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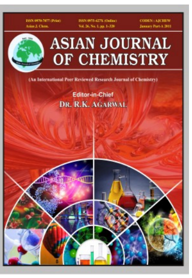

Prediction of Solubility of Sulfur in Hydrogen Sulfide Based on Molecular Dynamics Simulation

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A novel approach is presented to calculate the solubility of sulfur in hydrogen sulfide by molecular dynamics simulation. The dissolved sulfur in hydrogen sulfide is judged by the help of model of solvation shell. The tendency of simulation result matches well with the experimental data. The simulation shows that there are more element sulfur around neighbor and less sulfur locating on the solvation shell of hydrogen sulfide leads to a low solubility. An improved potential model and larger simulation system is necessary to extend this method to predict solubility of sulfur in natural gas system.

Keywords: Solubility, Sulfur, Hydrogen sulfide, Solvation shell, Molecular dynamics simulation.

INTRODUCTION

The staggering advancement of modern society is followed by Energy Crisis and Greenhouse Effect. Thus, lower quality natural gas reservoirs are forced to exploit for filling the energy gap. However, many questions have emerged during the mining and transporting process due to the large amount acid components (for instance, element sulfur, hydrogen sulfide, carbon dioxide) in these low quality natural gas reservoirs. The notorious problem may be the sulfur precipitate at well bore. This will result in block and erosion in the pipeline. The solubility of sulfur is mostly regarded as driven by thermodynamics. The temperature and pressure of acid natural gas are continuously declined as the fluid moves from earth mantle to shaft bottom. Meanwhile, the solubility of element sulfur decreases in acid natural gas. Consequently, solid deposit will be generated and adhere on the tube surface which is usually accompanied with hydrogen attack or acid etching[1]. Eventually, industrial safety accidents occur due to sulfur clogging. Therefore, accurate prediction of sulfur solubility in geological fluid is important for mining process improvement and geochemical applications.

Many solubility data of sulfur have been reported[2-6] by different experimental methods. However, the experimental data is still insufficient due to toxic and corrosive components in inclement conditions underground. Therefore, numerical methods are employed to determine solubility. Chrastil[7] proposed a simple correlation for solubility of solid and liquid in supercritical gases. However, Carroll[8] confirmed that the empirical correlation was not applicable at the low pressure region. The equation of state is used to study the solubility. Karan *et al.*[9] used Peng-Robinson equation to describe the solubility of sulfur in natural gas mixtures. Their model was successfully tested over a wide range of temperature, pressure and gas composition when the octasulfur (S_8) was stable. Cezac *et al.*[10,11] established a reactive flash model to estimate the solubility of sulfur in natural gas transmission and distribution networks. The parameters in their works were from three thermodynamic intrinsic properties including the description of sulfur dissociation reactions. However, there is still not a universal method to calculate the solubility of sulfur.

Molecular dynamics simulation (MD) has been successfully adopted to study the solubility[12-16]. Consequently, in this paper, a model of solvation shell is proposed to evaluate the solubility of sulfur (S) in hydrogen sulfide (H_2S) based on molecular dynamics simulation.

EXPERIMENTAL

Methodology of simulation: Molecular dynamics is a computer simulation that obtains atomic or molecular trajectories by solving the Newton's equations of motion. The particle interaction complies with a given potential which is defined by molecular force fields. Since molecular dynamics could directly calculate the movement of particles at the atomic level, it can accurately describe the thermodynamic properties of studied gas, which is usually difficult to be performed experimentally at atomic scale.

Accurate intermolecular potential plays a pivotal role during molecular dynamics simulation process. In the present work, a three-point potential model for H_2S is adopted[17], while a simple LJ model which adopts the parameters from results of Ballone and Jones[18] is proposed for element sulfur. The different LJ interactions of particle are determined by Lorentz-Berthelot combing rules[19]. All these parameters are based on the hypothesis that there is not chemical reaction. Accordingly, the environmental condition for the simulation is chosen as the same as those of Gu *et al.*[5].

During the process of simulation, 8000 H_2S molecule and 4000 S atoms are interplayed in the box with parallelepiped periodic boundary whose initial volume is 1×10^{-24} m^3. Nose-Hoover's method is employed to achieve isothermal-isobaric (NPT) ensemble. Particle trajectories are obtained through the integral of velocity Verlet algorithms[20]. When the molecular velocity distribution is consistent with the Maxwell-Boltzmann velocity distribution, the simulation system is considered to reach an equilibrium state. Once the system reached a steady state, the necessary statistical parameters were evaluated within 50,000 steps. The simulation total runs 400,000 steps. During the simulation process, the time step is 1×10^{-15} s and a cut off radius of 1×10^{-10} m is chosen for each model. If the distance between two particles is beyond this cut off radius, the intermolecular forces are neglected for saving the computation time, as usual molecular dynamics simulation does.

For the analysis, the model of solvation shell, which is from reference[21], is used to judge the solvable sulfur. The model of solvation shell is shown as Fig. 1.

In Fig. 1, the sulfur linked with two hydrogen atoms denotes the H_2S molecule. The dotted line is the solvation shell of H_2S. Because the interaction between S_1 atom and H_2S molecular is very strong within this salvation shell region, the S_1 atom is always limited in solvation shell of H_2S under the given condition. Therefore, the S_1 is regarded as solvable sulfur. However, beyond this solvation shell region of H_2S, S_2 is the element sulfur that can not be dissolved in H_2S. Therefore, the solubility of sulfur in H_2S is determined by the statistics numbers of solvable sulfur atom in solvation shell.

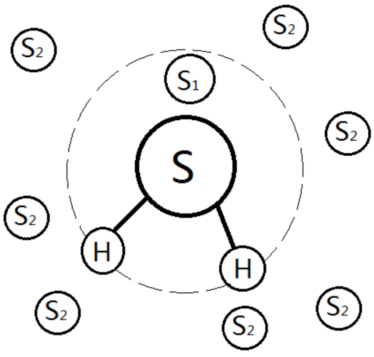

Fig. 1. Model of solvation shell

RESULTS AND DISCUSSION

Since there is no reference discussed about the sulfur solubility in hydrogen sulfide from microcosmic view, the model of solvation shell of H_2S is adopted to test the sulfur solubility of H_2S. It has been confirmed that the 3.37×10^{-10} m is the best radius of solvation shell for H_2S in this paper. As shown in Fig. 2, the mole fraction solubility of sulfur in hydrogen sulfide obtained by the model of salvation shell are compared with experimental results. From this figure, it is clearly shown that the solubility of simulation results have the same trend as those of experimental data when the pressure is varied between 10.0 MPa and 40.0 MPa and the simulation data is slight smaller than that of experimental data for a given pressure. Based on these simulation data, it is found that more sulfur atoms near the neighbor of given sulfur particle could result in a lower solubility of sulfur in hydrogen sulfide.

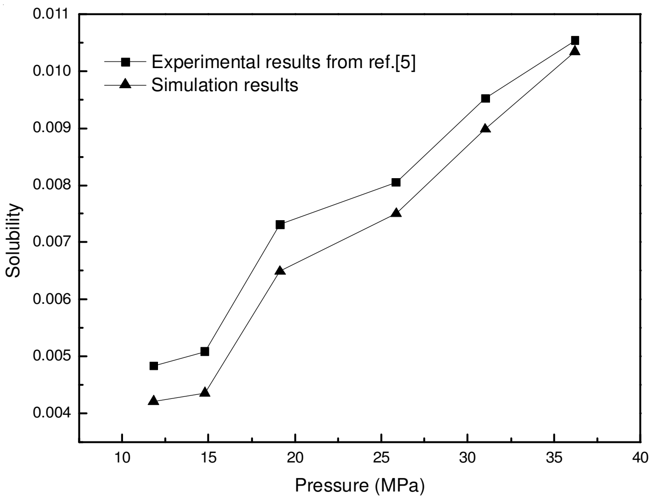

Fig. 2. Solubility of sulfur in hydrogen sulfide at 363.2 K

As shown in Fig. 3, the radial distribution function of element sulfur is presented. Since the two curves in this figure are not strictly in solid state, the potential model of sulfur in this paper is not suitable and this may result in the smaller solubility. On the other hand, since the size of simulation system is relatively small, it might bring some statistical error to predict the solubility of sulfur. Therefore, an improved potential model of sulfur is required to accurately predict the solubility of sulfur in the future work.

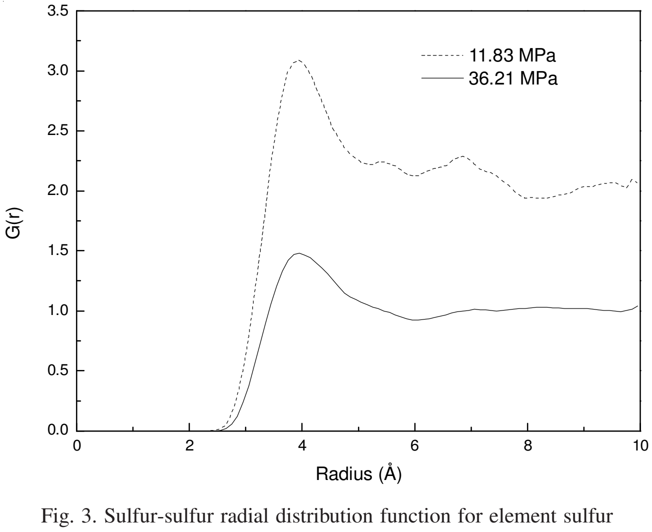

Fig. 3. Sulfur-sulfur radial distribution function for element sulfur

Conclusion

In this paper, an atom-level scheme based on molecular dynamic simulation is proposed to predict the solubility of sulfur in hydrogen sulfide. The model of solvation shell is applied to determine the number of solvable sulfur atom in hydrogen sulfide. It is demonstrated that the sulfur solubility of simulation model has the same trend as experimental data although the values of sulfur solubility are slight smaller than those of experiment for a given pressure. The radial distribution function of sulfur indicates that the state of sulfur is inappropriate due to the unsuitable potential model and more sulfur atoms near its neighbor region could result in a lower solubility of sulfur in hydrogen sulfide. Therefore, a more precise potential model of sulfur and a larger simulation system are demanded to apply this method to natural gas system.

ACKNOWLEDGEMENTS

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