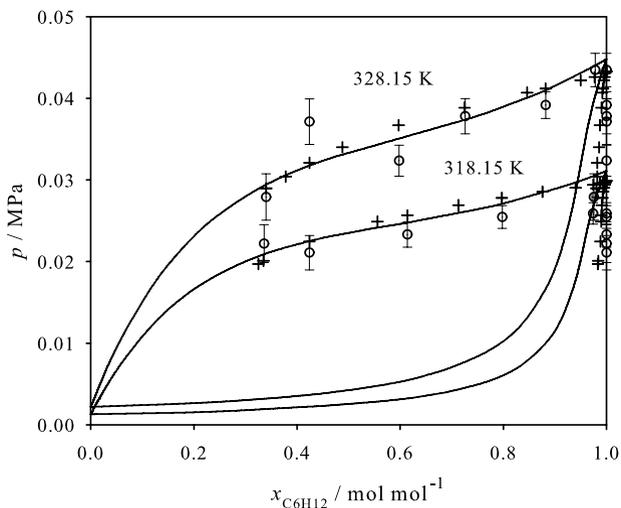


Fig. 5. Vapor-liquid equilibria of cyclohexane + cyclohexanol at 318.15 and 328.15 K: (●) present simulation data; (+) experimental data [19]; (—) Peng-Robinson equation of state with $k_{ij} = 0.0718$.

imental data, whereas the equation of state overpredicts the vapor pressure at high carbon dioxide contents in the liquid.

3.3 Cyclohexane + Cyclohexanol

The last binary mixture presented in this section is cyclohexane + cyclohexanol. Due to the fact that both molecules are large, which results in numerous interaction sites, and that cyclohexanol forms hydrogen bonds, simulating this mixture is computationally very demanding. It was not necessary to adjust ξ , thus the results presented in Fig. 5 are strictly predictive, i.e. $\xi = 1$. Figure 5 shows the simulation results together with experimental data [19] and the Peng-Robinson equation of state for 318.15 and 328.15 K. Note that experimental data is available for these temperatures only. Because these temperatures are near the triple point temperature of both components and thus the vapor pressure is low, the simulation results have high relative statistical uncertainties. Nevertheless, a good agreement with the experimental data was achieved. Also the predicted vapor phase composition from simulation is in a significantly better agreement with the experiment than the equation of state.

3.4 Carbon Dioxide + Cyclohexane + Cyclohexanol

Experimental data for ternary mixtures are very rare. For carbon dioxide + cyclohexane + cyclohexanol only a single VLE data point at 423 K and

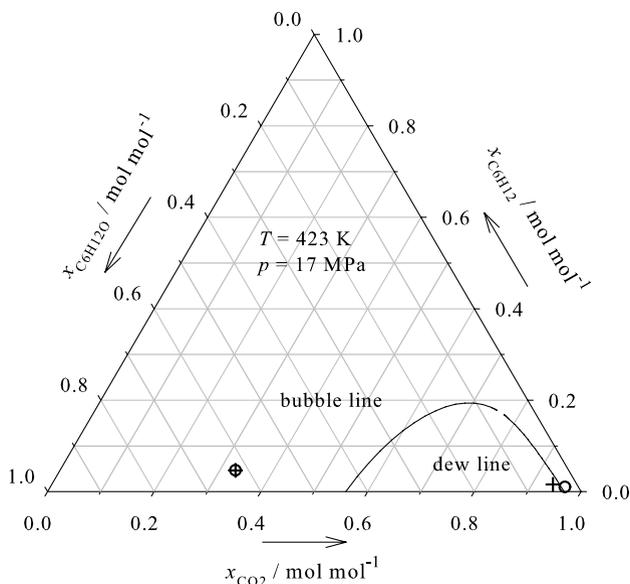


Fig. 6. Vapor-liquid equilibria of carbon dioxide + cyclohexane + cyclohexanol at 423 K and 17 MPa: (●) present simulation data; (+) experimental data [20]; (—) Peng-Robinson equation of state

17 MPa can be found [20]. The simulation result for this data point is predicted with the adjusted binary interaction parameters from the binary subsystems. In Fig. 6 the simulation result, the experimental data and the Peng-Robinson equation of state are compared. A good agreement for the vapor phase concentration between simulation and experiment was found. Nevertheless, the simulative vapor pressure is underpredicted by around 12 %. The Peng-Robinson equation of state is not capable to predict the ternary VLE of this mixture.

4 Conclusion

It was shown that molecular models which are based on quantum mechanical information on geometry and electrostatics and are optimized to experimental pure substance VLE data can be transferred to different predictive applications. Thereby, it was confirmed that hydrogen bonding can be described by eccentric point charges.

For liquid ammonia, transport data that describe the response of a system to external gradients were predicted over a wide range of temperature and pressure. Such data are generally rare, particularly for mixtures. Thus, it was confirmed that molecular modeling and simulation opens up a reliable route to such properties. Further work will investigate multi-component mixtures where hardly any experimental data is available.

The phase behavior of multi-component mixtures is essential for many process engineering applications, like reactions or separations. Particularly reactive, toxic or explosive mixtures are little attractive for experimental approaches so that *in silico* experiments are preferred. For the highly non-ideal mixture carbon dioxide+cyclohexan+cyclohexanol it was shown here that molecular modeling and simulation allow gaining access to necessary thermodynamic data. Subsequent work will include the component oxygen which is reactive and thus problematic *in vivo*, but can well be handled in computer experiments.

References

1. Allen, M.P. *Introduction to Molecular Dynamics Simulation*, Computational Soft Matter, Vol. 23, John von Neumann-Institute for Computing, Julich, 2004
2. Guevara-Carrion, G., Vrabec, J., Hasse, H. *J. Phys. Chem. B* **2008**, *112*, 16664.
3. Impey, R.W., Klein, M.L. *Chem. Phys. Lett.* **1984**, *104*, 579.
4. Sagarik, K.P., Ahlrichs, R., Brode, S. *Mol. Phys.* **1986**, *57*, 1247.
5. Mansour, K.A., Murad, S. *Fluid Phase Equil.* **1987**, *37*, 305.
6. Eckl, B., Vrabec, J., Hasse, H. *Mol. Phys.* **2008**, *106*, 1039.
7. Schnabel, T., Vrabec, J., Hasse, H. in Nagel, W. E.; Jäger, W.; Resch, M. (Eds.). *High Performance Computing in Science and Engineering '05* **2006**, 319.
8. Gross, T., Buchhauser, J., Price, W., Tarasov, I.N., Lüdemann, H. *J. Mol. Liq.* **1997**, *73*, 433.
9. Lemmon, E.W., Huber, M.L., McLinden, M.O. *Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties -REFPROP*; NIST: 2007.
10. Merker T., Guevara-Carrion G., Vrabec J., Hasse H. in Nagel, W. E.; Kröner, D. B.; Resch, M. (Eds.). *High Performance Computing in Science and Engineering '08* **2009**, 529.
11. Vrabec, J., Stoll, J., Hasse, H. *J. Phys. Chem. B* **2001** *105*, 12126.
12. Eckl, B., Vrabec, J., Hasse H. *J. Phys. Chem. B* **2008** *112*, 12710.
13. Schnabel, T., Vrabec, J., Hasse H. *J. Mol. Liq.* **2007**, *135*, 170.
14. Nagarajan, N., Robinson, R.L. Jr. *J. Chem. Eng. Data* **1987**, *32*, 369.
15. Shibata, S.K., Sandler, S.I. *J. Chem. Eng. Data* **1989**, *34*, 419.
16. Krichevski, I.R., Sorina, G.A. *Russ. J. Phys. Chem.* **1960**, *34*, 679.
17. Smith, J.M., Van Ness, H.C., Abbott, M.M. *Introduction to chemical engineering thermodynamics*, McGraw-Hill, New York, 1996.
18. Chen, J.-T., Lee, M.-J. *J. Chem. Eng. Data* **1996**, *41*, 339.
19. Chevalley, J. *Bull. Soc. Chim. Fr.* **1961**, *52*, 510.
20. Mukhapadhy, M., Srinivas, P. *Ind. Eng. Chem. Res.* **1996**, *35*, 4713.