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An NPT Monte Carlo Molecular Simulation-Based Approach to Investigate Solid-Vapor Equilibrium: Application to Elemental Sulfur-H$_2$S System

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Abstract

In this work, a method to estimate solid elemental sulfur solubility in pure and gas mixtures using Monte Carlo (MC) molecular simulation is proposed. This method is based on Isobaric-Isothermal (NPT) ensemble and the Widom insertion technique for the gas phase and a continuum model for the solid phase. This method avoids the difficulty of having to deal with high rejection rates that are usually encountered when simulating using Gibbs ensemble. The application of this method is tested with a system made of pure hydrogen sulfide gas (H$_2$S) and solid elemental sulfur. However, this technique may be used for other solid-vapor systems provided the fugacity of the solid phase is known (e.g., through experimental work). Given solid fugacity at the desired pressure and temperature, the mole fraction of the solid dissolved in gas that would be in chemical equilibrium with the solid phase might be obtained. In other words a set of MC molecular simulation experiments is conducted on a single box given the pressure and temperature and for different mole fractions of the solute. The fugacity of the gas mixture is determined using the Widom insertion method and is compared with that predetermined for the solid phase until one finds the mole fraction which achieves the required fugacity. In this work, several examples of MC have been conducted and compared with experimental data. The Lennard-Jones parameters related to the sulfur molecule model (ε, σ) have been optimized to achieve better match with the experimental work.

Keywords: Molecular simulation; Monte Carlo simulation; NPT ensemble; Widom insertion; Solid-vapor equilibria

1. Introduction

In petroleum industry, the problem of sulfur deposition in down hole tubulars and in above surface facilities such as gas pipelines represents a great challenge [1-3]. Sulfur, in small amounts, usually exists in sour gas, however, with the larger volume of gas produced, considerable amounts of sulfur may deposit upon changes in

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operating conditions namely pressure and/or temperature. The solubility of sulfur in sour gas is a function of many factors including the pressure, temperature, and gas composition. In particular, the pressure represents one of the primary factors affecting sulfur solubility. At relatively low pressures and temperatures that are found in gas pipelines, the solubility of sulfur can be very small to measure directly. This motivated the search for predictive techniques including molecular simulation that can predict small amounts of deposited sulfur. The study of phase equilibrium has been extensively implemented in molecular simulation using Gibbs ensemble [4-12] in which each phase is simulated in a separate box allowing particle interchange between the two boxes. Apparently when one of these phases is solid this represents a great challenge as most of the swapped particles to the solid phase box will be rejected. Swapping moves are responsible for equilibrating the chemical potential between the two phases. Therefore, the Gibbs ensemble fails whenever such solid-vapor equilibrium state is considered. This leaves little hope for the use of molecular simulation to investigate such an important phenomenon. Hence, several algorithms based on molecular simulations have been introduced to investigate systems where solid-fluid phase equilibria exist. For instance, Gibbs-Duhem integration [13, 14] and histogram reweighting [15].

In this work, we propose another methodology in which each phase is handled separately. It is based on the fact that, at the state of thermodynamic equilibrium, the sulfur in both phases must possess the same fugacity. Apparently, the fugacity of sulfur in gas phase can be determined using Monte-Carlo (MC) molecular simulation; however, for the solid phase, MC may not work. Instead it might be determined experimentally and indeed one can find in the literature a number of correlations to evaluate the fugacity of solid elemental sulfur at certain temperatures and pressures [16, 17]. On the other hand, only the vapor phase of the system under interest is simulated in Isobaric-Isothermal ensemble at the desired pressures and temperatures. Several simulations are run at the specified conditions with different mole fractions of elemental sulfur. For each simulation, the fugacity is evaluated using the Widom insertion method [18, 19]. The mole fraction which succeeds in achieving an equal value of fugacity as the one evaluated by the chosen correlation is taken as the true one.

In the following sections, all the aspects and elements of the method are discussed and explained. The methodology is introduced and then followed by the experimental work scheme used, where 4 groups of experiments made of at least 15 simulations were conducted. The results obtained showed a good agreement with the reproduced experimental data.

2. Methodology

2.1. Elemental Sulfur

Sulfur [20] is ranked as the second by the number of allotropes after carbon. Thus it has a complex chemistry. It exists in polymeric species ranging from S_2 to S_8. However for simplicity, only S_8 molecules of sulfur were simulated where the other forms are neglected as S_8 is detected to be the dominant form in vapor species [16].

2.2. Isobaric -Isothermal Ensemble, NPT

As have been stated earlier, only the vapor phase is to be simulated, thus only one simulation box is created. The Isobaric-Isothermal ensemble [10] is a statistical mechanical ensemble that maintains constant temperature, T, and constant pressure, P; where the number of particles N is preserved in the simulation box throughout the whole simulation. Therefore it is frequently referred to as NPT ensemble.

2.3. Molecular Models

The first critical and significantly important aspect in molecular simulation is the specification of suitable model parameters for the molecules to be simulated. Table 1 summarizes the details of the molecular models used for S_8 and H_2S. For both molecules the Lennard-Jones model is adopted to evaluate dispersion-repulsion

interactions. The cutoff radius for both dispersion-repulsion and columbic interactions was taken as half of the simulation box length.

$$U_{ij} = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\varepsilon_o r_{ij}} \qquad (1)$$

S_8 is considered as a flexible ring (Fig. 1a) while internal rotation is allowed. The intramolecular potential [21] for bending angels S-S-S is considered harmonic with $C_\beta = 25725 \ k_B/rad^2$, $\beta_o = 108 \ deg$, where k_B is Boltzmann constant.

$$V(\beta) = \frac{1}{2} C_\beta (\beta - \beta_o)^2 \qquad (2)$$

Double well intramolecular potential[21] for torsion $V(\tau)$ is computed with parameters $A_\tau = 57.192$, $B_\tau = 738.415$, $C_\tau = 2297.880 k_B$ and $D_\tau = 557.255 k_B$.

$$V(\tau) = A_\tau + B_\tau \cos\cos(\tau) + C_\tau \cos^2 \cos^2(\tau) + D_\tau \cos^3 \cos^3(\tau) \qquad (3)$$

However, H_2S (Fig. 1b) is simulated as a rigid molecule where only rigid rotation for the whole molecule is allowed. Therefore, in total four MC moves were performed, internal rotation for S_8 only, rigid molecular rotation and translation for both molecules and volume change to allow pressure adjustments.
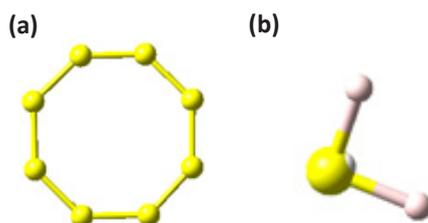
(a)   **(b)**

Fig.1. Yellow marbles for S atoms and white ones for H atoms and imaginary one (a) S_8 molecule created; (b) H_2S molecule created

Table 1. Model parameters for both S_8 and H_2S molecules, X is an imaginary atom near the sulfur atom with zero mass

Molecules	Molar mass (g/mol)	Atom	σ (A)	ε/k$_B$ (K)	q (e)	Reference
S_8	256.104	S	3.39	204.461	0	[21]
H_2S	34.013	S	3.73	250	0.4	[22]
		H1			0.25	
		H2			0.25	
		X			-0.9	

2.4. Widom Insertion Method

The method was firstly presented [19] to evaluate the chemical potential of certain pure specie or a component in a mixture. It works by inserting a test or "ghost" molecule of the same type of the component under interest into the simulation volume. The chemical potential is directly evaluated based on the energy calculations of the inserted molecule due to its interaction with the surrounding ones. However, the uncertainty of the calculation increases with dense fluids. Accuracy is improved within limits by increasing test molecules

insertions throughout the simulation. It is important to note that, these inserted molecules are performed as MC moves during the simulation even though this move is always rejected as the number of molecules in the simulation volume is always kept fixed.

$$\mu_i = k_B T \ln \left\langle \exp\left(-\Delta U_i / k_B T\right) \right\rangle \tag{4}$$

2.5. Solid Phase Elemental Sulfur Fugacity

An empirical formula to evaluate solid sulfur fugacity has been proposed earlier [16].

$$\ln f_s = \frac{A}{T} + B + \frac{P v_s}{RT} \tag{5}$$

The first two terms express the fugacity of sulfur at its sublimation pressure, while the last term is the Poynting correction for higher pressures. v_s is the molar volume of solid sulfur and assumed to be independent of pressure. A, B and even v_s are considered as empirical coefficients to be optimized to fit the data. After fitting, two correlations were proposed by the same group. In our work, we considered only the most recent one which was developed in 2001.

Developed in 1998 [16]:

$$\ln f_s = -\frac{13846.797}{T} + 22.83572 + \frac{0.122479P}{RT} \tag{6}$$

Developed in 2001 [17]:

$$\ln f_s = -\frac{14499.48}{T} + 24.4814 + \frac{0.127454P}{RT} \tag{7}$$

3. Experimental Work

Based on the described approach, the vapor phase will be solely simulated in a single box NPT ensemble. To determine the solubility of solid S_8 in vapor H_2S at certain temperature and pressure, a group of 15 simulations were generated using MedeA software from Material Design.

Each 5 of these simulations corresponds to the same mole fraction of S_8. The number of molecules of H_2S for all of the simulations was fixed to be 2000, while the number of molecules of S_8 was tuned between 5 and 20 molecules to achieve various desired mole fractions.

As the simulation box is set, the simulation was run through three stages. In the first stage, only rigid translations and rotations were allowed for 10 million MC cycles in order to relax the molecules with in the initial volume. In the second stage, all other moves are allowed for 15 million MC steps to allow the system to reach equilibrium. At the last stage, the insertion move of only S_8 molecules is allowed, with a probability of around 0.6, in addition to the previous moves for 80 million MC cycles more.

The probabilities for each of the performed MC moves and the number of steps are carefully selected in order to attain equilibrium and guarantee convergence at the lowest computational cost possible. The average simulation time for each simulation is around 80 CPU hours using 1 Intel Xeon processor on Dell PC.

The huge number of iterations is indeed needed due to the complexity of the system under investigation. The large number of molecules (more than 2000) used, significantly increases the time needed. Moreover, both of

the existing molecules are complex, as each S_8 molecule is made of 8 L-J sites and H_2S molecules require columbic interactions evaluation.

Widom insertion method is also affected by S_8 molecule complexity as it is the specie to evaluate its fugacity and it is the specie to be inserted. Therefore, to achieve the most accurate fugacity calculation, the runs has to be long. However, and even with these long runs, the fugacities evaluated by the insertion method were in general estimated with high uncertainties.

As a result, 5 experiments for each of the different mole fractions were run under the same temperature and pressure, leading to the total 15 experiments to determine a point. For each of these 5 experiments, started at the exact same conditions but with different initial molecular configuration, the average of the most accurate fugacities was taken as the true value at the specified molar fraction and thermodynamic conditions.

4. Results and Discussion

As an application for the proposed scheme four groups of experiments were conducted to reproduce the solubility of solid elemental sulfur in vapor H_2S at 338.9 K isotherm as reported by experimental data in literature [23]. Each of these groups is made up of at least 15 simulations and corresponds to a different pressure at the targeted isotherm.

For each group two plots were generated, one corresponds to results obtained based on the original model [21], and the other on a slightly modified one using $\varepsilon/k_B = 199.461\ K$ instead of $\varepsilon/k_B = 204.461\ K$ as it matches the experimental data better.

In all generated plots, dots represent the most accurate fugacities of S_8 in vapor phase obtained by NPT simulations. Dotted horizontal line corresponds to the fugacity obtained by correlation at the specified temperature and pressure. On the other hand, dotted vertical line refers to the true mole fraction expected. Hence the intersection between these two lines determines the true expected value. The dashed line is the average line of the chosen fugacities computed by the simulation and its intersection with the horizontal dotted line determine the estimated mole fraction by the proposed method.

4.1. First Group (T = 338.9 K and P = 30.7 MPa)

At these thermodynamic conditions, the true value of S_8 solubility reported is 0.0045 mole fraction. The calculated fugacity using correlation is 0.0451 Pa. The average line of calculated fugacities by simulation intersects with the calculated fugacity line at 0.0049 mole fraction (Fig. 2a) when using the original model. For repeated simulations with new model parameter, the results (Fig. 2b) were improved with an estimated mole fraction of 0.0046.
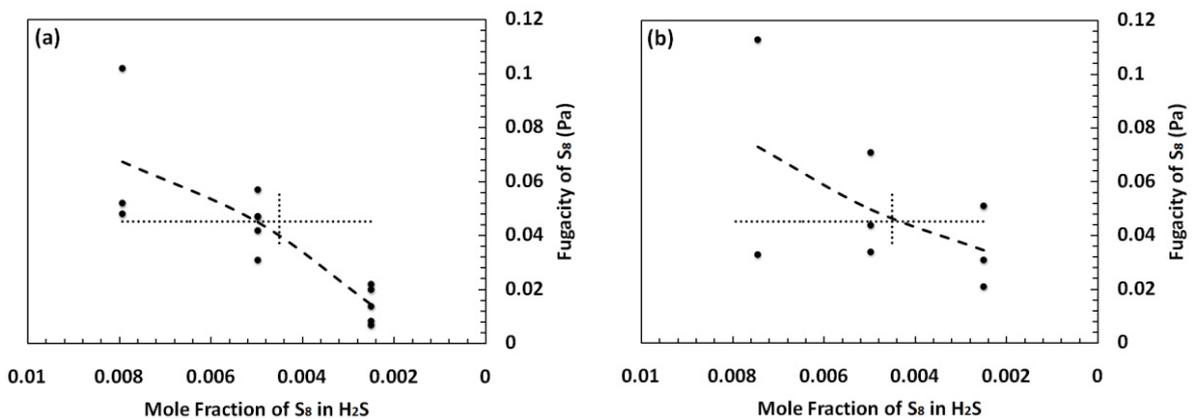

Fig. 2. First group of experiments at 338.9 K isotherm and *P = 30.7 MPa* (a) with $\varepsilon/k_B = 204.461\ K$; (b) with $\varepsilon/k_B = 199.461\ K$

4.2. Second Group (T = 338.9 K and P = 24.7 MPa)

In this group, the solubility reported in mole fraction is 0.0042. The calculated fugacity using correlation is 0.0344 Pa. The estimated mole fraction by original model (Fig. 3a) was 0.0065, and is significantly improved by the modified model (Fig. 3b) to reach 0.0044 mole fraction.
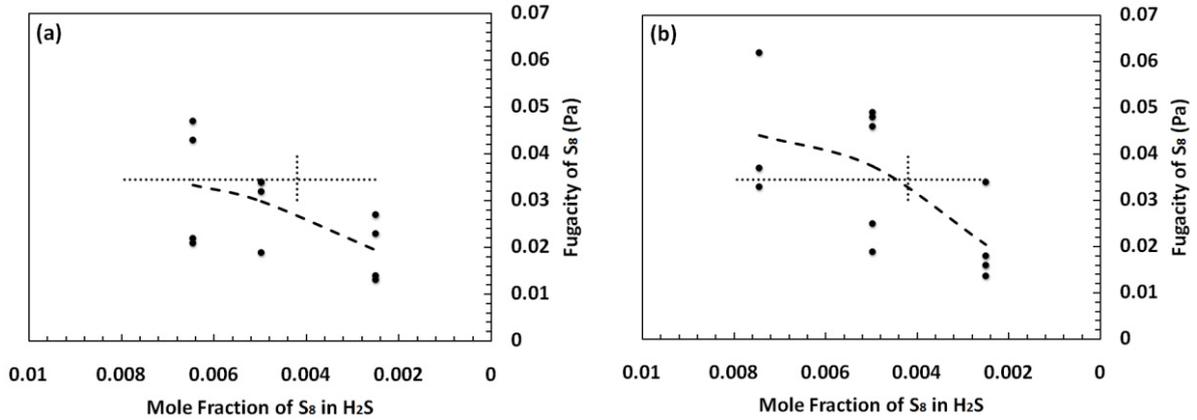

Fig. 3. Second group of experiments at 338.9 K isotherm and $P = 24.7$ MPa (a) with $\varepsilon/k_B = 204.461$ K; (b) with $\varepsilon/k_B = 199.461$ K

4.3. Third Group (T = 338.9 K and P = 17 MPa)

Also for this group the result has improved from 116 % deviation error (Fig. 4a) to around 32 % (Fig. 4b) with final estimated mole fraction of 0.0049.
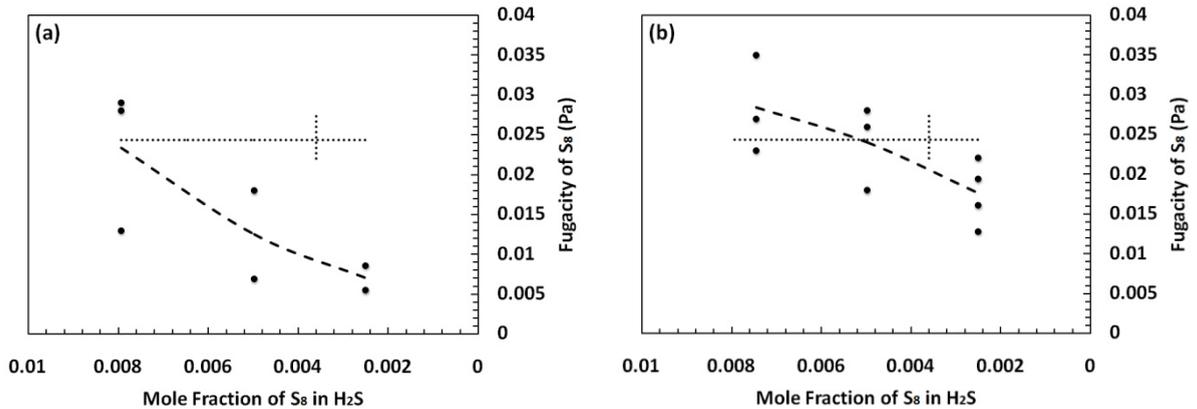

Fig. 4. Third group of experiments at 338.9 K isotherm and $P = 17$ MPa (a) with $\varepsilon/k_B = 204.461$ K; (b) with $\varepsilon/k_B = 199.461$ K

4.4. Fourth Group (T = 338.9 K and P = 10.4 MPa)

In the final group, same procedure was repeated and the results were much improved with the optimized parameter. The true experimental mole fraction is 0.0029 while the value obtained by the modified model (Fig. 5b) was 0.0036 and much better than the value obtained by original one (Fig. 5a).
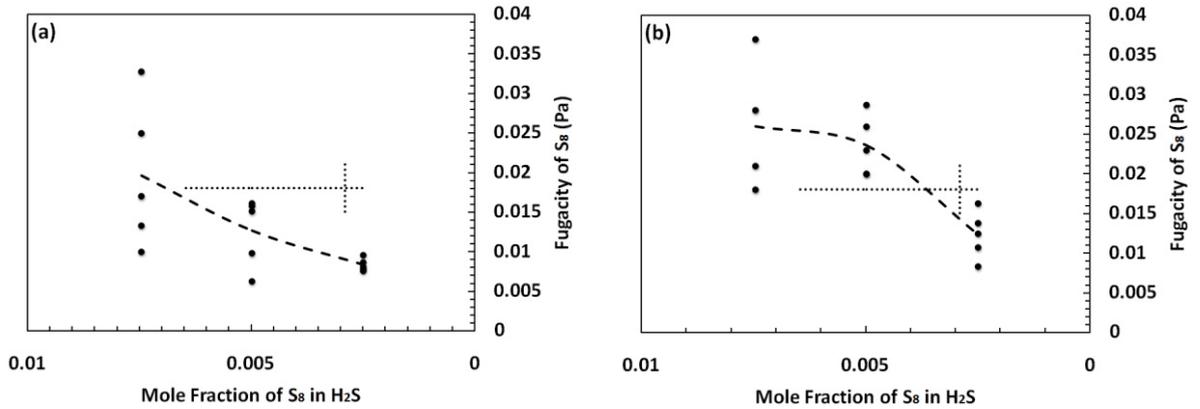
Fig. 5. Fourth group of experiments at 338.9 K isotherm and $P = 10.4$ MPa (a) with $\varepsilon/k_B = 204.461$ K; (b) with $\varepsilon/k_B = 199.461$ K

Table 2. Summary of all results obtained in comparison with the true experimental data [23]

Groups	True mole fraction	Mole fraction with $\varepsilon/k_B = 204.461$	Deviation from true (%)	Mole fraction with $\varepsilon/k_B = 199.461$	Deviation from true (%)
1	0.0045	0.0049	8.89	0.0046	2.22
2	0.0042	0.0065	54.76	0.0044	4.76
3	0.0037	0.008	116.22	0.0049	32.43
4	0.0029	0.0069	137.93	0.0036	24.14

4.5. Evaluated Fugacity at True Mole Fractions

Assuming that the true mole fraction is given, as in the case analyzed, the intersection of the fugacity average line obtained by simulation with the dotted vertical line corresponds to the fugacity value by simulation at the true fraction. The fugacities at true molar fractions for the 8 cases presented earlier were plotted (Fig. 6) against the fugacity values evaluated by the correlation. In theory, at the true molar fraction the two fugacities should be equal; however a deviation is detected with much less significance when ε/k_B was changed.

According to the plot, even though the error is small (no more than15% when model was optimized) while estimating fugacities, the simulation results for solubility were worse. This sensitivity to fugacity changes can be explained by the low solubility profiles we are trying to estimate.
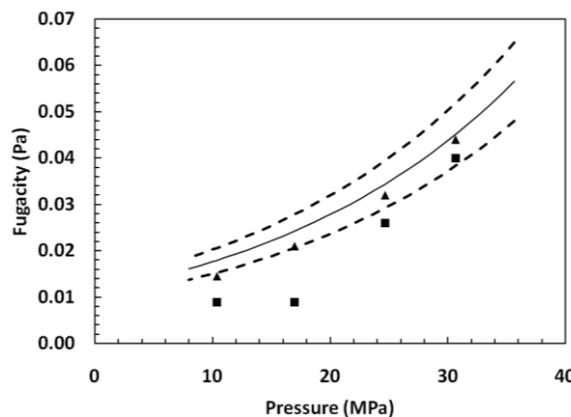

Fig. 6. Estimated fugacities with $\varepsilon/k_B = 204.461$ K (squares) and $\varepsilon/k_B = 199.461$ K (triangles) compared to true values (solid line) with 15% upper and lower margins (dashed lines)

5. Conclusion

Monte Carlo molecular simulation has been used in this work to estimate the solubility of elemental sulfur in H_2S gas. The fugacity of pure solid elemental sulfur was determined based on an experimentally developed correlation [17]. The fugacity of elemental sulfur in H_2S gas was evaluated using Widom insertion in an NPT ensemble simulation. The solubility of elemental sulfur in H_2S was determined as the fugacities of each phase are equated.

The results obtained, proved that indeed this approach could potentially be employed to estimate the solubility of solid species in vapor phase by avoiding particle insertions to the dense solid phase. In addition, S_8 molecule parameters as needed by molecular simulation were optimized to match best the experimental data.

Acknowledgements

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