Hydrogen Bonding of Methanol in Supercritical CO\textsubscript{2}: Comparison between \textsuperscript{1}H NMR Spectroscopic Data and Molecular Simulation Results

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Molecular dynamics simulation results on hydrogen bonding in mixtures of methanol with CO\textsubscript{2} at supercritical, liquid-like conditions are compared to \textsuperscript{1}H NMR spectroscopic data that have recently become available. The molecular models are parametrized using vapor—liquid equilibrium data only, which they reliably describe. A new molecular model for methanol of Lennard-Jones plus point charge type is presented. This molecular methanol model is investigated in terms of its capability to yield hydrogen-bonding statistics. Simple assumptions are made regarding the assignment of NMR chemical shifts to the different types of hydrogen-bonded species. Only two state-independent parameters are fitted to the large NMR data set on the basis of hydrogen-bonding statistics from molecular simulations. Excellent agreement between the molecular simulation results and the NMR data is found. This shows that the molecular models of the simple type studied here cannot only describe thermodynamic properties but also structural effects of hydrogen bonding in solutions.

1. Introduction

Despite long-standing efforts with different approaches, modeling thermophysical properties of strongly hydrogen-bonding systems remains a challenge. Phenomenological models often fail to describe the interplay between the energetics of hydrogen bonding and its structural effects. Molecular force field models are much better suited for solving that task. However, most of the presently available molecular models use crude assumptions. In many cases, hydrogen bonding is simply described by point charges which are eccentrically superimposed on Lennard-Jones potentials. That simple approach has, however, turned out to be fruitful in many ways. For example, the thermodynamic properties of many hydrogen-bonding fluids such as alcohols\textsuperscript{1,2}, amines\textsuperscript{3}, and thiols\textsuperscript{4} can be represented well with that model class.

As a first step, such a simple rigid united-atom Lennard-Jones plus point charge model for methanol (MeOH) was reparameterized here to optimally describe the experimental vapor—liquid equilibria properties. The focus of the present work, however, lies on a study of the structural properties of the new methanol model, namely, the hydrogen-bonded species distribution in mixtures with CO\textsubscript{2}. As no structural data were used in the model development, the hydrogen-bonding statistics from molecular dynamics simulation are predictions.

The new methanol model, which is composed out of a rigid set of two Lennard-Jones sites and three point charges, is described in Appendix A. It is shown there that it yields reliable results for vapor—liquid equilibria over the whole relevant temperature range. The molecular model for CO\textsubscript{2} was taken from previous work of our group and was also adjusted to vapor—liquid equilibria\textsuperscript{5}. The unlike Lennard-Jones energy parameter of the mixture methanol + CO\textsubscript{2} was adjusted to one binary vapor pressure data point following previous work\textsuperscript{6,7}. The resulting model describes vapor—liquid equilibria of the mixture well, as shown in Appendix A.

Molecular dynamics simulations for the mixture methanol + CO\textsubscript{2} were carried out here to obtain hydrogen-bonding statistics for methanol, which are compared to experimental data of \textsuperscript{1}H NMR chemical shifts from recent work of our group.\textsuperscript{8} Those data were taken at 293.15, 308.15, 323.15, and 338.15 K, starting from small methanol mole fractions and covering the full composition range up to pure methanol for pressures between 10 and 20 MPa. The experimental setup and the procedure used for obtaining the NMR data at the studied liquid-like supercritical conditions for methanol + CO\textsubscript{2} are described in ref 9.

The relative NMR chemical shift δ of the protons in the hydroxyl group to those in the methyl group of the methanol molecule is used in the present investigation of the hydrogen-bonding properties. This relative quantity is studied to eliminate effects from changes in the bulk magnetic susceptibility\textsuperscript{10} and to avoid density effects on other nonspecific contributions to the nuclear shielding of the hydroxyl group.\textsuperscript{11,12} The word “relative” is omitted in the following for the sake of brevity, and we simply refer to the chemical shift. The chemical shift is a weight-average over all methanol species since the lifetime of a hydrogen bond, being on the order of a few picoseconds,\textsuperscript{13} is much shorter than the NMR resolution time. For example, Astley et al.\textsuperscript{14} found good agreement between the lifetime of hydrogen bonds obtained by molecular simulations and that from experiment. Hence, molecular dynamics simulation is appropriate to yield hydrogen-bonding statistics as it can resolve this time scale straightforwardly.

In order to allow a comparison between the NMR data of Maiwald et al.\textsuperscript{9} and present hydrogen-bonding statistics from molecular simulation, parameters for the chemical shifts have to be assigned to the different hydrogen-bonded methanol species. The characterization of the different species types is described in section 2. The state-independent parameter for the chemical shift of the methanol monomer was directly obtained...
from the experimental NMR data. The species are grouped so that only two further chemical shifts have to be assigned, one for methanol molecules acting as a proton donor and one for methanol molecules acting as an acceptor. These two state-independent parameters were determined from a fit to the extensive experimental NMR data set on the basis of the hydrogen-bonding statistics from molecular simulation. The very good description of the NMR data obtained in this work shows that the new molecular model of methanol describes structural properties well and, more generally, supports the concept of modeling hydrogen bonding with point charges eccentrically superimposed on Lennard-Jones potentials. Other work on NMR chemical shifts for methanol + CO$_2$, for example, by Kanakubo et al.\textsuperscript{13} as well as Bai and Yonker\textsuperscript{16} presents databases that would have been too narrow for such a study.

Molecular models were previously tested using NMR data on hydrogen bonding, for example, by Bai and Yonker\textsuperscript{16} as well as Wallen et al.\textsuperscript{11,12} Furthermore, phenomenological methods were often used to describe that type of data. A review of phenomenological self-association models based on physical and chemical theory, which were published before 1996, is given by Hasse.\textsuperscript{17} More recent investigations on different phenomenological self-association models for NMR data were carried out, for example, by Asprion et al.,\textsuperscript{18} Shekaari et al.,\textsuperscript{19} Asahi and Nakamura,\textsuperscript{20} or Wallen et al.\textsuperscript{11,12}

### 2. Hydrogen-Bonding Criteria and Types of Hydrogen-Bonded Species

Several geometric or energetic criteria were proposed in the literature to identify hydrogen bonds in molecular simulation studies. Probably the most commonly applied criterion for hydrogen bonding of methanol is the geometric criterion introduced by Haughney et al.\textsuperscript{13} It was also used in the present study. This criterion was developed on the basis of experimental pair distribution functions of pure liquid methanol from X-ray and neutron scattering experiments. According to the geometric criterion of Haughney et al.,\textsuperscript{13} two methanol molecules in a molecular simulation are regarded as hydrogen-bonded if their oxygen site-site separation distance $r_{OO}$ is below 3.5 Å, the hydrogen site to oxygen site distance $r_{OH}$ is below 2.6 Å, and the angle between oxygen-oxygen alignment and the oxygen-hydrogen bond $\theta_{OO-OH}$ is below 30°. The molecular dynamics investigation of Chaliris and Samios\textsuperscript{21} on hydrogen bonding in supercritical methanol supports the usefulness of this criterion at high-pressure conditions.

Other authors suggested modifications of this geometric criterion. For example, Wallen et al.\textsuperscript{11} used the simple assumption that a hydrogen bond is established if $r_{OH}$ is below 2.5 Å, arguing that this distance corresponds to the first minimum of the hydrogen-bonding peak in the oxygen-hydroxyl hydrogen atom pair distribution function. In the Monte Carlo simulation study on self-association of methanol in supercritical CO$_2$ by Stubbs and Siepmann,\textsuperscript{22} the distance criterion for hydrogen bonds between methanol molecules is the same as the criterion proposed by Haughney et al.\textsuperscript{13} However, Stubbs and Siepmann used other limits for the orientation between hydrogen-bonded methanol molecules. A slightly modified geometric criterion for the self-association was applied by Chatzis and Samios\textsuperscript{23} in a simulation study of methanol in supercritical CO$_2$, $r_{OO}$ below 3.6 Å, $r_{OH}$ below 2.5 Å, and $\theta_{OO-OH}$ below 30°. Note that these two studies\textsuperscript{22,23} used other molecular models than that of the present work. Furthermore, Chatzis and Samios\textsuperscript{23} additionally investigated hydrogen bonding between methanol and CO$_2$, which was not done here.

In the present work, $NpT$ molecular dynamics simulations of methanol + CO$_2$ at a specified temperature, pressure, and composition were carried out. The distribution of hydrogen-bonded methanol species, with $i = 0, 1, 2$, and 3 hydrogen bonds per molecule, was determined using the hydrogen-bonding criterion of Haughney et al.\textsuperscript{13} The species fraction $f_i$ is the number of methanol molecules with $i$ hydrogen bonds divided by the total number of methanol molecules. In Figure 1, some important configurations of hydrogen-bonded methanol molecules are illustrated. The reference molecule for which the hydrogen bond status is classified is labeled by $*$ in Figure 1. The $f_0$ relates to methanol molecules that are not hydrogen bonded, thus, methanol monomers; see Figure 1a. Molecules being part of dimers, compare Figure 1b and c, as well as molecules at the two ends of a hydrogen-bonded chain (not shown in Figure 1) contribute to $f_1$. Molecules within a chain, for example, the central molecule of a trimer, contribute to $f_2$; see Figure 1d and e. Note that the present statistics does not evaluate whether a chain of hydrogen-bonded methanol molecules is linear or cyclic. Molecules that cross-link chains or central molecules in tetramers contribute to $f_3$; see Figure 1f.

The experimental chemical shift $\delta$ is assumed here to be a superposition of the signal of three different methanol species, monomers, methanol molecules, which act as proton donors, and methanol molecules, which act as proton acceptors in a hydrogen bond. The chemical shifts of these three methanol species are labeled as $\delta_m$, $\delta_D$, and $\delta_A$, respectively.

The contribution of the monomers to the observed chemical shift is $f_0\delta_m$; see Figure 1a. Half of the species with one hydrogen bond are donors; the other half acceptors. This holds both for dimers and the two ends of a chain; compare Figure 1b and c. Thus, their contributions are $0.5 f_1\delta_A + 0.5 f_1\delta_D$. The assignment of $f_2$ is not straightforward. For molecules acting both as proton donors and acceptors as in Figure 1d, it is
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TABLE 1: NMR Chemical Shifts between Hydroxyl and Methyl Signals Resulting from an Interpolation of Experimental Data from Maiwald et al.³

<table>
<thead>
<tr>
<th>$T$ K</th>
<th>$\delta_{\text{MeOH}}$ mol mol⁻¹</th>
<th>10 MPa</th>
<th>15 MPa</th>
<th>20 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>0.0052</td>
<td>-2.682</td>
<td>-2.721</td>
<td>-2.644</td>
</tr>
<tr>
<td>0.0531</td>
<td>-2.534</td>
<td>-2.623</td>
<td>-2.510</td>
<td></td>
</tr>
<tr>
<td>0.1552</td>
<td>0.0436</td>
<td>0.267</td>
<td>0.404</td>
<td></td>
</tr>
<tr>
<td>0.1857</td>
<td>0.829</td>
<td>0.600</td>
<td>0.827</td>
<td></td>
</tr>
<tr>
<td>0.6607</td>
<td>1.511</td>
<td>n.a.</td>
<td>1.515</td>
<td></td>
</tr>
<tr>
<td>1.0000</td>
<td>1.604</td>
<td>1.565</td>
<td>1.617</td>
<td></td>
</tr>
<tr>
<td>308.15</td>
<td>0.0091</td>
<td>-2.623</td>
<td>-2.608</td>
<td>-2.589</td>
</tr>
<tr>
<td>0.0350</td>
<td>-1.547</td>
<td>-1.567</td>
<td>-1.519</td>
<td></td>
</tr>
<tr>
<td>0.1857</td>
<td>0.584</td>
<td>0.346</td>
<td>0.351</td>
<td></td>
</tr>
<tr>
<td>0.6607</td>
<td>1.382</td>
<td>1.381</td>
<td>1.384</td>
<td></td>
</tr>
<tr>
<td>1.0000</td>
<td>1.501</td>
<td>1.505</td>
<td>1.504</td>
<td></td>
</tr>
<tr>
<td>338.15</td>
<td>0.0091</td>
<td>-2.730</td>
<td>-2.657</td>
<td>-2.579</td>
</tr>
<tr>
<td>0.0141</td>
<td>-2.567</td>
<td>n.a.</td>
<td>-2.670</td>
<td></td>
</tr>
<tr>
<td>0.0244</td>
<td>-2.181</td>
<td>-2.201</td>
<td>-2.204</td>
<td></td>
</tr>
<tr>
<td>0.0591</td>
<td>-1.121</td>
<td>-1.192</td>
<td>-1.210</td>
<td></td>
</tr>
<tr>
<td>0.0675</td>
<td>-0.484</td>
<td>-0.918</td>
<td>-1.137</td>
<td></td>
</tr>
<tr>
<td>0.0746</td>
<td>n.a.</td>
<td>-0.892</td>
<td>-0.908</td>
<td></td>
</tr>
<tr>
<td>0.1003</td>
<td>-0.391</td>
<td>-0.399</td>
<td>-0.253</td>
<td></td>
</tr>
<tr>
<td>0.1632</td>
<td>0.128</td>
<td>0.104</td>
<td>0.087</td>
<td></td>
</tr>
<tr>
<td>0.2454</td>
<td>0.571</td>
<td>0.550</td>
<td>0.556</td>
<td></td>
</tr>
<tr>
<td>0.4784</td>
<td>0.941</td>
<td>0.964</td>
<td>0.978</td>
<td></td>
</tr>
<tr>
<td>1.0000</td>
<td>1.340</td>
<td>1.343</td>
<td>1.346</td>
<td></td>
</tr>
</tbody>
</table>

As expected, it can be seen from Figure 2 that the fraction of methane gas-phase studies, Hoffmann and Conradi⁴ also found a monomer chemical shift of −3.40 ppm.

3. Results

3.1. Experimental Data. On the basis of eq 1, results from molecular simulation can be compared to experimental chemical shifts. The chemical shift data used in the present work is given in Table 1, covering four temperatures 293.15, 308.15, 323.15, and 338.15 K at pressures of 10, 15, and 20 MPa in the full composition range. To obtain isobaric data, the original data were linearly interpolated. Uncertainties due to this interpolation are well within the experimental scatter. Despite that interpolation, the chemical shifts in Table 1 are called “experimental” in the following. The chemical shifts refer to tetramethylsilane (TMS).⁹

The experimental chemical shift of a hydroxyl group, which participates in a hydrogen bond, is significantly larger than that of a non-hydrogen-bonded hydroxyl group as the protons of the hydrogen-bonded hydroxyl group are deshielded. Hence, from the experimental data used here, it can directly be deduced that with increasing temperature, the extent of hydrogen bonding decreases; see Table 1. The data also show that more hydrogen bonds are present when the methanol mole fraction increases.

In the investigated range of liquid-like states, no pressure effect on hydrogen bonding was found. NMR investigations of liquid methanol up to 280 MPa by Wallen et al.¹¹ showed a weak increase of hydrogen bonding with increasing pressure at constant temperature. Similar findings on the pressure effect were published by Stubbs and Siepmann,² who observed a weak pressure dependence of methanol hydrogen bonds in liquid-like supercritical CO₂ going up to 40 MPa with a molecular simulation study.

A simple analytic function is used to fit the experimental NMR chemical shifts at constant pressure and temperature

$$\delta = a - \frac{b_{\text{MeOH}}}{1 + c_{\text{MeOH}}}.$$  (2)

This function is not based on any chemical or physical consideration, and eq 2 was found as the best simple analytic function among several fit approaches. Nevertheless, it is useful for extrapolating the chemical shift of infinite diluted methanol, that is, for finding the monomer chemical shift $\delta_M$. Thus, from fitting the parameters $a$, $b$, and $c$ of eq 2 to the chemical shifts at constant temperature and pressure from Table 1, monomer chemical shifts in the range of −3.2 to −3.9 ppm were found. The arithmetic mean for all temperatures and pressures yields −3.356 ppm and was used subsequently. The monomer chemical shift $\delta_M$ found here is in good agreement with the findings of Asahi and Nakamura,²⁰ who obtained $\delta_M = -3.45$ ppm.

From methanol gas-phase studies, Hoffmann and Conradi⁴ also found a monomer chemical shift of −3.40 ppm.

Only $\delta_D$ and $\delta_A$ from eq 1 need to be determined on the basis of hydrogen-bonding statistics here.

3.2. Hydrogen Bonding Statistics from Molecular Simulation. Detailed information on the fractions of differently hydrogen-bonded species can be obtained from molecular simulation. The quality of these predictions is assessed here by a comparison of calculated and experimental NMR chemical shifts. The distribution of methanol molecules $f_i$ was calculated from $NpT$ ensemble molecular dynamics simulations at experimental temperatures, pressures, and methanol mole fractions specified in Table 1. Additional simulations were performed at methanol mole fractions of 0.1, 0.2, 0.4, 0.6, and 0.8 mol/mol. Tables I–IV in the Supporting Information summarize the simulation results for the distribution of differently hydrogen-bonded methanol species at these conditions. Figures 2–5 show the dependence of $f_0$–$f_3$ on the methanol mole fraction and temperature at a pressure of 15 MPa. Due to the weak pressure influence, plots for the other pressures show only very little differences compared to those of Figures 2–5 and are omitted here.

As expected, it can be seen from Figure 2 that the fraction of methanol monomers $f_0$ increases with increasing temperature and decreasing methanol mole fraction. The fraction $f_1$, that is, one hydrogen bond per methanol molecule, increases with increasing temperature; see Figure 3. The influence of the methanol mole fraction on $f_1$ is not monotonous, and a maximum is observed at methanol mole fractions between about 0.1 and 0.2 mol/mol. Consistent with $f_0$ and $f_1$, the fraction $f_2$ increases with decreasing temperature and increasing methanol mole
fraction; see Figure 4. At small methanol mole fractions close to infinite dilution, practically no chains were observed. The fraction of cross-linking molecules in branched chains or tetramers increases with increasing methanol mole fraction but decreases with temperature; see Figure 5. The fraction of this type of species is small compared to the other species.

As for the experimental data in Table 1, the pressure influence cannot be resolved in the hydrogen-bonding statistics from simulation results; compare Tables I–IV in the Supporting Information.

3.3. Comparison of Molecular Simulation Results with Experimental NMR Data. To compare the simulation results with the experimental NMR data, chemical shifts were assigned to the different species based on eq 1, as discussed in section 2. Only three chemical shifts were assigned, that of the monomers $\delta_M$, that of hydrogen-bonded donors $\delta_D$, and that of acceptors $\delta_A$. Note that the assignment of a value for $\delta_M$ is unrelated to simulation data as it was directly found from an extrapolation of the experimental data to infinite dilution, as explained in section 3.1. Only the fit of the state-independent parameters $\delta_D$ and $\delta_A$ to the experimental data from Table 1 relies on the simulation data. The results are summarized in Table 2.

The predictions of the NMR chemical shifts applying $\delta_M$, $\delta_D$, and $\delta_A$ from Table 2 and the hydrogen-bonding statistics from Tables I–IV (Supporting Information) for 15 MPa and...
for 293.15, 308.15, 323.15, and 338.15 K are compared to the experimental NMR data in Figure 6. The agreement is very favorable. Figure 6 also includes the correlation of the experimental data based on eq 2 and predictions of NMR chemical shifts at methanol mole fractions 0.1, 0.2, 0.4, 0.6, and 0.8 mol/mol with molecular simulation, which also fit well. The results for the pressures 10 and 20 MPa are not shown here, but they are of the same quality.

The results from the NMR measurements are excellently described regarding the effects of both temperature and methanol mole fraction on hydrogen bonding.

TABLE 2: NMR Chemical Shifts Assigned to Different Methanol Species; See Equation 1

<table>
<thead>
<tr>
<th>äM ppm</th>
<th>äA ppm</th>
<th>äD ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3.356</td>
<td>-1.845</td>
<td>1.876</td>
</tr>
</tbody>
</table>

TABLE 3: Lennard-Jones, Point Charge, Internal Hard-Sphere Diameter, and Geometry Parameters of the New Methanol Model

<table>
<thead>
<tr>
<th>site</th>
<th>σaa Å</th>
<th>εaa/kB K</th>
<th>qaa e</th>
<th>σ2aa Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>S CH3</td>
<td>3.7543</td>
<td>120.592</td>
<td>+0.24746</td>
<td>1.5020</td>
</tr>
<tr>
<td>S OH</td>
<td>3.0300</td>
<td>87.879</td>
<td>-0.67874</td>
<td>1.2120</td>
</tr>
<tr>
<td>S H</td>
<td>0</td>
<td>0</td>
<td>+0.43128</td>
<td>0.4000</td>
</tr>
</tbody>
</table>

h1 Å  h2 Å  γ°
1.42460  0.94510  108.530

a Compare eq 3 and Figure 7. Boltzmann’s Constant is kB, and the electronic charge is e.

Figure 8. Saturated densities of methanol; ● present simulation; ○ critical point derived from present simulation data; ∆ simulation data from Chen et al.; † — experimental data.35

Figure 9. Vapor pressure of methanol; ● present simulation; ○ critical point derived from present simulation data; ▲ simulation data from Chen et al.; † — experimental data.35

Figure 10. Site-site radial distribution functions gxx over the site-site distance r for liquid methanol at 0.1 MPa and 298.15 K; — present simulation results; — — results from neutron diffraction experiments.36,37

Figure 11. Vapor—liquid equilibria of the mixture methanol + CO2; ● present simulation with ξ = 1.010; + experimental data.41

4. Conclusion

A simple molecular force field model for methanol was reparameterized to accurately describe the vapor—liquid equilibria of pure methanol. Its ability to describe hydrogen bonding in mixtures of methanol and CO2 was studied here, in detail, based on results of NMR chemical shifts from an extensive experimental study. A simple approach was used for assigning NMR chemical shifts to the different hydrogen-bonded species; only monomers, proton donors, and acceptors are distinguished. Only two state-independent parameters for the NMR chemical shifts of the donors and acceptors were fitted to experimental data based on hydrogen-bonding statistics from molecular
simulation. Despite the simplicity of that approach, an excellent agreement between the simulation results and the experimental NMR data was found. This agreement shows that with simple molecular models based on Lennard-Jones and point charge potentials, not only thermophysical properties of hydrogen-bonding substances can be described but also structural quantities.

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Appendix

A. Molecular Methanol and Mixture Models. The present molecular model of methanol is a reparameterization of an existing one from van Leeuwen and Smit. It consists of two united-atom Lennard-Jones sites, accounting for dispersion and repulsion of the methylene and hydroxyl groups and three point charges located at the Lennard-Jones sites and at the hydroxyl hydrogen atom to model both polarity and hydrogen bonding. Hence, the potential energy $u_{ij}$ between two methanol molecules $i$ and $j$ is given by

$$u_{ij}(r_{ij}) = \sum_{a,b=1}^{3} 4\varepsilon_{ab} \left[ \left( \frac{\sigma_{ab}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ab}}{r_{ij}} \right)^{6} \right] + \frac{q_{ia}q_{jb}}{4\pi\varepsilon_{ij}r_{ij}},$$

(3)

where $a$ is the site index of molecule $i$ and $b$ is the site index of molecule $j$, respectively. The site–site distance between molecules $i$ and $j$ is denoted by $r_{ij}$. $\sigma_{ab}$ and $\varepsilon_{ab}$ are the Lennard-Jones size and energy parameters, and $q_{ia}$ 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 of two methanol molecules is defined by the Lorentz–Berthelot combining rules:

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

(4)

$$\varepsilon_{ab} = \sqrt{\varepsilon_{aa}\varepsilon_{bb}},$$

(5)

To obtain a parameter set of a rigid methanol model which favorably describes the vapor–liquid equilibrium, the optimization procedure of Stoll was applied. The optimization procedure employs the sensitivity of the model parameters on pure substance bubble density and vapor pressure over a wide temperature range. As a starting model for this procedure, the molecular model of van Leeuwen and Smit was used. In the course of the optimization, it turned out that the geometry of the model did not need to be changed. A description of the optimized methanol model is given by Figure 7 and Table 3.

To avoid nonphysical interactions due to the superposition of the 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 were employed. Such internal hard-sphere cutoffs were also used, for example, by Lisal et al. 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 Lisal et al. 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 and Stoll. The diameter of an internal hard-sphere located at site $a$ is termed $\sigma_{ia}$ in the following. The internal hard-sphere diameter $\sigma_{ij}$ 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 $r_{ij} \leq \sigma_{ij}$. The like internal hard-sphere diameters of the present methanol model are included in Table 3.

The vapor–liquid equilibrium calculations of the methanol model used in this work were obtained with the $NpT + test$ particle method. To determine the chemical potential of the liquid and vapor phase, the Monte Carlo-based gradual insertion method was applied with 864 molecules in each phase. The liquid runs were equilibrated in the $NpT$ ensemble over 10 000 cycles without fluctuating molecules and adjusting the maximum displacement of translation, rotation, and volume to yield acceptance rates of 50%. After that, 5 000 Monte Carlo cycles with fluctuating molecules were performed 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 displacement of translation, rotation, and volume. Due to the formation of hydrogen-bonded clusters in the vapor phase, particularly at low temperatures, the equilibration phase was carried out significantly longer than the liquid phase.

Figures 8 and 9 depict the vapor–liquid equilibrium simulations of the present model, including the TraPPE-UA simulation data taken from Chen et al. This TraPPE-UA model consists of united atoms and point charges, considering internal degrees of freedom. The agreement between the new model and the experimental data is favorable, even better than that for the more complex TraPPE-UA methanol model. The simulation results of the present methanol model yield mean unsigned errors compared to vapor pressure, saturated liquid density, and heat of vaporization experimental data of 1.1, 0.6, and 5.5%, respectively, in the temperature range from 280 to 490 K, which is about 55 to 95% of the critical temperature. The numerical values of vapor–liquid equilibrium simulations of the present methanol model are given in Table V of the Supporting Information.

To investigate the capability of the new methanol model regarding other structural properties, site–site radial distribution functions were determined with $NpT$ molecular simulations at 0.1 MPa for temperatures of 193.15 and 298.15 K. These molecular simulation results are compared to the site–site radial distribution functions of Yamaguchi et al. who used neutron diffraction experiments and empirical potential structure refinement (EPSR) to determine the entire set of 10 site–site radial distribution functions $g_{ij}$, only six site–site radial distribution functions can be distinguished here, namely, $g_{CC}, g_{CO}, g_{CH}, g_{OO}, g_{OH}$, and $g_{HH}$. The site–site radial distribution functions determined here from molecular simulation are compared in Figure 10 to data of Yamaguchi et al. at 298.15 K. Similar results were found for the isotherm at 193.15 K. The excellent agreement strongly supports the findings of the present NMR study that the new molecular model for methanol yields not only vapor–liquid equilibria accurately but also structural properties. Note that the present site–site radial distribution function $g_{HH}$ at 298.15 K agrees even better with the data of Weitkamp et al. who
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derived this site—site radial distribution function directly from neutron diffraction experiments. As the data of Weitkamp et al. are only available graphically, they are not shown in Figure 10.

The molecular model for CO₂ was developed in previous work of our group. The model was derived from a comprehensive study of the symmetric two-center Lennard-Jones plus point quadrupole (2CLJQ) model by Stoll et al. The mean unsigned error of vapor pressure, saturated liquid density, and heat of vaporization of the 2CLJQ model is typically smaller than 1, 3, and 3%, respectively, over the whole vapor—liquid equilibrium temperature range. In molecular simulations of a binary mixture A + B with pairwise additive potentials, three different interactions occur, two like interactions between molecules of the same type A—A and B—B, which are fully defined by the pure component models, and the unlike interaction between molecules of different type A—B. In mixtures consisting of polar molecules, the electrostatic part of the unlike interaction is fully determined by the laws of electrostatics. However, there is no rigorous physical framework that yields reliable unlike dispersion parameters and thus unlike Lennard-Jones parameters. For this purpose, combining rules were developed in the past based on physical and mathematical intuition or on empirical approaches. Following a recent investigation on combining rules and of the sensitivity of vapor—liquid equilibrium mixture properties on unlike Lennard-Jones parameters by Schnabel et al., the modified Lorentz—Berthelot combining rules between interactions of molecules of different type

\[ \sigma_{ab} = \frac{\sigma_{aa} + \sigma_{bb}}{2} \]

and

\[ \varepsilon_{ab} = \xi \varepsilon_{aa} \varepsilon_{bb} \]

were used. The state-independent binary parameter \( \xi \) in eq 7 is introduced to account for polarizability effects and is adjusted to one reliable experimental vapor pressure of the mixture or one Henry’s law constant. For the binary mixture methanol + CO₂, \( \xi \) was adjusted here at 323.15 K and the bubble point CO₂ mole fraction of 0.2368 mol/mol to 1.01. Figure 11 depicts the vapor—liquid equilibrium simulations for pure methanol and methanol + CO₂ at the isotherms of 293.15, 308.15, 323.15, and 338.15 K are listed in Tables V and VI, respectively. The numerical data for the vapor—liquid equilibrium simulations for pure methanol and methanol + CO₂ are given in Tables V and VI, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

For the present molecular simulations, the Lennard-Jones long-range interactions beyond the cutoff radius were corrected by employing angle averaging as proposed by Lustig. The Coulombic interactions were corrected using the reaction field method.

Supporting Information Available: The numerical results for the hydrogen-bonding statistics from the \( NpT \) molecular dynamics simulations at the isotherms of 293.15, 308.15, 323.15, and 338.15 K are listed in Tables I–IV. The numerical data for the vapor—liquid equilibrium simulations for pure methanol and methanol + CO₂ are given in Tables V and VI, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes