

Molecular Simulation of Vapor–Liquid Phase Equilibria of Hydrogen Sulfide and Its Mixtures with Alkanes

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A new set of force field parameters for a three-point potential model of hydrogen sulfide (H_2S) is proposed, based on fitting of the experimental saturation densities. The proposed model also reproduces well the critical properties and vapor-phase dipole moment of the substance. The new model is used to study vapor–liquid phase equilibria of binary mixtures of hydrogen sulfide with alkanes of various lengths. Results of binary phase equilibria simulations are found to be in good agreement with available experimental data.

1. Introduction

In the petrochemical industry, sulfur-containing molecules constitute a very important class, besides hydrocarbons. Sulfur-related compounds are polluting agents in petroleum fluid and must be removed. A proper understanding of the phase equilibria of these compounds and their mixtures with hydrocarbons is thus required for efficient design of oil-refining processes.

Hydrogen sulfide often occurs in the petroleum reservoirs, in a multicomponent mixture with various alkanes. To understand the multicomponent hydrogen sulfide–alkane mixtures, knowledge of the phase equilibria of the binary subsystems is important. Recently, Feng and Mather^{1–4} have performed a series of experimental studies to extend our understanding of the H_2S –alkane binary mixtures up to *n*-eicosane. Despite these experimental studies, it remains a fact that at high temperatures and pressures experimental studies of such systems are very difficult and often unsafe. Equations of state methods are often used to estimate phase equilibria of such systems. However, due to the empirical nature of these equations, they are heavily dependent on experimental inputs.

In recent years, since the appearance of the Gibbs ensemble simulation technique,⁵ molecular simulation is increasingly becoming a popular tool for studying phase equilibria of complex fluids. From simple Lennard-Jones fluids to fairly realistic models of molecules, coexistence properties can now be simulated with unprecedented levels of accuracy. A number of recent studies^{6–9} have demonstrated the ability of molecular simulations to estimate the phase equilibria of various alkane mixtures with quantitative accuracy when a suitable force field model is available. However, to date, simulation studies of mixtures containing non-hydrocarbon molecules have been limited. For H_2S –alkane systems, molecular simulation of only an H_2S –pentane system has appeared, reported by Delhommelle et al.¹⁰ In the current work, one of our objectives is to demonstrate the ability of molecular simulations in predicting phase equilibria of binary mixtures of H_2S with longer alkane systems.

Quantitative predictions of phase equilibria from simulation studies are highly dependent on the development of accurate force field models. With the development of sophisticated techniques for phase equilibria simulations, a number of new

potential models and parameter sets for alkanes have been devised in recent years.^{9,11–13} In this work we use the Nath–Escobedo–de Pablo revised (NERD)¹¹ force field to model the alkanes studied. NERD is a united-atom force field model, in which an *n*-alkane molecule is described as a flexible linear chain of methylene (CH_2) pseudoatoms, terminating at both ends with methyl (CH_3) pseudoatoms. NERD force field parameters have been demonstrated to provide accurate descriptions of phase equilibria of pure components and mixtures of various linear and branched alkanes.^{6,7,11}

Unlike the situation for alkanes, studies to estimate the force field parameters for hydrogen sulfide are limited. The most accurate of these force fields in predicting pure component phase equilibria is the model given by Kristof and Liszi.¹⁴ The model for H_2S used by Kristof and Liszi is a four-site model, in which, besides the three atomic sites, a fourth point charge was placed on the bisector of the H–S–H angle. Although, the Kristof–Liszi model works reasonably well in predicting the phase equilibria of H_2S , we found their model to be unsuitable for application with our atom-type-based software.¹⁵ In this work, we thus propose a new three-site model for H_2S by fitting to the experimental orthobaric densities of the pure component system. With the introduction of the H_2S model, NERD is now a semi-united-atom force field model in which hydrogen atoms are explicitly represented when nonzero point charges are required to model them.

Complete prediction of a P – x or T – x binary phase diagram from Gibbs ensemble simulation requires the simulation to be conducted at several state points. Due to the high demand of computational resources in conducting these simulations, often only four or five simulation points are calculated to produce a diagram. Thermodynamic data reduction methods¹⁶ can be easily used to extend the simulated phase equilibria points to other state points where simulation had not been conducted. Although various thermodynamic data reduction methods to analyze mixture phase equilibria data are available and are used by the experimental community, application of such methods with molecular simulation is nonexistent. In this work, we demonstrate the use of thermodynamic methods to extend and refine simulated binary phase equilibria data.

2. Modeling and Simulation Methodology

The NERD force field model uses a united-atom representation of the alkanes. In the NERD model, the nonbonded potential

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TABLE 1: Nonbonded Energy Parameters

pseudoatom	σ (Å)	ϵ/k_B (K)	charge
CH ₃	3.91	104.0	
CH ₂	3.93	45.8	
H (in H ₂ S)	0.98	3.9	+0.124
S	3.72	250.0	−0.248

between interaction sites that either are separated by more than three bonds or belong to different molecules is described by the Lennard-Jones 12-6 potential. For bonded interactions, NERD uses a harmonic potential for bond stretching and bond bending and a cosine series expression for torsions. In the NERD model, electrostatic potentials are considered negligible for alkanes. Complete details of the NERD parameters used for alkanes are available in the original publications.¹¹

In this work, we model hydrogen sulfide using a three-site model: interaction sites are placed at each of the hydrogen and sulfur atom nuclei. We use the same potential forms to describe the bonded and nonbonded parameters as were used to model alkanes in NERD. Electrostatic terms are represented by point charges at each of the interaction sites, and energies are calculated using the Coulombic interaction potentials. Although the usual practice in the united-atom force fields is to place Lennard-Jones interaction terms only on the heavy atoms of polar molecules and the point charges on both heavy atoms and hydrogens, in our model all of the interaction sites contain Lennard-Jones interactions. We believe that having additional Lennard-Jones terms on the hydrogen atoms can improve flexibility in modeling of these molecules. Besides, since calculation of interaction energies due to Lennard-Jones terms is computationally much less demanding (or at the most equally demanding) than the calculation of the Coulombic energies, we believe that having explicit parameters on these hydrogen atoms does not make this model computationally inferior to the other “united-atom” polar molecule models.

To obtain force field parameters for H₂S, we first obtained the optimal molecular geometry and the atomic point charges on each interaction site by fitting the ab initio ESP charges, using the Accelrys DMol³ software.¹⁷ The DMol³ calculations were conducted using the double numerical plus d-functions (DND) basis set. From our calculations, we obtained optimum values for the H–S bond and the H–S–H angle to be 1.365 Å and 91.5°, respectively. Fitting of the ESP charges gave point charges of 0.124 and −0.248 on H and S sites, respectively. Note that our values of point charges are much smaller than the charges used by Jorgensen¹⁸ in his three-point model of H₂S (point charge of −0.47 on sulfur, and so on). From our model, we predict a molecular dipole moment of 1.134 for H₂S, which is slightly higher than the experimentally predicted value of 1.0.¹⁹ The Jorgensen model predicts a dipole moment of 2.1, whereas the Kristof–Liszi model predicts a value of 1.4. For bond-stretching and bond-bending interaction energies, we use the same values as those used in NERD for alkanes.

In determining the nonbonded Lennard-Jones (LJ) parameters for H₂S, we obtained the parameters for hydrogen from the CFF force field.²⁰ We modified the LJ 9-6 parameters from CFF to fit to a LJ 12-6 model such that the maximum well depth of the model is preserved. At this point we are left with the LJ parameters for the sulfur atom, which we obtained by trial-and-error fitting of the experimental pure component H₂S phase equilibria data to the Gibbs ensemble simulation results. Nonbonded parameters for all the molecules studied in this work are listed in Table 1.

In all our calculations, a cutoff radius of 10.0 Å was employed for both the Lennard-Jones interactions and the Coulomb

interactions. For the Lennard-Jones interactions we used an atom-based cutoff, and for the Coulomb interactions we used a group-based cutoff.²¹ In applying group-based cutoffs, charge groups are first defined, which are small groups of atoms close to one another with a net charge of zero or almost zero. Often, charge groups are identical to common chemical functional groups. For H₂S, there is only one charge group. Thus, for H₂S, a group-based cutoff is identical to a molecule-based cutoff. It has been shown that if a group-based cutoff is employed with a safe (about 9.0 Å) cutoff radius, long-range corrections to Coulomb energy calculations are negligible.²¹ Delhommelle et al.¹⁰ have also demonstrated that Coulomb long-range corrections have no effect on the predicted phase equilibria from systems involving H₂S. We used a standard tail correction for Lennard-Jones interactions and did not employ any long-range corrections to our Coulomb interactions. As in our previous works,⁶ we used simple Lorentz–Brethelot combining rules for the interaction parameters between unlike pairs and did not use any adjustable mixing parameters.

All the coexistence curve simulations were conducted in the Gibbs ensemble. For pure components, all simulations were conducted at constant volume and temperature, and for mixtures, simulation were conducted at constant pressure and temperature. All molecule-transfer moves were supplemented by the continuum configurational bias method.^{22,23} For equilibration during Gibbs ensemble simulation, we used a combination of translation and rotation moves for pure H₂S. In these simulations, about 20% translation moves, 20% rotation moves, 5% volume moves, and the rest of transfer moves were employed. For mixture simulations, hybrid Monte Carlo (HMC) moves were added to enhance equilibration. Within the HMC procedure, five molecular dynamics steps were used to generate a global trial Monte Carlo move. A time step of 2.0 fs was used for the molecular dynamics part of the HMC move. For mixture simulations, about 10% translation moves, 10% rotation moves, 5% HMC moves, 5% volume moves, and the rest of transfer moves were employed.

The size of the systems investigated ranged from 300 molecules for pure H₂S to 100–200 H₂S and 20–100 alkane molecules for mixtures. The lengths of each pure component simulation were 2×10^6 steps for equilibration and 5×10^6 steps for production. The lengths of each mixture simulation ranged from 1×10^7 to 5×10^7 steps for equilibration and from 3×10^7 to 10×10^7 steps for production. It was observed from simulation of the binary H₂S–alkane mixtures that the acceptance of the transfer moves for the H₂S molecules is about 5%, which is high compared to that obtained for simulation of alkane mixtures. Using a HP ES45 Quad Alpha 1000-MHz Tru64 computer, the time required for a typical binary mixture simulation containing 20 *n*-eicosane molecules and 150 H₂S molecules, and with 5×10^7 equilibration steps and 10×10^7 production steps, is about 50 CPU hours.

3. Results and Discussions

Pure Component H₂S. To demonstrate the performance of the newly developed NERD force field parameters for hydrogen sulfide in this work, we begin by comparing experimental and simulated vapor–liquid orthobaric densities in Figure 1. For comparison purposes, simulation predictions from the Kristof–Liszi model (from their original publication)¹⁴ are also shown in the figure. As is evident from the figure, the agreement between the experimental data and our simulation results is excellent. Predictions from the Kristof–Liszi model are also quite reasonable; however, they give slightly higher liquid

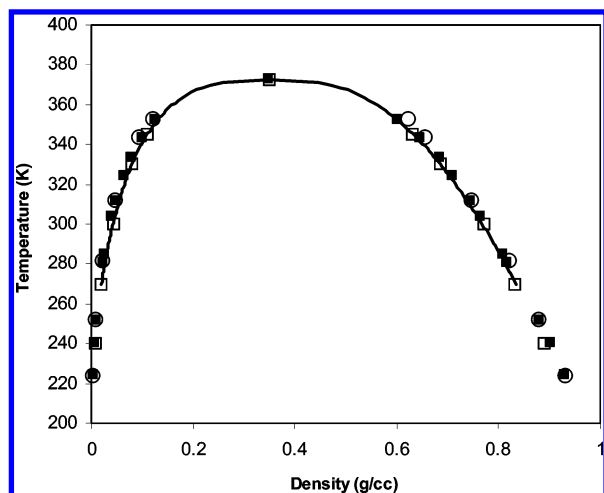


Figure 1. Orthobaric densities for hydrogen sulfide. The filled symbols are experimental results,¹⁹ the open squares are simulation results from the current model, the open circles are simulation results from the Kristof–Liszi model,¹⁴ and the lines show an Ising fit to the simulation data from current model. The error bars near the critical point are less than 3 times the size of the symbols. Error bars at lower temperature are less than twice the size of the symbols.

TABLE 2: Simulation Results for the Orthobaric Densities of H₂S

<i>T</i> (K)	ρ_{liq} (g/cm ³)	ρ_{vap} (g/cm ³)
345	0.632 (22)	0.109 (9)
330	0.685 (17)	0.079 (6)
300	0.772 (12)	0.044 (4)
270	0.831 (9)	0.020 (2)
240	0.889 (8)	0.009 (1)

densities as we approach the critical region. From our observations in Figure 1, we estimate that, near the critical region, the performance of the NERD model (new model) is slightly superior compared to that of the Kristof–Liszi model. Simulated coexistence densities and their statistical accuracies for the current model are also given in Table 2.

Since Gibbs ensemble simulation becomes difficult near the critical point due to large fluctuations in the simulated systems, a common practice is to estimate the critical points from a weighted linear fit of the subcritical simulation data, using the Ising scaling law. It has been established that, for hydrocarbon systems, the Ising scaling law, with the universal constant of $\beta = 0.32$, can fit the experimental data very well.²⁴ However, for polar systems, the exponent β starts deviating from ideality.²⁵ In this work, we thus fit the experimental phase equilibria data for hydrogen sulfide to estimate the Ising scaling constant and use it to estimate critical constants from our simulation. More accurate estimates of critical constants can be obtained by applying crossover or finite-size corrections to grand canonical ensemble simulation data; however, such calculations are beyond the scope of this article, as they require simulations over a wide range of system sizes. From our fitting of the experimental data from hydrogen sulfide, we found that an exponent of 0.336 describes the data well. Fitting of the NERD model simulation data with an exponent of 0.336 gives us a critical temperature of 372.43 K and a critical density of 0.351 g/cm³, which compare well with the experimental predictions of 373.4 K and 0.3476 g/cm³,¹⁹ respectively. The Ising fit curve to the simulation data is also shown in Figure 1.

Figure 2 presents experimental and simulated results for the saturation pressures of H₂S. A plot of the logarithm of saturation pressure versus the inverse temperature is chosen to allow fitting of the data to estimate the critical pressure following the

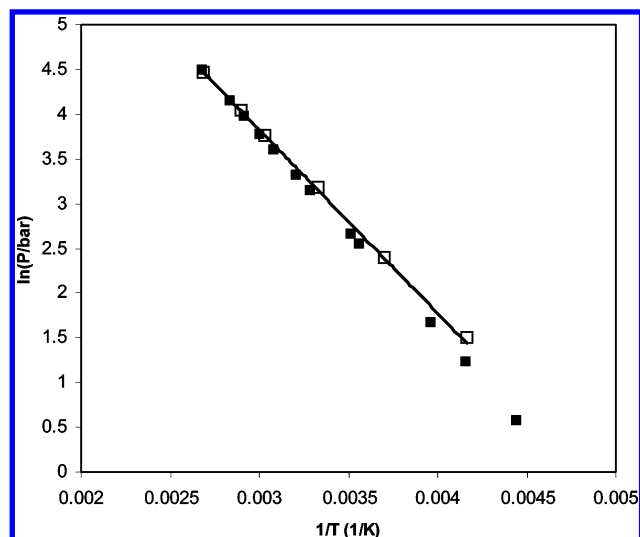


Figure 2. Plots of the logarithm of saturated vapor pressure versus the inverse temperature. The filled symbols are experimental results,¹⁹ the open squares are simulation results, and the lines show a Clausius–Clapeyron fit to the simulation data. The error bars in simulated vapor pressures are less than twice the size of the symbols.

Clausius–Clapeyron equation.²⁶ The Clausius–Clapeyron equation fit curve to the simulation data is also shown in Figure 2. In general, agreement between the experimental and simulation data for the current model is good; however, at low temperatures the simulated pressures are slightly higher compared to the experimental values. The estimated critical pressure from Clausius–Clapeyron fit to the simulation data is 87.6 bar, which agrees reasonably well with the experimental value of 89.6 bar.¹⁹ We also estimate a boiling point temperature of 205.8 K for our model on the basis of the Clausius–Clapeyron fit to the simulation data, which is slightly lower than the experimental value of 212.8 K.

Binary Mixtures. One of our main objectives in this work is to demonstrate the ability of molecular simulation in determining phase equilibria of H₂S–alkane mixtures. In this section we show simulation results of binary mixtures of H₂S with linear alkanes of various size and compare them with available experimental data.

Figure 3 shows a pressure versus composition diagram for a binary H₂S–pentane mixture at $T = 377.6$ K. The simulations are conducted without the use of any binary mixing parameters; agreement with experiment is satisfactory at all pressures. In general, simulations seem to slightly overpredict the solubility of H₂S in both the vapor and the liquid phases at all pressures. Delhommelle et al.,¹⁰ using the Kristof–Liszi model for H₂S¹⁴ and the Ungerer et al. anisotropic united-atom model¹³ for alkanes, had also previously attempted simulation of this H₂S–pentane mixture. For comparison purposes, results from their simulation study are also shown in Figure 3. Comparison with experimental data shows that their predictions of the H₂S mole fractions are in good agreement at low pressures but are severely underpredicted at high pressures in both phases. On the basis of our observations in Figure 3, NERD model predictions are in better agreement with experimental data²⁷ compared to the predictions from Delhommelle et al.

Thermodynamic data reduction methods can be useful in extending the simulated phase equilibria points to other state points where simulation had not been conducted. We fit our H₂S–pentane simulation data to generate a continuous diagram from $x(\text{H}_2\text{S}) = 0.0$ to $x(\text{H}_2\text{S}) = 0.70$, the highest concentration at which simulations were conducted. In most cases, thermo-

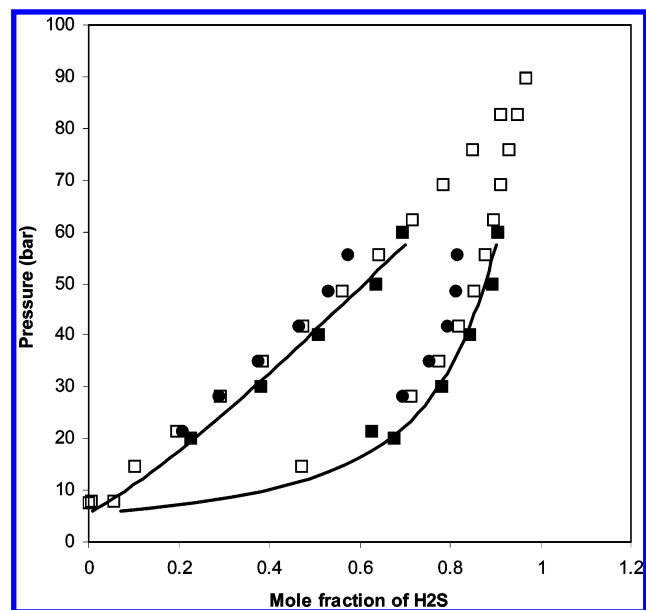


Figure 3. Pressure vs composition diagram for a binary mixture of hydrogen sulfide and pentane at $T = 377.6$ K. The open symbols are experimental data,²⁷ the closed squares are simulation results from current model, the closed circles are simulation results from Delhom-melle et al.,¹⁰ and the lines show a thermodynamic fit to the simulation results from current model. Simulation error bars are less than 3 times the size of the symbols.

dynamic data reduction methods are used only with low-pressure phase equilibria data due to our lack of knowledge of the Poynting factor.¹⁶ Recently we devised an iterative technique to obtain the Poynting factor from vapor–liquid equilibrium data,²⁸ which can be used in data reduction methods for high-pressure systems. Brief details of the data reduction method are described in Appendix A. For a subcritical mixture, data reduction methods can be used to generate curves for the full range of compositions, from $x = 0$ to 1. However, since knowledge of a critical region is not built within the thermodynamic relations used in these data reduction process, extrapolation beyond the highest available concentration point is not possible for a mixture containing supercritical components. The data reduction fit curve to the simulation results is also shown in Figure 3. We used the simple Van Laar equation¹⁶ for excess free energy expression in our calculation. NERD model predictions are in reasonable agreement with experimental data for the entire range of the fitted curve.

Figure 4 shows the Poynting factors obtained as a part of the thermodynamic fitting of the simulation data. Thermodynamic data reduction techniques require the knowledge of vapor pressure of the components. When a critical component is present in the system (H₂S, in our case), the critical pressure is used instead of the vapor pressure. Use of the critical pressure only shifts the calculated Poynting factors by some constant factor and has no effect on the data reduction method. From Figure 4, it is obvious that the use of a constant (unity) value for the Poynting factors would severely affect the calculated mixture concentrations.

We have also conducted Gibbs ensemble simulations to estimate the solubility of H₂S in longer alkanes at a series of temperatures and pressures. We first look at the effect of alkane chain length on the solubility of H₂S at a fixed temperature. Before presenting the simulation results, we would like to point out an interesting observation from experimental solubility data of H₂S in alkanes of various lengths at a fixed temperature. Experimental data^{1,2} show that the solubility values of H₂S

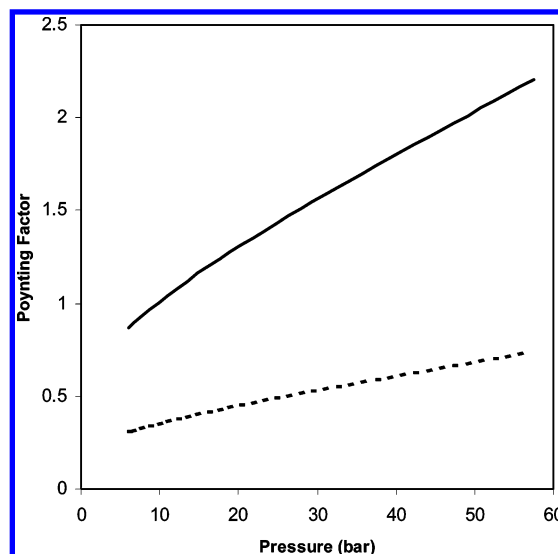


Figure 4. Poynting factor data as a function of pressure from thermodynamic data fit of the simulation results for a binary H₂S–pentane mixture at 377.6 K. The solid line corresponds to pentane, and the dotted line corresponds to hydrogen sulfide.

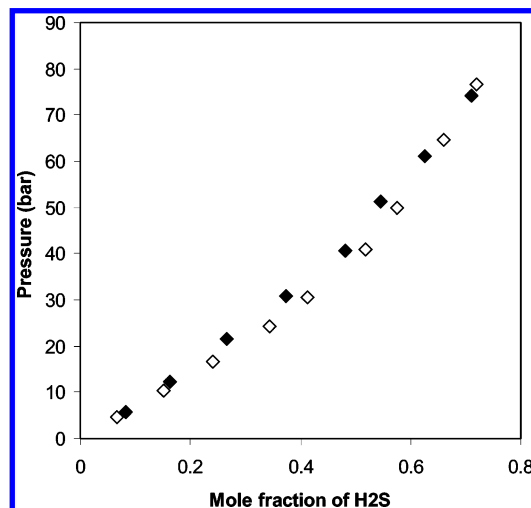


Figure 5. Comparison of experimentally predicted pressure vs composition diagrams for H₂S–*n*-hexadecane² and H₂S–*n*-eicosane¹ binary mixtures at 423.2 K. The closed symbols are for systems containing *n*-hexadecane, and the open symbols are for systems containing *n*-eicosane.

(presented in mole fraction of H₂S in the alkane) in *n*-hexadecane and *n*-eicosane at 423.2 K and 0–80 bar are almost identical (Figure 5), differing slightly only in the middle pressure range. Our simulation results for the solubility of H₂S in *n*-dodecane, *n*-hexadecane, and *n*-eicosane at 423.2 K show the same trend; the differences in observed solubilities in various alkanes are within the simulation error bars. To better represent the simulation data and compare them with experimental predictions, we have thus plotted our simulation results in units of grams of gas per 100 grams of alkane in Figure 6. Our simulation results compare well with available experimental data. The solubility of H₂S (in grams of gas per 100 grams of alkanes) increases with a decrease in the alkane chain length and increases with an increase in the system pressure.

Thermodynamic methods can also be used in extending simulation results for solubility of small molecules in polymeric liquids. The Krichevsky–Kasarnovsky equation (Appendix B) is one of the widely used equations for fitting solubility data, due to its simplicity. Feng and Mather^{1,2} used this equation to

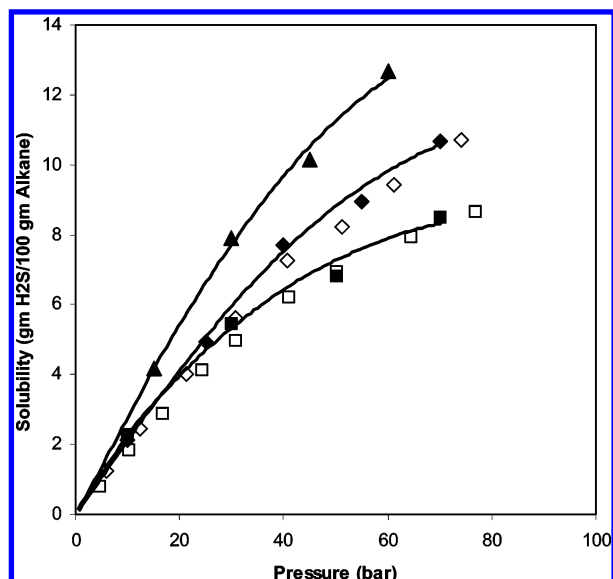


Figure 6. Solubility of H₂S in normal alkanes of various lengths at 423.2 K. The open symbols are experimental data,^{1–3} the closed symbols are simulation results from the current model, and the lines show a Krichevsky–Ilinskaya fit to simulation data. The triangles are for solubility data in *n*-dodecane, the diamonds are for *n*-hexadecane, and the squares are for *n*-eicosane. Simulation error bars are less than 3 times the size of the symbols.

TABLE 3: Henry's Constants of H₂S in Various Alkanes

alkane	<i>T</i> (K)	<i>H</i> (MPa) ^a	<i>H</i> (MPa) ^b
<i>n</i> -dodecane	352.2	3.829	4.52
<i>n</i> -dodecane	423.2	7.585	-
<i>n</i> -hexadecane	423.2	7.549	7.01
<i>n</i> -eicosane	423.2	5.126	6.42

^a This work with Krichevsky–Ilinskaya equation. ^b From experimental data with Krichevsky–Kasarnovsky equation.

fit their experimental solubility data of H₂S in alkanes and estimate Henry's constants. However, as pointed out in Appendix B, the Krichevsky–Kasarnovsky equation is accurate only at very low pressures. In this work we use the Krichevsky–Ilinskaya equation to fit the simulation data and estimate Henry's constants. The data reduction fit curve to the simulation results is also shown in Figure 6. Estimates of Henry's constants obtained from our fitting are given in Table 3.

The estimates for Henry's constants from this work should be considered with caution since the estimates strongly depend on the slope of the fitted curves (Krichevsky–Ilinskaya fitting to Gibbs ensemble simulation data) near zero pressure and a very small deviation in the trend of the simulation data at low pressure would have a strong impact on the resulting value. Note that a much simpler approach, such as the use of Widom particle transfer with the configurational bias technique, is a more accurate technique to estimate Henry's constants from simulation. However, such studies are not within the scope of this work. Better estimates of Henry's constants from the method used in this work would require performing more simulations at low pressures.

We also studied the effects of temperature on the solubility of H₂S in alkanes at various pressures. Figure 7 shows the solubility of H₂S in *n*-dodecane at 352.7 and 423.2 K over a range of pressures. Again, our simulation results compare well with available experimental data. We observe that the solubility of H₂S in *n*-dodecane increases with a decrease in temperature. Simulation results are fitted using the Krichevsky–Ilinskaya equation, and the fitting curves are also shown in the figure.

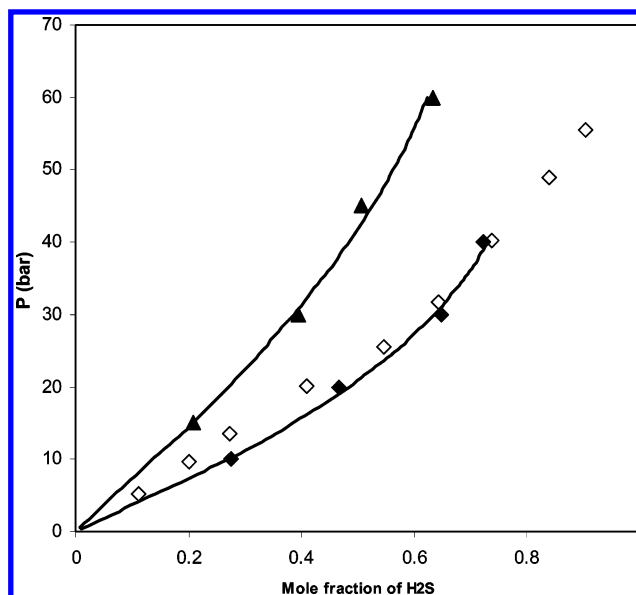


Figure 7. Solubility of H₂S in *n*-dodecane at various temperatures. The open symbols are experimental data,³ the closed symbols are simulation results from the current model, and the lines show a Krichevsky–Ilinskaya fit to simulation data. The triangles are at *T* = 423.2 K, and the diamonds are at *T* = 352.2 K. Simulation error bars are less than 3 times the size of the symbols.

Estimated Henry's constants of H₂S in *n*-dodecane are also presented in Table 3.

4. Conclusions

We have proposed a new set of force field parameters for a three-point model of hydrogen sulfide. This is the first step in extending the NERD force field for molecules containing electrostatic charges. Until now, NERD had been developed as a united-atom force field model for hydrocarbon molecules that provides accurate descriptions of phase equilibria of pure components and mixtures. With the addition of hydrogen sulfide, NERD is now a semi-united-atom model, in which hydrogens are explicitly modeled when explicit charges on the hydrogen atoms are required. Unlike the earlier practices in extending united-atom force fields into polar molecules, all of the interaction sites in our model contain Lennard-Jones interactions.

The newly developed set of parameters provides an accurate description of the phase coexistence densities for pure hydrogen sulfide. Simulations were also conducted to study the ability of the proposed model to describe low- and high-pressure phase equilibria in mixtures with alkanes of various lengths. The system studied here included mixtures of hydrogen sulfide with pentane, *n*-dodecane, *n*-hexadecane, and *n*-eicosane. The simulation results for mixtures were compared with experimental data; it was found that, for these mixtures, simulations provide quantitative agreement with experimental data without a need for adjustable parameters.

Thermodynamic data reduction methods were used to fit the simulated mixture compositions at constant temperature and over a pressure range. It was shown that data reduction methods could be used, even for supercritical mixtures, in extending simulated phase equilibria results over state points where simulations were not conducted.

Extension of the NERD force field for other sulfides and thiols is currently under study.

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Appendix A: Phase Equilibria Thermodynamics of Binary Mixtures

The fundamental equation for the coexistence of a component i in two phases is given by

$$f_i^V = f_i^L \quad (\text{A-1})$$

where f is the fugacity and the superscripts “V” and “L” refer to the vapor phase and liquid phase, respectively. Without any simplifications and applying thermodynamic relations, eq A-1 can be rewritten as¹⁶

$$y_i P = \gamma_i x_i P_{\text{vp}i} \mathcal{P}_i \quad (\text{A-2})$$

where the Poynting factor

$$\mathcal{P}_i = \frac{\phi_i^s}{\phi_i} \int_{P_{\text{vp}i}}^P \frac{V_i^L}{RT} dP \quad (\text{A-3})$$

P is the total pressure, V is the molar volume, P_{vp} is the vapor pressure, γ is the activity coefficient, ϕ is the fugacity coefficient, and x and y are the liquid-phase and vapor-phase mole fractions, respectively. The superscript “s” refers to saturation in eq A-3. If the Poynting factor and activity coefficient for component i are known at a given pressure and temperature, then eq A-2 can be easily used to obtain the equilibrium mole fractions of that component in a mixture.

For subcritical components and for low total pressures, the value of the Poynting factor in eq A-2 is near unity. Since calculation of the Poynting factor is not straightforward, use of eq A-2 has so far been limited to mixtures of subcritical components at low pressures where the Poynting factor is set to unity.

Vapor–liquid data reduction using eq A-2 requires the use of an empirical equation for the molar excess Gibbs free energy. Experimental or simulated vapor–liquid phase equilibria data at known points can be used to fit the expression for molar excess free energy and the activity coefficients calculated from direct manipulation of the free energy expression.

An iterative approach to solve eq A-2 for a system in which the Poynting factor is not unity is described below:²⁸

(1) Estimate activity coefficients from eq A-2 with initial estimates of the Poynting factors to be unity.

(2) Using the obtained activity coefficients from (1) and using available simulation results, calculate the coefficients of the Gibbs energy expression.

(3) Recalculate the activity coefficients from the Gibbs energy expression.

(4) If our assumptions about the Poynting factors being unity were correct, activity coefficients calculated from step (3) should exactly match those calculated in step (1). If the activity coefficients are different, repeat steps (2) and (3) using these new values of activity coefficients in step (2).

(5) If we denote the activity coefficients obtained from step (1) as the ideal activity coefficients, the Poynting factors can now be obtained from the ratio of the actual activity coefficients and the ideal activity coefficients.

Appendix B: Thermodynamics of Solubilities of Gases in Liquids

On the basis of the simplifying assumptions that the activity coefficient of the solute is nearly constant and that the partial

molar volume of the solute in the liquid solution at infinite dilution is nearly incompressible, eq A-1 can be written to describe the solubility of a gas in a liquid at constant temperature, according to Krichevsky and Kasarnovsky:²⁹

$$\ln \frac{f_2}{x_2} = \ln H_{2,1} + \frac{v_2^\infty (P - P_{\text{vp}1})}{RT} \quad (\text{B-1})$$

where $H_{2,1}$ is the Henry’s constant of component 2 in component 1, v_2^∞ is the partial molar volume of the solute in the liquid solution at infinite dilution, and subscripts “1” and “2” refer to the solvent and the solute, respectively. The assumption that v_2^∞ is independent of pressure is reasonable if the solution temperature is well below the critical temperature of the solute, which is often the case of our interests. However, the activity coefficient is a constant only at very low solute mole fractions. Consequently, eq B-1 can be successfully used only for systems in which the gas solubility is low.

By using an expression for free energy of the solution, eq B-1 can be corrected to account for the variation of the activity coefficient of the solute with mole fraction. Using the two-suffix Margules equation for the free energy,¹⁶ the Krichevsky–Ilinskaya equation for solubility of a gas in a liquid at constant temperature is³⁰

$$\ln \frac{f_2}{x_2} = \ln H_{2,1} + \frac{v_2^\infty (P - P_{\text{vp}1})}{RT} + \frac{A}{RT} (x_1^2 - 1) \quad (\text{B-2})$$

where A is the constant from the free energy expression.

Although eq B-2 is very accurate in describing gas solubility in liquids, application of the equation is limited due to difficulties in estimation of the three required constants ($H_{2,1}$, A , and v_2^∞) of this equation from solubility data reduction. A numerical method for solution of eq B-2 to obtain the constants, when only the solubility data are present, is described below:²⁸

(1) Calculate the gas-phase fugacity for the solute constituent using the thermodynamic relationship:

$$\ln \left(\frac{f}{P} \right)_{\text{pure } i} = \int_0^P \frac{z - 1}{P} dP \quad (\text{B-3})$$

where z is the compressibility factor. If a series of Gibbs ensemble simulation are carried out to generate the solubility data, the gas-phase densities are available as a byproduct of those simulations. For numerical integration of eq B-3, we use cubic splines to interpolate densities (i.e., compressibility factors) at intermediate pressures.

(2) To solve eq B-2, we recognize that it is a linear equation with three unknowns, of the form:

$$Y = A + B\alpha + C\beta \quad (\text{B-4})$$

where A , B , and C are unknowns and the values of $Y = \ln(f_2/x_2)$, $\alpha = (P - P_{\text{vp}1})$ and $\beta = (x_1^2 - 1)$ are known at the given data points. Perform a multiple linear regression using least-squares method³¹ to solve for A , B , and C (i.e., $H_{2,1}$, A , and v_2^∞).

References and Notes

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