Molecular Model for Formic Acid adjusted to Vapor-Liquid Equilibria

Thorsten Schnabel\textsuperscript{1}, María Cortada\textsuperscript{2}, Jadran Vrabec\textsuperscript{1}\textsuperscript{*}, Santiago Lago\textsuperscript{2}, Hans Hasse\textsuperscript{1}

\textsuperscript{1}Institut für Technische Thermodynamik und Thermische Verfahrenstechnik, Universität Stuttgart, 70550 Stuttgart, Germany

\textsuperscript{2}Departamento de Ciencias Ambientales, Universidad Pablo de Olavide, Carretera de Utrera Km 1, 41013 Sevilla, Spain

Abstract

A new molecular model for formic acid is proposed which favorably describes vapor-liquid equilibrium properties in the full temperature range. The geometry of the model was determined by quantum chemical calculations of the \textit{cis}-conformer. The model is rigid and consists of anisotropic united atom Lennard-Jones sites and point charges, so that it requires relatively little computational effort.

Keywords: formic acid, molecular modeling, vapor-liquid equilibrium

\textsuperscript{*}author to whom correspondence should be addressed, Email: vrabec@itt.uni-stuttgart.de
1 Introduction

Formic acid plays an important role in industrial applications, as in food and chemical industry it is an intermediate from which a large variety of products are obtained. It is, e.g., directly used as a preservative and antibacterial in livestock feed. Also carbon monoxide is often produced in laboratories by the decarbonylation of formic acid with sulfuric acid where the kinetics of the decarbonylation was quantitatively understood recently [1].

Formic acid is the simplest carboxylic molecule and has exceptional thermophysical properties due to its strong ability to act both as hydrogen bond donor and acceptor. Since both hydrogen atoms of formic acid can act as proton donors and both oxygen atoms provide proton acceptance, four unlike hydrogen bond types yield the basis for a complex self-association which is the reason for its exceptional thermophysical behavior. In the gas phase, formic acid tends to form cyclic dimers rather than polymeric chain aggregates. These dimers contain primarily the cis-conformer as investigated by Turi [2] and Roszak et al. [3]. At elevated temperatures and pressures as well as in the crystal phase, the trans-conformer could play an important role [3]. But due to the lower stability of the trans-conformer, the frequently employed rigid molecular model for formic acid of Jedlovszky and Turi [4, 5] is based on the cis-conformer. The energetic and structural properties of the liquid phase are also described favorably by the cis-conformer model of Jedlovszky and Turi [6], which, however, shows significant deviations to experimental data regarding vapor-liquid equilibria. Hence, the present rigid molecular model is introduced to overcome this problem. It also applies the cis-geometry.

2 Molecular Model

Molecular models which accurately describe vapor-liquid equilibria in the full temperature range usually have a good predictive power in most of the fluid region [7, 8]. Hence, for re-
search and industrial applications such molecular models are of great interest. Following this, a simple new formic acid model was developed with the aim to yield a favorable description of the vapor-liquid equilibrium at relatively low computational cost. It neglects the internal degrees of freedom and uses anisotropic united atom Lennard-Jones sites accounting for repulsive and dispersive interactions. Point charges were used to model both polarity and hydrogen bonding of formic acid. In total, three Lennard-Jones sites and four point charge sites at five positions were chosen. Thus, the potential energy $u_{ij}$ between two formic acid molecules $i$ and $j$ is given by

$$u_{ij}(r_{ijab}) = \sum_{a=1}^{5} \sum_{b=1}^{5} 4\varepsilon_{ab} \left[ \left( \frac{\sigma_{ab}}{r_{ijab}} \right)^{12} - \left( \frac{\sigma_{ab}}{r_{ijab}} \right)^{6} \right] + \frac{q_{ia}q_{jb}}{4\pi\varepsilon_0 r_{ijab}},$$

where $a$ is the site index of molecule $i$ and $b$ the site index of molecule $j$, respectively. The site-site distance between molecules $i$ and $j$ is denoted by $r_{ijab}$. $\sigma_{ab}$ and $\varepsilon_{ab}$ are the Lennard-Jones size and energy parameters, $q_{ia}$ and $q_{jb}$ are the point charges located at the sites $a$ and $b$ on the molecules $i$ and $j$, respectively. Finally, $\varepsilon_0$ is the permittivity of vacuum. The interaction between unlike Lennard-Jones sites is defined by the Lorentz-Berthelot combining rule [9, 10]

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

$$\varepsilon_{ab} = \sqrt{\varepsilon_{aa}\varepsilon_{bb}}. \quad (3)$$

Figure 1 depicts the positions of the interaction sites of the present molecular model and Table 1 gives the model parameters according to Equation (1). In order to avoid unphysical interactions due to the superposition of point charge and Lennard-Jones potentials at very small site-site distances, which primarily may occur in Monte Carlo simulations, internal hard-sphere cutoffs at the point charge sites are employed. Such internal hard-sphere cutoffs were also used
e.g. by Lísal et al. [11] for vapor-liquid equilibrium simulations of hydrogen bonding components. However, their internal hard-sphere cutoffs were located at the Lennard-Jones sites, hence, the cutoffs chosen by Lísal et al. [11] were considerably larger than the present ones, which are located directly at the point charge sites. Such an approach was previously proposed by Möller and Fischer [12] and Stoll [13]. The diameter of an internal hard-sphere located at site \( a \) is termed \( \sigma_{aa}^c \) in the following. The internal hard-sphere diameter \( \sigma_{ab}^c \) between unlike point charges is set to the arithmetic mean of the like internal hard-sphere cutoff diameters. During a simulation, the pair potential between molecules \( i \) and \( j \) is set to infinity if \( r_{ijab} \leq \sigma_{ab}^c \).

The like internal hard-sphere diameters of the present formic acid model are included in Table 1.

In the following, a few remarks on the model development are given. Nuclei positions of the formic acid atoms were calculated using the quantum chemistry software package GAMESS (US) [14]. For the geometry optimization, the Hartree-Fock, i.e. self-consistent field (SCF), method was applied using the basis set 6-31G, which is a split-valence orbital basis set without polarizable terms. Figure 1 includes these nuclei positions, labeled \( \text{N}_C, \text{N}_O \) and \( \text{N}_H \), obtained by the geometry optimization. This optimized geometry was only used to deduce the geometry of the present model. However, the interaction sites of the formic acid model do not coincide with the nuclei positions of the quantum chemistry calculations since offsets for the anisotropic united atom sites were used.

To obtain a parameter set of a formic acid model which favorably describes the vapor-liquid equilibrium in the full temperature range, the optimization procedure of Stoll [13] was applied. This procedure employs the sensitivity of the model parameters on bubble density and vapor pressure over a wide temperature range. An initial model based on nuclei positions from quantum chemical calculation was used as a starting point for the systematical variation of the model parameters. The Lennard-Jones and offset parameters of the hydroxyl and CH group as well
as the Lennard-Jones parameters of the carboxylic oxygen were taken from models previously
developed for other molecules. For the initial model, four point charges were employed, three
of them were placed at the Lennard-Jones centers and one at the acidic hydrogen. Thus, for the
starting model the positive formic hydrogen point charge was concentrically superimposed to
the anisotropic united atom Lennard-Jones CH site. Since the formic hydrogen atom also forms
weak hydrogen bonds (C–H···O), as investigated by Roszak et al. [3] as well as Jedlovszky and
Turi [6], the positive formic hydrogen point charge was shifted during the optimization proce-
dure into the direction of the formic hydrogen nucleus, cf. Figure 1. Note that the superposition
of positive point charges to excentrical Lennard-Jones sites is commonly used to model hydro-
gen bonding. All vapor-liquid equilibrium calculations of the models used in this work were
obtained by molecular simulations, technical details are given in the following section.

3 Simulation Details

In all simulations \( N = 864 \) molecules were used. The calculation of the vapor-liquid equilibrium
of formic acid was done with the \( NpT+ \) test particle method [12, 15, 16] based on the Monte
Carlo technique. In order to determine the chemical potential of the liquid and vapor phase,
the gradual insertion method [17, 18, 19] was applied. The liquid runs were equilibrated in the
\( NpT \) ensemble over 10 000 cycles and the maximum displacements for translation, rotation and
volume were adjusted to yield acceptance rates of 50 \%. After that, gradual insertions and dele-
tions were performed over 5 000 Monte Carlo cycles with fluctuating molecules to equilibrate
the weights of the transition states. The production phase was performed over 50 000 Monte
Carlo cycles with constant weights of the transition states and constant maximum displacements
for translation, rotation and volume.

Due to the formation of hydrogen bonded clusters, particularly in the vapor phase at low
temperatures, the equilibration phase was carried out significantly longer than for the liquid phase. However, the sampling of the chemical potential in the production phase was 60 000 Monte Carlo cycles for the vapor. The cutoff radius was set to 18 Å in all liquid phase runs. For the simulation of the vapor phase, the radius of the cutoff sphere was chosen close to half of the length of the cubic simulation box to obtain faster equilibration yielding hydrogen bonded aggregates and a more accurate sampling. The Lennard-Jones long range interactions beyond the cut-off radius were corrected employing angle averaging proposed as by Lustig [20]. The coulombic interactions were corrected using the reaction field method [21].

4 Vapor-Liquid Equilibrium Results

Vapor-liquid equilibrium results of the present molecular model for formic acid are compared to experimental data [22] in Figures 2 to 4. These figures also include the results of Chialvo et al. [23] who used the molecular model of Jedlovszky and Turi [4, 5]. The results of Chialvo et al. [23] had to be extracted from the published graphs since the numerical data were not accessible to us. For the saturated densities in Figure 2, also Gibbs ensemble Monte Carlo results for the model of Jedlovszky and Turi [4, 5] are available from Mináry et al. [24, 25]. The present numerical simulation results together with experimental data [22] are given in Table 2. Simulation results were tested for thermodynamic consistency with the Clausius-Clapeyron equation and consistency is given for the present model in the scope of the simulation uncertainties.

The present bubble densities agree well with the experiment, the mean unsigned error is only 0.8 %. Note that the bubble density of the present model at 290 K shown in Figure 2 was estimated by a $NpT$ simulation at vanishing pressure. However, the agreement of the dew densities with a mean unsigned error of 29 % is poor. The “experimental” dew densities were obtained from the Clausius-Clapeyron equation using experimental vapor pressure, bubble den-
sity and heat of vaporization [22]. These “experimental” dew densities are in good agreement with dew densities evaluated with the dimerization constant for formic acid proposed by Büttner and Maurer [27] up to 400 K. Figure 2 indicates that the new molecular model is significantly more precise regarding the saturated densities than the model of Jedlovszky and Turi [4, 5].

The new molecular model is also much more accurate for the vapor pressure and the heat of vaporization, cf. Figures 3 and 4. The vapor pressure is described by the new molecular model with a mean unsigned error of 5.1 %. However, the heat of vaporization shows a reasonable temperature dependence, but significant deviations are present, where the mean unsigned error is 20 %. It can be speculated that this is due to the inability of the present model to yield accurate vapor configurations. Following the procedure suggested by Lotfi et al. [26], the critical values of temperature, density and pressure were determined (experimental value in parentheses): \( T_c = 604.90 \) (588.00) K, \( \rho_c = 8.21 \) (8.00) mol/l and \( p_c = 7.02 \) (5.81) MPa. The critical temperature is predicted too high predominantly due to the deviations in the dew density.

5  Conclusion

A new molecular model for formic acid based on the cis-conformer was developed. The advantages of this model are that it accurately describes bubble densities and vapor pressures from temperatures near to the triple point up to the critical point and that it requires relatively little computational resources. Although a simple modeling approach was employed to describe hydrogen bonding and polarity, it is capable to describe these effects in terms of the regarded thermodynamic properties. However, limitations of such a simple modeling approach for the strongly hydrogen bonding formic acid were found which are visible here in the unsatisfying representation of the dew density and the heat of vaporization. Compared to the frequently used molecular model of Jedlovszky and Turi [4, 5] it is much more precise for vapor-liquid
equilibrium properties.

6 Acknowledgment

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References


Table 1: Lennard-Jones, point charge, internal hard-sphere and geometry parameters of the present formic acid model, cf. Equation (1) and Figure 1; the electronic charge is $e = 1.6021 \ldots \times 10^{-19}$ C.

<table>
<thead>
<tr>
<th>Site</th>
<th>$\sigma_{aa}$ Å</th>
<th>$\varepsilon_{aa}/k_B$ K</th>
<th>$q_{ia}$ $e$</th>
<th>$\sigma_{aa}^c$ Å</th>
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<tr>
<td>S_O</td>
<td>2.9953</td>
<td>96.696</td>
<td>−0.42186</td>
<td>0.2995</td>
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<tr>
<td>S_C_H</td>
<td>3.2335</td>
<td>59.993</td>
<td>0</td>
<td>0</td>
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<tr>
<td>S_H(C)</td>
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<td>S_O_H</td>
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<td>85.053</td>
<td>−0.31574</td>
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<td>S_H(O)</td>
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<td>0</td>
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<tr>
<th>$h_1$ Å</th>
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<th>$h_3$ Å</th>
<th>$h_4$ Å</th>
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<table>
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<th>$\gamma_1$</th>
<th>$\gamma_2$</th>
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<tr>
<td>125.545</td>
<td>120.255</td>
<td>110.804</td>
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</table>
Table 2: Vapor-liquid equilibrium of formic acid: simulation results compared to experimental data [22] for vapor pressure, saturated densities and heat of vaporization. The numbers in parentheses indicate the statistical uncertainty in last digit. The “experimental” dew densities were derived from the Clausius-Clapeyron equation.

<table>
<thead>
<tr>
<th>$T$ K</th>
<th>$p_{\text{sim}}$ MPa</th>
<th>$p_{\text{exp}}$ MPa</th>
<th>$\rho'_{\text{sim}}$ mol/l</th>
<th>$\rho'_{\text{exp}}$ mol/l</th>
<th>$\rho''_{\text{sim}}$ mol/l</th>
<th>$\rho''_{\text{exp}}$ mol/l</th>
<th>$\Delta h^v_{\text{sim}}$ kJ/mol</th>
<th>$\Delta h^v_{\text{exp}}$ kJ/mol</th>
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<tr>
<td>335</td>
<td>0.030(1)</td>
<td>0.027</td>
<td>25.18(2)</td>
<td>25.36</td>
<td>0.0197(1)</td>
<td>0.0165</td>
<td>18.12(8)</td>
<td>20.97</td>
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<tr>
<td>360</td>
<td>0.067(1)</td>
<td>0.066</td>
<td>24.48(3)</td>
<td>24.64</td>
<td>0.0428(3)</td>
<td>0.0352</td>
<td>17.96(7)</td>
<td>21.68</td>
</tr>
<tr>
<td>385</td>
<td>0.145(3)</td>
<td>0.140</td>
<td>23.76(2)</td>
<td>23.87</td>
<td>0.0933(5)</td>
<td>0.0672</td>
<td>17.69(7)</td>
<td>22.36</td>
</tr>
<tr>
<td>410</td>
<td>0.267(5)</td>
<td>0.269</td>
<td>22.90(3)</td>
<td>23.06</td>
<td>0.153 (1)</td>
<td>0.1177</td>
<td>17.95(9)</td>
<td>22.93</td>
</tr>
<tr>
<td>435</td>
<td>0.513(6)</td>
<td>0.480</td>
<td>22.08(3)</td>
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<td>0.803</td>
<td>21.15(3)</td>
<td>21.25</td>
<td>0.393 (2)</td>
<td>0.3033</td>
<td>18.09(7)</td>
<td>23.37</td>
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<tr>
<td>485</td>
<td>1.36 (2)</td>
<td>1.275</td>
<td>20.23(3)</td>
<td>20.20</td>
<td>0.615 (4)</td>
<td>0.4617</td>
<td>17.98(8)</td>
<td>22.98</td>
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<tr>
<td>510</td>
<td>1.92 (3)</td>
<td>1.937</td>
<td>18.96(5)</td>
<td>19.01</td>
<td>0.914 (6)</td>
<td>0.6933</td>
<td>17.01(8)</td>
<td>21.93</td>
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<td>2.839</td>
<td>17.74(5)</td>
<td>17.58</td>
<td>1.36 (1)</td>
<td>1.0465</td>
<td>15.93(9)</td>
<td>19.99</td>
</tr>
<tr>
<td>560</td>
<td>4.4 (1)</td>
<td>4.036</td>
<td>16.17(7)</td>
<td>15.69</td>
<td>2.01 (2)</td>
<td>1.6384</td>
<td>14.2 (1)</td>
<td>16.72</td>
</tr>
</tbody>
</table>
List of Figures

1 Geometry of the present formic acid model: $S_i$ indicates the model interaction site $i$ and $N_j$ the nucleus position of atom $j$ of the cis-conformer obtained from quantum chemical calculations. Note that all sites of the present model are within a plane.

2 Saturated densities of formic acid: ● present simulation results, ▼ simulation results of Chialvo et al. [23] using the model of Jedlovszky and Turi [4, 5], □ simulation results of Mináry et al. [24, 25] using the model of Jedlovszky and Turi [4, 5], — experimental data [22]. Present simulation uncertainties are within symbol size.

3 Vapor pressure of formic acid: ● present simulation results, ▼ simulation results of Chialvo et al. [23] using the model of Jedlovszky and Turi [4, 5], — experimental data [22]. Present simulation uncertainties are within symbol size.

4 Heat of vaporization of formic acid: ● present simulation results, ▼ simulation results of Chialvo et al. [23] using the model of Jedlovszky and Turi [4, 5], — experimental data [22]. Present simulation uncertainties are within symbol size.
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Figure 2: Schnabel et al.
Figure 3: Schnabel et al.
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