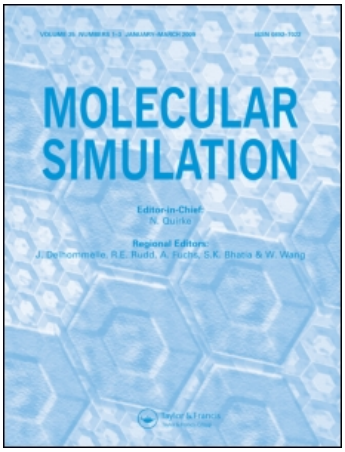

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Molecular Simulation of Vapour-Liquid Coexistence Curves for Hydrogen Sulfide-Alkane and Carbon Dioxide-Alkane Mixtures

Jérôme Delhommelle[a]; Anne Boutin[a]; Alain H. Fuchs[a]
[a] Department of Physical Chemistry, Laboratoire de Chimie-Physique des Matériaux Amorphes, France

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MOLECULAR SIMULATION OF VAPOUR–LIQUID COEXISTENCE CURVES FOR HYDROGEN SULFIDE–ALKANE AND CARBON DIOXIDE–ALKANE MIXTURES

JÉRÔME DELHOMMELLE, ANNE BOUTIN and ALAIN H. FUCHS*

Laboratoire de Chimie-Physique des Matériaux Amorphes,
Department of Physical Chemistry, UMR 8611 CNRS, Bâtiment 490,
Université Paris-Sud, 91405 ORSAY, France

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Gibbs ensemble Monte Carlo simulations, combined with the configurational-bias technique applied to alkane chains, were performed to calculate hydrogen sulfide–alkane and carbon dioxide–alkane liquid–vapour phase equilibria for several *n*-alkane molecules (propane, pentane and decane). Recently proposed effective pair potentials that describe accurately the pure components coexistence curves were used in the simulations. It is shown that the use of these force fields together with the Lorentz-Berthelot mixing rules yield a description of the coexistence curves of these binary mixtures that is in good agreement with the experimental data is most cases. Some deviations from the experimental results were observed in the range of high H_2S mole fraction and high pressure. Further work is needed in order to improve the level of accuracy of potential models for fluid mixtures of non polar and multipolar molecules.

Keywords: Gibbs ensemble Monte Carlo simulations; liquid–vapour equilibria; polar and non-polar molecules mixtures

1. INTRODUCTION

The knowledge of thermodynamic properties of alkane fluids and mixtures of alkanes with multipolar molecules such as water, hydrogen sulfide, nitrogen and carbon dioxide is important for the petrochemical industry. Certain areas remain extremely difficult to access by experimentation (systems under

*Corresponding author.

high pressure and temperature and/or containing poisonous substances). Equations of state are often used to estimate the thermodynamic properties of these systems. Since the interaction parameters used in these equations need to be fitted to many experimental values, equations of state are not always suited to deal with systems for which few experimental data are available. This is the case, for instance, for mixtures of alkanes and hydrogen sulfide [1, 2]. Molecular simulation is thus, in principle, of great interest as a tool for predicting thermophysical properties of fluids in these systems.

Simple potential models have been proposed recently for hydrogen sulfide [3] and for carbon dioxide [4]. The parameters in both models were initially fitted to reproduce experimental data for the liquid phase. They were then readjusted to yield an accurate agreement with the experimental coexistence curve of the pure fluid. These models seemed therefore well adapted to the study of mixtures with alkanes.

Several different models for alkane molecules have been proposed in the last two decades for use in computer simulations. A successful approach has been to reduce the complexity of the alkane molecule by introducing a united atom (UA) approximation in which groups of CH_n atoms ($n = 0-4$) are represented by one "pseudoatom" interaction site [5]. These site–site interaction models have been applied with good results to pure systems of alkanes [6–12]. The lack of explicit hydrogens becomes significant if systems at high pressures are considered where the alkanes start to pack together. Toxvaerd [13, 14] proposed an Anisotropic United-Atom (AUA) in which the interaction site is moved from being located directly on the original carbon atom site to the geometrical centre of the atoms that have been united together. This AUA model has been shown to perform better for predicting equation of state of alkanes at high pressure. AUA force fields also yield transport coefficients (viscosity, thermal conductivity and intradiffusion coefficients) in acceptable agreement with experiments [15]. We have recently shown that the AUA force field performs rather well in predicting vapor–liquid coexistence curves (VLCC) for alkane mixtures [16]. We have thus used the more recent version of the AUA model (called AUA-3 [14]) in this study.

Details of the potential models are given in the following section. The simulation techniques are described in Section 3, namely the Gibbs-Ensemble technique combined with the configurational-bias Monte Carlo method. A reaction field approach was implemented in the case of H_2S, in order to address the issue of performing simulations in two phases having different densities *i.e.*, dielectric media of different permittivities. In Section 4 we present the simulation results of the liquid–vapour phase diagram for pure

H_2S, CO_2, propane, pentane and decane, and for binary mixtures of these *n*-alkanes with H_2S and CO_2 and compare these predicted phase diagrams to experimental values. We finish in Section 5 with the main conclusions from this work.

2. POTENTIAL MODELS

2.1. Hydrogen Sulfide

Few studies have been devoted to the development of an accurate effective pair potential for hydrogen sulfide [3, 17, 18]. Liquid hydrogen sulfide, unlike water, seems to have all the characteristics of a non-associated system. It is therefore expected that simple potential models can accurately describe the liquid phase and the coexistence curve of hydrogen sulfide. The first site–site potential model was proposed by Jorgensen [17]. It is quite similar to the TIP3P model for water [19]. Hydrogen sulfide is modeled as a Lennard-Jones sphere on the sulfur atom, two positive point charges on hydrogen atoms and one negative point charge on the sulfur atom. The parameters of the model have been fitted to a few experimental properties of liquid hydrogen sulfide. However, as pointed out by Forrester *et al.* [18], the electrostatic component of the total interaction energy seems too strong. The dipole moment of 2.1 D in this model is more than twice the experimental value of 1.0 D. A more refined model was then proposed by Forrester *et al.* [18] on the basis of the results of a distributed multipole analysis [20]. In this model, an additional partial charge, located on the bissector of the HSH angle, is taken into account. This model yields a good description of the structure and energetics of liquid hydrogen sulfide and also of the high-temperature solid phase. Induction forces are still not taken explicitely into account in this model, which has been recently readjusted by Kristof *et al.* [3] to reproduce the VLCC of hydrogen sulfide. In this latter model the dipole moment is 1.4 D. The parameters of this model, used in all this work, are listed in Table I.

TABLE I Parameters of the potential model for H_2S [3]

Site	$(\varepsilon/k_b)(K)$	$\sigma(\AA)$	$q(e)$	$x(\AA)$	$y(\AA)$	$z(\AA)$
S	250	3.73	0.4	0.0	0.0	0.0
H	0	0	0.25	0.9639	0.9308	0.0
H	0	0	0.25	−0.9639	0.9308	0.0
X	0	0	−0.9	0.0	0.1862	0.0

TABLE II EPM2 model for CO_2 [4]

Site	$(\varepsilon/k_b)(K)$	$\sigma(\AA)$	$q(e)$	$x(\AA)$	$y(\AA)$	$z(\AA)$
C	28.129	2.757	0.6512	0	0	0
O	80.507	3.033	−0.3256	1.166	0	0
O	80.507	3.033	−0.3256	−1.166	0	0

2.2. Carbon Dioxide

Many models have been proposed for carbon dioxide. The EPM2 model, developed by Harris *et al.* [4], is a simple and efficient model which performs quite well for predicting VLCC. In this model, carbon dioxide is described by a 3-sites model: one Lennard-Jones sphere per atom and one point charge per atom. The 3 point charges were fitted in order to reproduce the experimental value of the quadrupole moment ($-4.3\,D\cdot\AA$ [21]). The parameters of the Lennard-Jones centres of force were initially fitted by Murthy *et al.* [22] to a few experimental data (second virial coefficient, lattice vibrational frequencies and some densities of liquid carbon dioxide). Using the corresponding states theorem, Harris *et al.*, have obtained nearly exact agreement between the experimental and calculated critical properties by multiplying the Lennard-Jones well depths of the model of Murthy *et al.* [22], the length parameters (bond lengths and Lennard-Jones core sizes) and charges by 0.97, 0.99 and 0.98 respectively. In this work, we have used a rigid version of the EPM2 model (parameters are listed in Tab. II).

2.3. Alkanes

In the anisotropic united atom (AUA) model, molecules are represented by chains of interaction sites standing for each CH_3 and CH_2 group. Nonbonded interactions, described by Lennard-Jones potential form, take place between two united atoms of different molecules or within the same molecule if the two sites are separated by more than three chemical bonds. In order to take into account the excluded volume effect due to the hydrogen atoms in a dense fluid without using an explicit all atoms description, Toxvaerd has suggested displacing the position of the interaction site from the carbon atom to the geometrical centre of the group of atoms [13]. In a more recent model, the AUA-3 model used in this work, the positions of the interaction site for the methyl and methylene groups have been considered as fitting parameters [14]. The values of the interaction force displacements with respect to the carbon atom, d_{AUA}, and the potential parameters are given in Table III.

TABLE III Lennard-Jones parameters for AUA-3 model [14]

	$(\varepsilon/k_b)(K)$	$\sigma(\AA)$	$d_{AUA}(\AA)$
CH_3	119.8	3.516	0.18
CH_2	79.87	3.516	0.4

In the AUA models, the bond-bending potential (Eq. (1)) and torsion potential (Eq. (2)) have the following forms (parameters given in Tab. IV):

$$U^{\text{bend}}(\theta) = \frac{1}{2}k_\theta(\cos\theta - \cos\theta_0)^2 \tag{1}$$

$$U^{\text{tors}}(\phi) = \sum_{k=0}^{n} c_n \cos^k(\phi). \tag{2}$$

The C—C bond length was fixed to 1.533 Å for propane and pentane and 1.545 Å for decane.

For all molecules studied in this work, repulsion-dispersion interactions between two centres of force, i and j, are described by a Lennard-Jones pair potential (Eq. (3)):

$$U^{LJ}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \tag{3}$$

using Lorentz-Berthelot mixing rules (Eq. (4)):

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad \sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{4}$$

TABLE IV Bond-bending and torsion potential parameters for AUA-3 model [14]

Bond-bending potential parameters	$k_\theta(K) = 62500$ and $\theta_0(\text{deg}) = 113.3$ (for propane and pentane) or 114.6 (for decane)
Torsion potential parameters (K)	$c_0 = 1001.35$, $c_1 = 2129.52$, $c_2 = -303.06$, $c_3 = -3612.27$, $c_4 = 2226.71$, $c_5 = 1965.93$, $c_6 = -4489.34$, $c_7 = -1736.22$ and $c_8 = 2817.37$

2.4. Mixtures of Non Polar and Multipolar Molecules

In the simulations of H_2S–alkane and CO_2–alkane binary mixtures, the interactions between unlike molecules were calculated using the Lorentz-Berthelot mixing rules (Eq. (4)). No additional effects, such as the electrostatic and/or induction interaction has been taken into account here. It was one of the purpose of this work to test the performance of this highly simplified approach of intermolecular interactions between a polar and a multipolar molecule. In a recent work Errington *et al.* [23] have shown that the phase equilibria for water-methane and water-ethane mixtures could be fairly well reproduced using such a simplified force field, although some deviations between simulation and experiments were observed.

3. SIMULATION DETAILS

The Gibbs Ensemble (GE) technique was introduced by Panagiotopoulos [24–26] to study liquid–vapour or liquid–liquid phase equilibria. In this method, a Monte-Carlo simulation is achieved simultaneously in two boxes, one standing for the gas phase and the other one for the liquid phase. Three different types of Monte-Carlo steps are allowed: displacement of a molecule in its own phase, change of volume of boxes and transfer of a molecule from one phase to the other.

The step of transfering a molecule from the gas phase to the liquid phase may lead to low acceptance probabilities in the case of chain molecules such as alkanes. Smit *et al.* [6] have suggested using the configurational-bias Monte Carlo technique which rebuilds bead by bead the transferred molecule avoiding areas of unfavourable energy. We have also included an additional bias for the insertion of the first bead [9, 27] in the procedure described by Smit *et al.* In this work, we have chosen 10 random sites for the insertion of the first bead and a number of 6 trial orientations for the insertion of each bead during the configurational-bias scheme. No configurational bias was used for hydrogen sulfide and carbon dioxide.

In the case of pure components, equilibrium was typically reached after $5 \cdot 10^5$ MC moves. A further 10^6 production steps were performed to average quantities. In the case of mixtures, the number of steps had to be increased by an order of magnitude. This is due to a large increase of the configuration hyperspace complexity for mixtures. Thus a larger number of configurations needed to be generated in order to compute thermodynamics averages properly (typically 10^7 production steps in order to average quantities).

Most of the simulations performed in this work involved a total of 400 molecules. Spherical potential truncations at $r_{cut} = 9$ Å were used and the usual tail corrections were applied [28]. An atom-based truncation is used for the van der Waals interactions whereas a centre of mass-based cutoff is used for Coulombic interactions.

In the case of hydrogen sulfide, we have introduced in our calculation the Barker-Watts reaction field approach [29], generalized by Neumann [30] to molecules bearing partial charges. In this method, electrostatic interactions between partial charges of two different dipolar molecules are calculated explicitely within a spherical cutoff radius r_{cut}, embedded in dielectric medium defined by its macroscopic permittivity ε_{RF}. Since the cavity has to be neutral, r_{cut} is a centre of mass-based cutoff radius.

The electrostatic contribution to the total interaction energy becomes (Eq. (5)) [31]:

$$V^{\text{élec}} = \sum_{I<J} \sum_{i\in I, j\in J} q_i q_j \left[\frac{1}{r_{ij}} + \left(\frac{\varepsilon_{RF} - 1}{2\varepsilon_{RF} + 1} \right) \frac{r_{ij}^2}{r_{cut}^3} \right] \tag{5}$$

In this formula, the interaction of a dipole with its own reaction field is neglected:

$$\frac{-\mu^2}{r_{cut}^3} \left(\frac{\varepsilon_{RF} - 1}{2\varepsilon_{RF} + 1} \right)$$

Using this formula requires a knowledge of the dielectric constant value ε_{RF} and its dependence upon temperature and density, since we are dealing with both the liquid and the vapour phases in the VLCC computation. To do this, we have used an iterative procedure. Given an initial value of the dielectric constant $\varepsilon_{RF}(0)$, a GE simulation is performed during $5 \cdot 10^5$ steps. Average densities for both phases are estimated and a canonical Monte-Carlo simulation of a system of 100 molecules of hydrogen sulfide is performed for each calculated density. The fluctuations of the total dipole moment of the simulation cell are estimated and the Kirkwood factor is obtained (Eq. (6)) [28]:

$$g(\varepsilon_{RF}(0)) = \frac{\langle |M|^2 \rangle - \langle |M| \rangle^2}{N|\mu|^2} \tag{6}$$

where M stands for the total dipole moment of the simulation cell and μ the molecular dipole moment of H_2S.

The value of the dielectric constant is then estimated thanks to the following fluctuation formula (Eq. (7)) [31, 32]:

$$\varepsilon_{RF}(1) = \frac{1 + 2\varepsilon_{RF}(0) + 6\varepsilon_{RF}(0)yg(\varepsilon_{RF}(0))}{1 + 2\varepsilon_{RF}(0) - 3yg(\varepsilon_{RF}(0))} \tag{7}$$

where $y = (4\pi\mu^2 N/9kTV)$.

The calculated value $\varepsilon_{RF}(1)$ is then introduced in the GE simulation. This procedure has been repeated three times, at each temperature, in the case of the coexistence curve of H_2S. The dielectric constants were then kept fixed during the production runs. The ε_{RF} values used are given in Table V.

Average densities, mass fractions and molecular fractions were calculated and their errors were estimated using standard block averaging [28]. We have also calculated the critical point of pure compounds (critical temperature T_c and density ρ_c) by fitting the simulation data to the density scaling law for the critical temperature (Eq. (8)) and the law of rectilinear diameters for the critical density (Eq. (9)) [33]

$$\rho_l - \rho_v = B(T - T_c)^{\beta} \tag{8}$$

$$\frac{\rho_l + \rho_v}{2} = \rho_c + A(T - T_c) \tag{9}$$

where ρ_l and ρ_v are the liquid and the vapour density respectively and β stands for the critical exponent of the order parameter. Such fits have been made here by fixing the value of β to the Ising-type critical exponent of 0.32.

TABLE V Dielectric constants used in the reaction field method (simulation of pure H_2S, model of Kristof *et al.* [3], see text)

Temperature (K)	ε_{RF} *(liquid phase)*	ε_{RF} *(vapour phase)*
252.9	7.5_2	1.07_2
285	5.7_2	1.11_4
304.2	5.3_1	1.14_3
312	5.1_2	1.15_3
325	4.8_1	1.20_3
333.6	4.5_1	1.30_4
343.6	4.1_1	1.4_1
352	3.8_1	1.41_4

4. RESULTS

4.1. Pure Fluids

We have performed a GE-NVT simulation of the coexistence curve of hydrogen sulfide with the model proposed by Kristof *et al.* [3] and applied the reaction field technique described above in Section 3. The results obtained in this work are in excellent agreement with those obtained by Kristof *et al.*, with a GE-NPH technique and using a spherical truncation for long-range interactions (Fig. 1). The estimated critical temperature and density values from our calculations are of $T_c = 370.5\,\mathrm{K}$ and $\rho_c = 0.339\,\mathrm{g/cm^3}$ which are in good agreement with the experimental data ($T_c = 373.4\,\mathrm{K}$

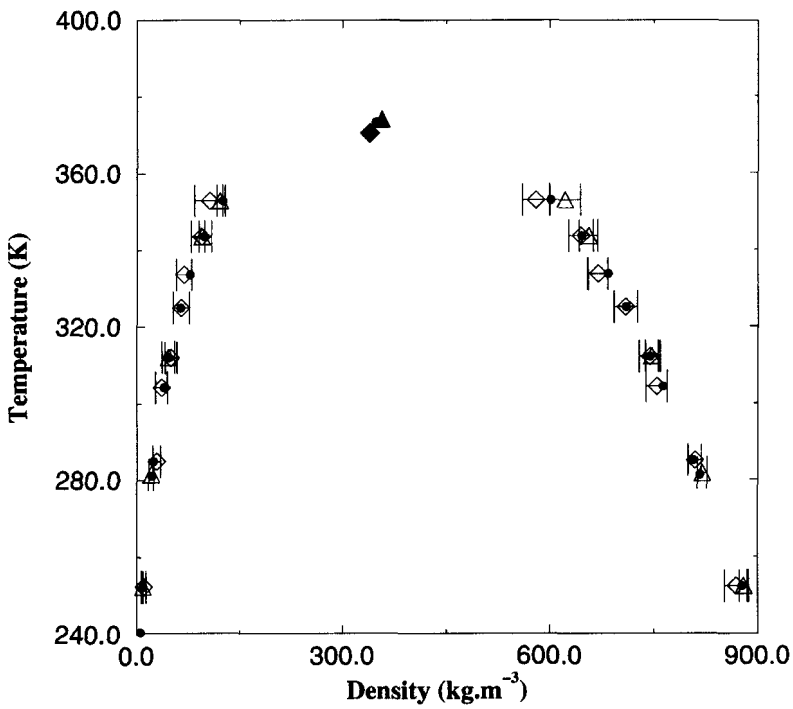

FIGURE 1 Hydrogen sulfide vapour–liquid coexistence curve (VLCC) using the model of Kristof *et al.* [3]. Results of this work (open diamonds) are compared with [3] (open triangles) and experiment (filled circles) [34]. The estimated critical points of the models are indicated by the filled triangle and filled diamond.

and $\rho_c = 0.3476\,\mathrm{g/cm^3}$ [34]) and with the computed values [3]: ($T_c = 374.1\,\mathrm{K}$ and $\rho_c = 0.3567\,\mathrm{g/cm^3}$). The difference between the critical parameters determined in this work (system of 400 molecules) and those of Kristof *et al.* (system of 512 molecules) is presumably related to a finite-size effect in the vicinity of the critical point. We conclude, by comparing these two simulations, that correcting for a spherical truncation of long range interactions has no noticeable effect on the calculated coexistence densities of hydrogen sulfide.

We have then performed GE-NVT simulation on carbon dioxide (Fig. 2) with the model of Harris *et al.* [4] without taking into account any long-range coulombic correction. In the original work of Harris *et al.* [4], long-range coulombic corrections were calculated thanks to a site–site reaction field method [35]. The estimated critical temperature and density values from our calculations are of $T_c = 301.2\,\mathrm{K}$ and $\rho_c = 0.453\,\mathrm{g/cm^3}$ which are in good agreement with the experimental data ($T_c = 304.2\,\mathrm{K}$ and

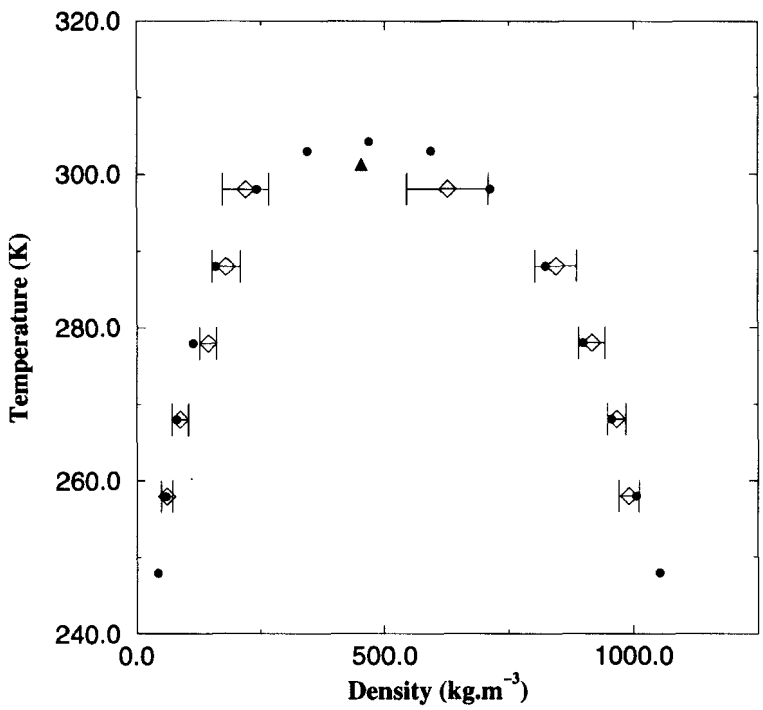

FIGURE 2 Pure carbon dioxide VLCC using the EPM2 [4]. Results of this work (open diamonds) are compared with experiments (filled circles) [43].

$\rho_c = 0.468\,g/cm^3$) and the computed values of [4]. The long range corrections have again no noticeable effect on the predicted coexistence densities as it could have been expected from the fact that the first non-zero multipole moment in carbon dioxide is a quadrupole. They were therefore dropped in our further calculations.

The coexistence curve of propane, pentane and decane, calculated using the AUA-3 model are shown in Figure 3. AUA-3 model accurately describes the VLCC of short alkanes like propane and pentane. Critical temperatures are slightly underpredicted by 1.9% for propane and by 1% for pentane. For propane, the estimated critical point is $T_c = 363.3\,K$ and $\rho_c = 0.215\,g/cm^3$ (experimental data: $T_c = 370.02\,K$ and $\rho_c = 0.223\,g/cm^3$ [36]). For pentane, the estimated critical constants are $T_c = 465\,K$ and $\rho_c = 0.247\,g/cm^3$ (experimental data: $T_c = 469.8\,K$ and $\rho_c = 0.230\,g/cm^3$ [36]). Larger deviations are observed between the simulation and the experimental critical data for decane. AUA-3 model underestimates the critical temperature by

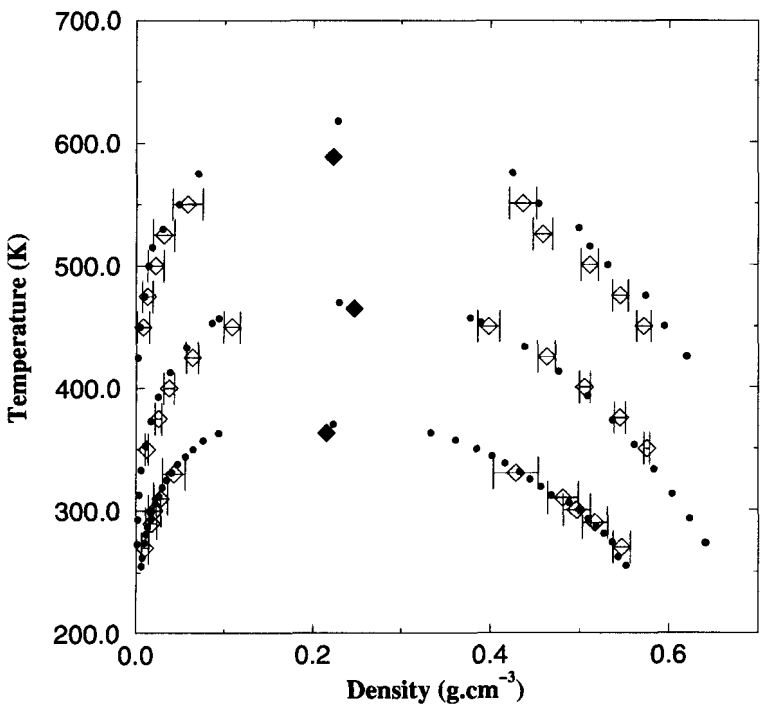

FIGURE 3 Pure propane, pentane and decane VLCC compared with experimental data or data estimated from an equation of state [44] (same legend as in Fig. 2).

4.7% (588.3 K compared with the experimental value of 617 K) and the critical density by 2.2% (0.223 g/cm^3 compared with the experimental value of 0.228 g/cm^3 [36]). AUA-3 model underpredicts the saturated liquid densities of decane though this trend is less pronounced than in the case of dodecane [16].

4.2. Mixtures

The hydrogen sulfide–propane coexistence curve in a temperature-H_2S mole fraction plot and hydrogen sulfide–pentane coexistence curve in a pressure-H_2S mole fraction plot are shown in Figures 4 and 5 respectively. In the case of the hydrogen sulfide–propane mixture, calculations overestimate the H_2S mole fraction in the liquid phase by 14% and underestimate the H_2S mole fraction in the vapour phase by 3.3%. The observed deviations take place in the range of high H_2S mole fraction

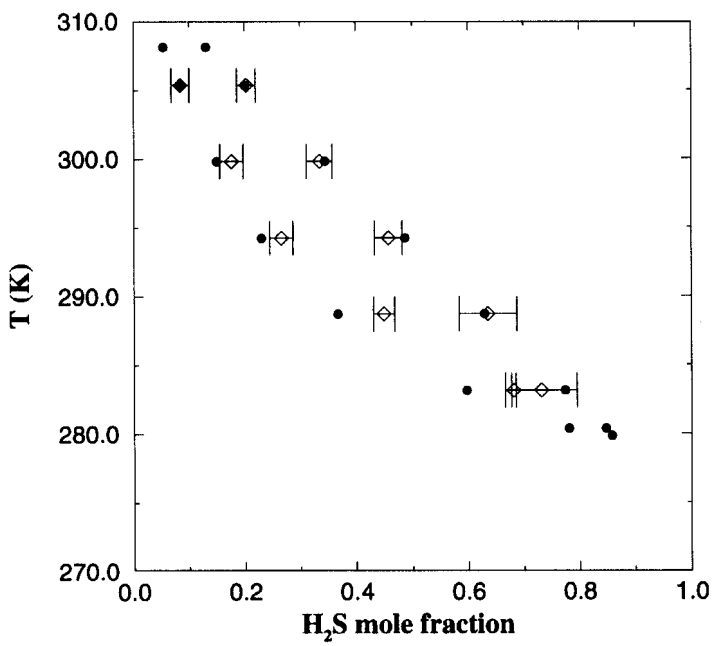

FIGURE 4 Temperature-composition VLCC for the hydrogen sulfide–propane mixture calculated at P = 1.3634 MPa and compared with experiments (same legend as in Fig. 2) [45].

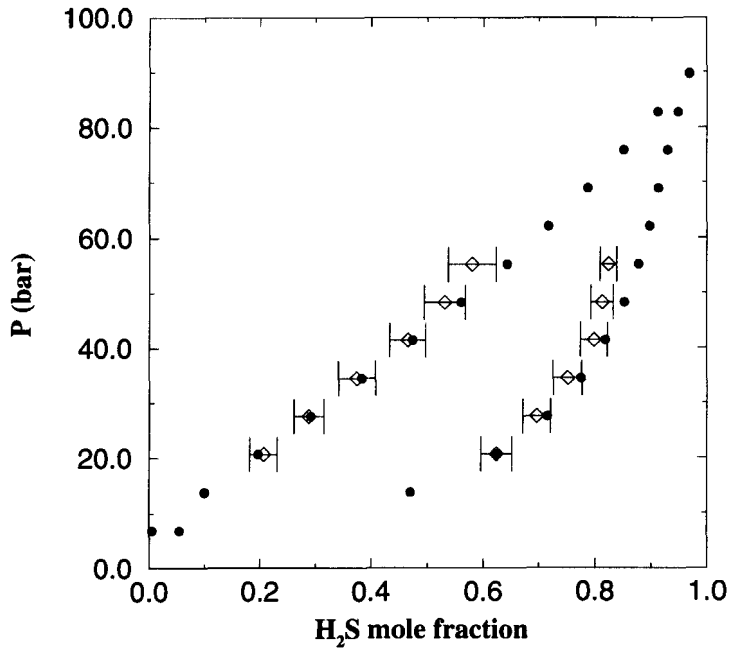

FIGURE 5 Pressure-composition VLCC for the hydrogen sulfide–pentane mixture calculated at $T = 377.59$ K and compared with experiments (same legend as in Fig. 2) [46].

($x > 0.5$) and low temperature ($T < 290$ K). In the case of the hydrogen sulfide–pentane mixture, a good agreement is obtained between simulation results and experiment for pressures up to 40 bar. The simulations tend to underestimate the H_2S mole fraction in both phases. Above 40 bar the simulated VLCC strongly disagrees with experiments. A critical point is predicted slightly above 50 bar and $x \sim 0.7$, while in the experiments the critical point is found at 90 bar and $x \sim 0.97$.

The carbon dioxide–pentane coexistence curve and the carbon dioxide–decane coexistence curve in a pressure-H_2S mole fraction plot are shown in Figures 6 and 7 respectively. In the case of the CO_2–pentane mixture, a good agreement is obtained with experiment: simulation results overestimate the CO_2 mole fraction in the liquid phase by 7% and underestimate the CO_2 mole fraction in the vapour phase by 2%. In the case of the CO_2–decane mixture, larger deviations are observed between simulation and experimental data, as can be seen in Figure 7.

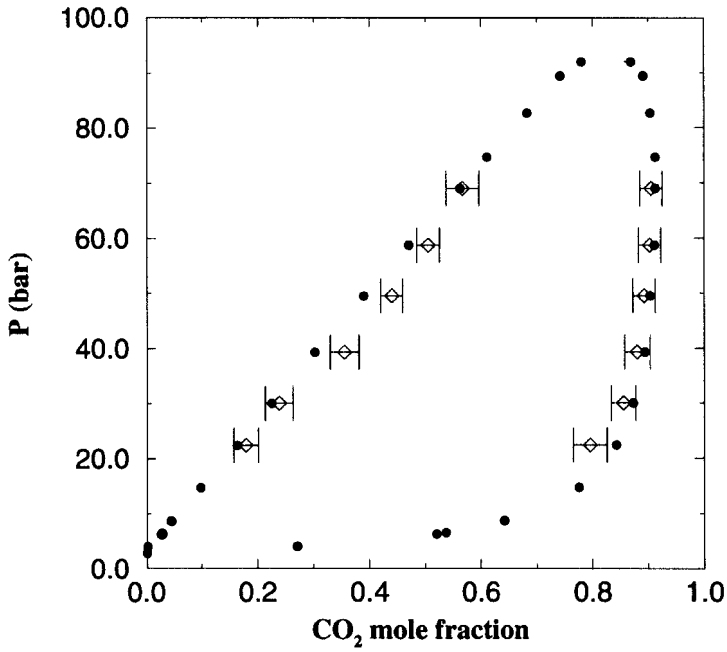

FIGURE 6 Pressure-composition VLCC for the carbon dioxide–pentane mixture calculated at $T = 344.16\,K$ and compared with experiments (same legend as in Fig. 2) [47].

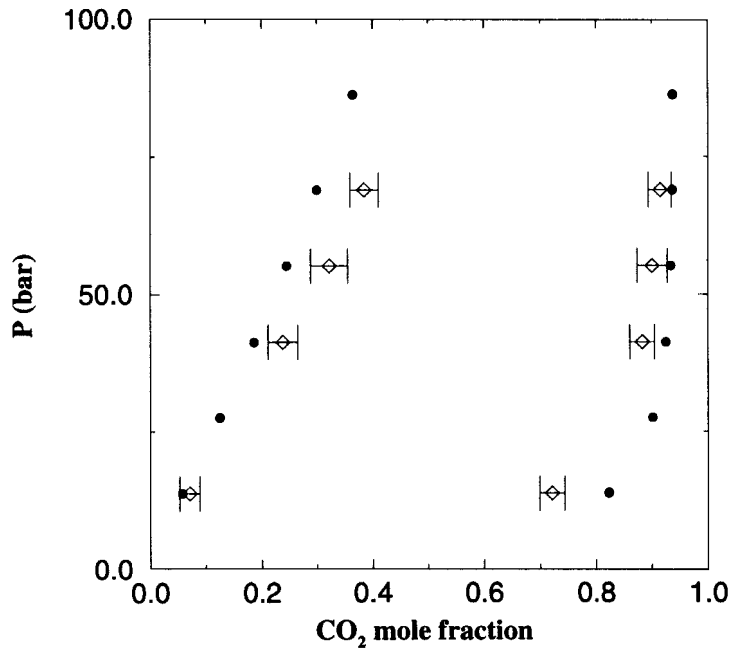

FIGURE 7 Pressure-composition VLCC for the carbon dioxide–decane mixture calculated at $T = 477\,K$ and compared with experiments (same legend as in Fig. 2) [48].

5. DISCUSSION AND CONCLUSION

The potential models used in this work accurately describe the coexistence curve of pure components. The ability of the AUA-3 model to predict several thermophysical properties (VLCC [16] and this work, transport properties [15]) with a fair accuracy has been demonstrated. It would be of great interest to improve this model for long chains such as $C_n, n \geq 10$. On the basis of the results obtained here for H_2S and CO_2, it seems that the long-range Coulombic corrections hardly have any effect on the calculated coexistence densities of weakly polar fluids or quadrupolar fluids.

The combination of the configurational bias with the Gibbs ensemble technique has made it possible to keep the acceptance rate of the transferring step high enough to reach thermodynamic equilibrium. Improving the accuracy of the calculations for mixtures is thus presumably related to a further refinement of the potential models. As shown in this work, the range of high H_2S mole fraction and high pressure for H_2S-pentane mixture or high H_2S mole fraction and low temperature for H_2S-propane mixture are not satisfactorily described by our calculations using the potential models of Kristof *et al.* [3] for H_2S and the AUA-3 model for alkane molecules. The accuracy of the potential models for both molecules should be increased. As stated in [18], induction forces may have a significant effect for H_2S since the polarizability of H_2S ($2.78 \cdot 10^{-24}\,cm^3$) is almost twice the one of H_2O ($1.45 \cdot 10^{-24}\,cm^3$) [37]. Moreover, the readjustment of the potential performed by Kristof *et al.* [3] in order to reproduce the VLCC of H_2S, assumes that the dipole moment of H_2S has the same enhanced value in both phases. As such a potential is obviously not appropriate for describing the gas phase since induction forces play a very minor role in this phase, the parameters, obtained by fitting the VLCC, may be affected. A polarizable model would avoid this effect. It might also be important to take into account the electrostatic interaction between alkanes and H_2S molecules. Distributions of partial charges for alkanes have been suggested in the literature [38, 39]. Chen *et al.* [40] have recently calculated the VLCC of pure alkanes using the OPLS-AA force field, with and without partial charges. Their results showed no significant difference in fluid-phase behaviour of pure alkanes when partial charges were included in the calculations. However, it is known that simple atomic point charges models are unable to accurately reproduce the electrostatic potential created by an alkane molecule [41]. Work is in progress to correctly describe the electrostatic interactions in such mixtures [42]. Finally, the use of simple Lorentz-Berthelot mixing rules may not be well suited to deal with interactions between centres of force that are very different in nature (the well-depth of

H_2S is 250 K whereas for CH_2, it is equal to 80 K). More elaborated mixing rules might improve this point.

Deviations between simulation and experimental data were also observed for the decane–CO_2 binary mixture. These deviations seem to be mainly due to the fact that AUA-3 model does not perform as well for decane as it does for shorter alkanes. For instance, calculations for the pentane–CO_2 binary mixture yield good agreement with experimental results. However, the electrostatic interactions between the alkane and CO_2 molecules, although they are expected to be weaker than in the case of H_2S, might not be negligible [42].

In this work, we have used potential models which were initially adjusted in order to reproduce some properties of the liquid phase. The parameters of AUA-3 for instance were fitted to reproduce diffusion coefficients and volumetric properties of liquid alkanes [14]. Models for CO_2 and H_2S were developed for liquid and solid phases before being readjusted to reproduce VLCC [3, 4]. As shown by Errington *et al.*, in the case of water–methane and water-ethane mixtures [23], using physically meaningful potential models, molecular simulation yields reliable predictions of mixture phase equilibria even in the case of very dissimilar components such as H_2S, CO_2 and alkane chains. An increase in the accuracy of the simulation results requires further work on the potential models.

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