Fluid Phase Equilibria 316 (2012) 46–54

Contents lists available at SciVerse ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

On the prediction of transport properties of monomethylamine, dimethylamine, dimethylether and hydrogen chloride by molecular simulation

G. Guevara-Carrion[a], J. Vrabec[b,*], H. Hasse[a]

[a] *Laboratory for Engineering Thermodynamics, Technical University of Kaiserslautern, Erwin-Schrödinger-Straße 44, 67663 Kaiserslautern, Germany*
[b] *Thermodynamics and Energy Technology, University of Paderborn, Warburger Straße 100, 33098 Paderborn, Germany*

ARTICLE INFO

Article history:
Received 19 September 2011
Received in revised form 7 November 2011
Accepted 5 December 2011
Available online 13 December 2011

Keywords:
Green–Kubo
Reverse non-equilibrium molecular dynamics
Diffusion coefficient
Shear viscosity
Thermal conductivity

ABSTRACT

Molecular modeling and simulation has emerged in recent years as a powerful engineering tool for the prediction of thermodynamic properties of fluids. In this work, transport properties of monomethylamine, dimethylamine, dimethylether and hydrogen chloride are predicted by molecular simulation, employing rigid, non-polarizable molecular models that were developed without using any transport property information. Equilibrium molecular dynamics as well as non-equilibrium molecular dynamics are used to predict self-diffusion coefficient, shear viscosity and thermal conductivity of the studied liquids for a wide range of thermodynamic conditions. In most cases, the reported predictions deviate on average by less than 10% from the available experimental data.

1. Introduction

In recent years, the need for transport data has increased in the chemical industry. Among others, this is due to the growing use of rate-based methods for process modeling. Traditionally, thermodynamic properties are obtained from experiments, however, despite the extensive effort devoted to their measurement, the data availability is still surprisingly low and the data sets are in many cases contradictory. This is associated with the significant effort to measure thermophysical properties, particularly at very high temperatures and pressures [1], or to deal experimentally with substances that are toxic or explosive. Compared to static properties like vapor–liquid equilibria, transport data are very scarce. Because traditional phenomenological models for transport properties are little reliable in the liquid state, molecular simulation has emerged as an alternative engineering tool for predictive applications.

The aim of this work is to demonstrate the capability of molecular modeling and simulation to predict the technically most relevant transport properties, i.e. self-diffusion coefficient, shear viscosity and thermal conductivity, of monomethylamine (MMA, $CH_3—NH_2$), dimethylamine (DMA, $(CH_3)_2—NH$), dimethylether (DME, $(CH_3)_2—O$) and hydrogen chloride (HCl). As in previous work of our group, rigid, non-polarizable molecular models were used. This model class is suitable to predict structural and thermodynamic properties of hydrogen bonding fluids with a good accuracy, e.g. water, methanol, ethanol, ammonia and some binary mixtures thereof [2–4]. Equilibrium molecular dynamics (EMD) simulation together with the Green–Kubo formalism was used to determine the self-diffusion coefficient and the shear viscosity. The shear viscosity and the thermal conductivity were calculated via the reverse non-equilibrium molecular dynamics (NEMD) algorithm by Müller-Plathe [5]. These transport properties were predicted in the liquid state for a wide range of thermodynamic conditions and a comparison between EMD and NEMD results is given for the shear viscosity.

The studied fluids have important industrial applications. The weakly hydrogen bonding amines MMA and DMA are widely used as intermediates in chemical synthesis, e.g. in the production of solvents, pesticides, pharmaceuticals, dyes or surfactants [6,7]. DME is largely used as a substitute for chlorofluorocarbons, i.e. as an aerosol propellant, refrigerant or petroleum gas [8–10]. It is also used as feedstock for the production of higher value chemicals, e.g. acetic acid or formaldehyde [11]. HCl is a very hazardous fluid that is widely used in the chemical, pharmaceutical, oil and food industry [12], e.g. as an intermediate or catalyst in the production of higher value chemicals [13]. The success of molecular simulation to predict thermodynamic properties is primarily determined by the force field that describes the molecular interactions. Many of the molecular models from the literature for MMA and DMA

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[*] Corresponding author. Tel.: +49 0 5251 60 2421; fax: +49 0 5251 60 3522.
E-mail addresses: jadran.vrabec@uni-paderborn.de, jadran.vrabec@upb.de (J. Vrabec).

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doi:10.1016/j.fluid.2011.12.009

are based on transferable force fields developed for biological systems, e.g. OPLS-AA [14], CFF [15] or CHARMM [7], which usually include Lennard–Jones (LJ) sites, point charges as well as internal degrees of freedom, i.e. bond stretching, angle and dihedral bending. Other molecular models are based on transferable force fields that were developed for chemical engineering applications, e.g. the anisotropic united atom force field (AUA) [16], the TraPPE-EH force field [17] or the discontinuous force field SPEAD [18]. They were primarily employed for studying the fluid structure [19] and thermodynamic properties like free energy of hydration [14] or vapor–liquid equilibria [17,18]. However, only a few models were assessed with respect to their capability to predict transport properties. Kosztolányi at al. [20] and Kusalik et al. [21] predicted the self-diffusion coefficient of MMA at 250 K using the rigid model by Impey et al. [22]. Bauer and Patel [7] also predicted the self-diffusion coefficient of MMA at 266.8 K based on their polarizable model. Recently, Feng et al. [23] predicted the self-diffusion coefficient of MMA for different thermodynamic conditions based on a modification of the OPLS-AA model [14]. To our knowledge, the self-diffusion coefficient of DMA as well as the shear viscosity and thermal conductivity of both amines were not studied by molecular simulation prior to this work.

A variety of molecular models for DME can be found in the literature, e.g. flexible models based on transferable [24–26], discontinuous [27] or polarizable [28] force fields as well as rigid models [29–31]. However, to our knowledge, none of them was employed to predict the transport properties of DME by molecular simulation.

HCl is the smallest molecule considered in this work and has therefore been subject to numerous molecular simulation and quantum mechanical studies in the last 30 years. For HCl, there are several molecular models of different complexity in the literature, e.g. [32–41]. Some of them were used to predict the self-diffusion coefficient [32,33,36,37,41] and the shear viscosity [42] by molecular simulation. The thermal conductivity was not studied prior to this work.

The molecular models employed here for MMA [43], DMA [43], DME [44] and HCl [13] were developed in preceding work of our group. These rigid, united-atom models were optimized to experimental data on vapor pressure and saturated liquid density only. No data on transport properties were taken into account during model parameterization so that all respective results are strictly predictive.

The outline of the present work is as follows: first, the employed molecular models and the simulation techniques are briefly described. Second, the predictions for self-diffusion coefficient, shear viscosity and thermal conductivity of the studied liquids are presented and compared to experimental data and correlations thereof as well as to other simulation results from the literature. Finally, conclusions are drawn. The simulation details are summarized in Appendix B.

2. Molecular models

Throughout this work, rigid, non-polarizable molecular models of united-atom type from earlier work of our group were used. The models account for the intermolecular interactions by one or more LJ sites and superimposed point charges or point dipoles. Thus, the total intermolecular interaction energy u_{ij} between two molecules i and j can be written as

$$u_{ij}(r_{ijab}) = \sum_{a=1}^{S_i^{LJ}}\sum_{b=1}^{S_j^{LJ}} 4\epsilon_{ijab}\left[\left(\frac{\sigma_{ijab}}{r_{ijab}}\right)^{12} - \left(\frac{\sigma_{ijab}}{r_{ijab}}\right)^{6}\right] + \sum_{c=1}^{S_i^e}\sum_{d=1}^{S_j^e} \frac{q_{ic}q_{jd}}{4\pi\varepsilon_0 r_{ijcd}} + \frac{\mu_{ic}\mu_{jd}}{4\pi\varepsilon_0 r_{ijcd}^3}\cdot f\left(\boldsymbol{\omega}_i, \boldsymbol{\omega}_j\right), \qquad (1)$$

where r_{ijab}, ϵ_{ijab} and σ_{ijab} are the distance, the LJ energy parameter and the LJ size parameter, respectively, for the pair-wise interaction between LJ site a on molecule i and LJ site b on molecule j. The permittivity of the vacuum is ε_0, whereas q_{ic} and μ_{ic} denote the point charge magnitude and the dipole moment of the electrostatic interaction site c on molecule i. The expression $f(\boldsymbol{\omega}_i, \boldsymbol{\omega}_j)$ stands for the dependency of the dipole interaction on the orientations $\boldsymbol{\omega}_i$ and $\boldsymbol{\omega}_j$ of the molecules i and j [45]. The pure substance model parameters were taken from [13,43,44] and are summarized in Table 1. The interactions between unlike LJ sites of different type were defined by the standard Lorentz–Berthelot combining rules

$$\sigma_{ab} = \frac{\sigma_{aa} + \sigma_{bb}}{2}, \qquad (2)$$

and

$$\epsilon_{ab} = \sqrt{\epsilon_{aa}\epsilon_{bb}}. \qquad (3)$$

3. Methodology

3.1. Equilibrium molecular dynamics

Transport properties can be determined from the time evolution of the autocorrelation function of a particular microscopic flux in

Table 1
Lennard–Jones and electrostatic parameters of the molecular models employed in this work. The orientation of the dipole moment is defined in standard Euler angles, where φ is the azimuthal angle with respect to the x–z plane and θ is the inclination angle with respect to the z axis. The spatial position of the sites can be found in the original publications [13,43,44].

Interaction sites	σ (Å)	ε/k_B (K)	θ (°)	φ (°)	μ (D)	q (e)
Monomethylamine						
CH_3	3.6072	120.150	–	–	–	+1.95250
NH_2	3.3151	141.147	–	–	–	–0.88653
H	–	–	–	–	–	+0.34564
Dimethylamine						
CH_3	3.6072	120.150	–	–	–	+0.03774
NH	3.4800	72.856	–	–	–	–0.45959
H	–	–	–	–	–	+0.38411
Dimethylether						
O	2.727	89.570	–	–	–	–
CH_3	3.6072	120.150	–	–	–	–
Dipole	–	–	180	0	1.7040	–
Hydrogen chloride						
HCl	3.520	179.00	–	–	–	–
H	–	–	–	–	–	+0.438
Cl	–	–	–	–	–	–0.438