

FULL PAPER

Absorbing behavior of hydrogen sulfide on ethylenediamine during sour gas sweetening

Mahdieh Nezamabadi^a | Abolghasem Shameli^{b,*} | Ebrahim Balali^a | Mahnaz Qomi^a | Sara Hallajian^a

^aDepartment of Organic Chemistry, Faculty of Pharmaceutical Chemistry, Tehran Medical sciences, Islamic Azad university, Tehran, Iran

^bDepartment of Chemistry, Faculty of Science, Omidyeh Branch, Islamic Azad University, Omidyeh, Iran

This research study discussed the hydrogen sulfide (H₂S) behavior during the absorption on ethylenediamine (H₂NCH₂CH₂NH₂) in the course of the sour gas sweetening process. For this purpose, the molecular dynamics simulation was conducted on methane, ethane, and hydrogen sulfide (as sour gas) and ethylenediamine for investigating the oil sweetening process. Quantum method of density-functional theory with B3LYP method and basis set 6-311(+)G** was also employed to calculate the charge. Simulation results revealed that, the ethylenediamine molecules could absorb the hydrogen sulfide molecule. Despite the six sites on the ethylenediamine, hydrogen sulfide molecules will interact just with two sites. It was also observed that each ethylenediamine molecule could absorb 3-7 hydrogen sulfide molecules, whereas hydrogen sulfide interacted only with two nitrogen sites. In addition to interaction with ethylenediamine, hydrogen sulfide molecules also interact with each other. This gives rise to the condition in which the number of hydrogen sulfide molecules acting with ethylenediamine would be more than two molecules. Investigating the behavior of the H₂S molecules absorbed on nitrogen showed the unique interacting behavior of these molecules and nitrogen of ethylenediamine. H₂S molecules are absorbed by nitrogen through one of its hydrogen molecules. However, it was observed that the two hydrogen atoms exchange their places with each other, and nitrogen will interact by another H atom of H₂S. At some steps of simulation, the hydrogen absorbed on one of the nitrogen atoms of ethylenediamine, will immigrate to the other nitrogen atom of ethylenediamine molecule and interact with that nitrogen.

***Corresponding Author:**

Abolghasem Shameli

Email: shameli678@gmail.com

Tel.: +98 (61) 52631034

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Introduction

Natural gas sweetening is an important topic for many grounds; the acid gas absorption in natural gas can cause pipeline corrosion problems in transport [1]. The removal of acid gases reduces the gas volume to be transported and increases the calorific value

of selling gas stream [2]. Chemical properties of the natural gas contain some complex contaminants such as CO₂, H₂S Mercaptan (acid gas). In the atmosphere, these materials constitute more significant environmental hazards for the human body. They are also hindered by natural gas processes [3]. Natural gas with H₂S or other sulfur

compounds is called sour gas, whereas gas with the only CO_2 is called sweet gas. Sour gas can do extensive harm to natural gas pipelines that is not correctly treated. The burning of sulfur compounds produces dangerous air pollutants and eventually produces acid rain when combined with water [5]. The main challenge of the natural gas sweetening process was to get rid of the acid gases and sulfur compounds from the natural gas to as low a point every bit possible, uniform with the prevailing emission regulations, and as economically as possible. A number of methods is available for the removal of acid gases from product gas streams. Yet, processes that remove hydrogen sulfide and carbon dioxide from natural gas are not efficient in removing mercaptans, disulfides, and carbonyl sulfide. It was due to the fact that, the aforementioned organic sulfur compounds did not readily ionize (hydrolyze) to organize that anions that react with caustic, amine, or metal oxide [5]. Acid gas removal processes are primarily of two types: adsorption and absorption. Adsorption is a physical-chemical phenomenon in which the gas is concentrated on the surface of a solid to remove impurities. Absorption differs from adsorption—for the reason that it is not a physical-chemical surface phenomenon. Absorption is dissolution (a physical phenomenon) or by reaction (a chemical phenomenon). There are several processes for natural gas sweetening. Because the concentrations of CO_2 and H_2S in the raw gas to be processed and allowable acid gas levels in the final product vary substantially, no single process is markedly superior in all circumstances and results, many processes are presently in employment. In chemical processes, absorption of acid gases is accomplished primarily by the use of amines or alkaline salts of various weak acids, such as sodium and potassium salts of carbonate [6]. Chemical solvents are especially suitable when contaminants at a relatively low partial pressure have to be

removed to deficient concentrations. In physical solvent processes, which utilize an organic solvent, no chemical reaction occurs, and acid gas/organic sulfur components removal depends entirely on physical absorption. In an increase, the physical solvent can usually be stripped of impurities by reducing the pressure without the increase of heat [7].

The H_2S reacts much quicker with the amine than the CO_2 , as the reaction between amine and H_2S appears gas film diffusion-rate limited, whereas the response between the amine and CO_2 is kinetically limited. Thus, if the absorber is designed in such a way to furnish an adequate number of contact points with sufficient contact time, the total absorption of H_2S and CO_2 can be achieved [6].

Modeling has been practiced for a really long time and also for the purpose and improved operation of gas processing and transmitting installations [27,28]. The function of steady-state models is universally admitted in all levels of the design and operation of gas processing plants. Dynamic simulation has been used for a long time. A rigorous dynamic simulation model is however computationally intensive, requiring software and hardware systems capable of running the model faster than real time. The advancements in hardware and software systems have allowed easy access to rigorous dynamic simulators that can be quickly configured and deployed with relative ease [5]. The fields of application have been parted into two great groups (plant design and plant operation) [8]. As an important tool exploring the structure and properties of materials at a detailed atomistic level, molecular dynamic (MD) simulation has been successfully applied to estimate the complicated interface properties of composites [9-20]. Although, some relevant researches have been polished by computer simulations, further and much more information is still necessary, especially before applying core-shell microspheres in

the oilfield. In the present study, we investigated the absorption of the H₂S molecule by ethylenediamine.

Simulation details

We employed the molecular dynamics simulations in the well-known large-scale atomic/molecular massively parallel simulator (LAMMPS) [21] and structures visualized using the VMD version 1.9.3 package [22]. All the simulations carried out in constant-volume and constant-temperature (NPT) ensemble and in the NPT-ensemble at 300 K and 15 bar, using a Nose-Hoover thermostat [23] with a relaxation time of 100 fs for the temperature and 1 ps for the pressure.

Time integration of the Newton's equation of motion undertaken by using a velocity Verlet algorithm with a time step of 0.5 fs. Non-bonded van der Waals interactions modeled in terms of 12-6 Lennard-Jones famous potentials $U_{LJ}(r_{ij})$ [24]. We applied the particle-particle particle-mesh (PPPM) method to minimize error in long-range terms in both Coulombic and Lennard-Jones potentials. Lennard-Jones and Coulombic cutoff radiuses were 10 Å and 12 Å, respectively. Each MD simulation was run for 5.0 ns.

All of the compounds in this work were parameterized on the basis of the OPLS force field [25]. SHAKE algorithm was used to keep the S-H distance fixed at 1.336 Å and H-S-H angle at 92.070°. The initial size of the simulation box was (80×80×80) Å³ with

compound percentage: methane 16.5%, ethane 72.1%, sulfide hydrogen (with title atomic H_s and S) 8.8% and ethylenediamine (EDA with title atomic H_namin and N_e) 2.6%.

We have performed the density-functional theory (DFT) calculations to optimize the structural models of ethylenediamine, and the hydrogen sulfide with systems has been studied in the gas. All the structures were optimized the B3LYP exchange-correlation functional, and the 6-311(+)G** standard basis set has been used to run all computations as implemented in the NWCHEM version 6.6 package [26].

Result and discussion

The aim of this study was to molecularly investigate the absorption of the H₂S molecule by ethylenediamine in a mixture of methane, ethane, ethylenediamine, and hydrogen sulfide. Results of our different simulations showed that although ethylenediamine has six interaction sites, however, the H₂S only interacts with this molecule via two sites, and also H₂S molecules are only absorbed by amine nitrogen atoms.

Electrostatic property of the system is one of the effective parameters of interaction, and it usually has a profound impact on system behavior. For this purpose, the first charge distribution was addressed. Figure 1 demonstrates the electrical charge distribution of the ethylenediamine and hydrogen sulfide molecules.

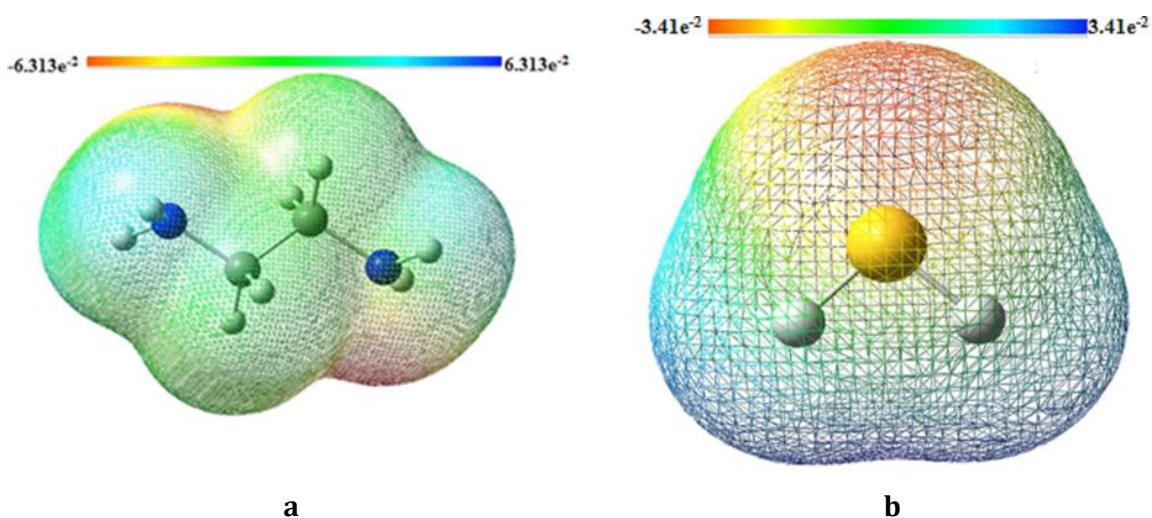


FIGURE 1 Electrical charge distribution around A) ethylenediamine and B) hydrogen sulfide, blue, yellow, turquoise and white colors represents nitrogen, sulfur, carbon and hydrogen, respectively

Figure 1 demonstrates that, the charge distribution of the ethylenediamine and hydrogen sulfide is different. In Figure 1-a, ethylenediamine possesses a negative charge in the amine part near hydrogen atoms. Charge distribution has lower dispersion in central regions of ethylenediamine and it is close to neutral range. However, in Figure 1-b,

it can be observed that the charge distribution of hydrogen sulfide is similar to dipole distribution.

The interaction between hydrogen sulfide and ethylenediamine will be examined; radial distribution function (RDF) can offer useful information about the interaction between particles. Figure 2 illustrates the RDF of ethylenediamine and hydrogen sulfide.

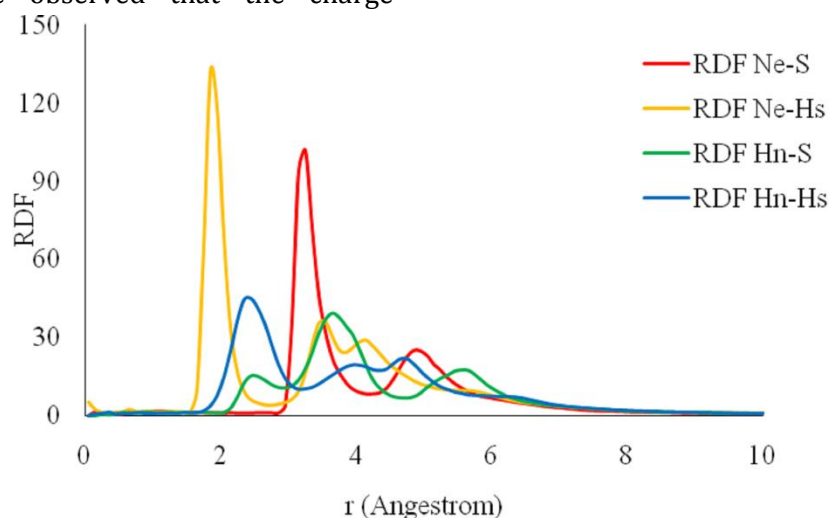


FIGURE 2 Radial distribution function of ethylenediamine and hydrogen sulfide. S, Hs, Hn and Ne represent sulfur and hydrogen atom of hydrogen sulfide molecule, amine hydrogen in ethylenediamine and amine nitrogen of ethylenediamine, respectively.

Figure 2 suggests that, the RDF of amine nitrogen (Ne) and hydrogen sulfide H (Hs) have a sharp peak in 1.8 with a height of 132

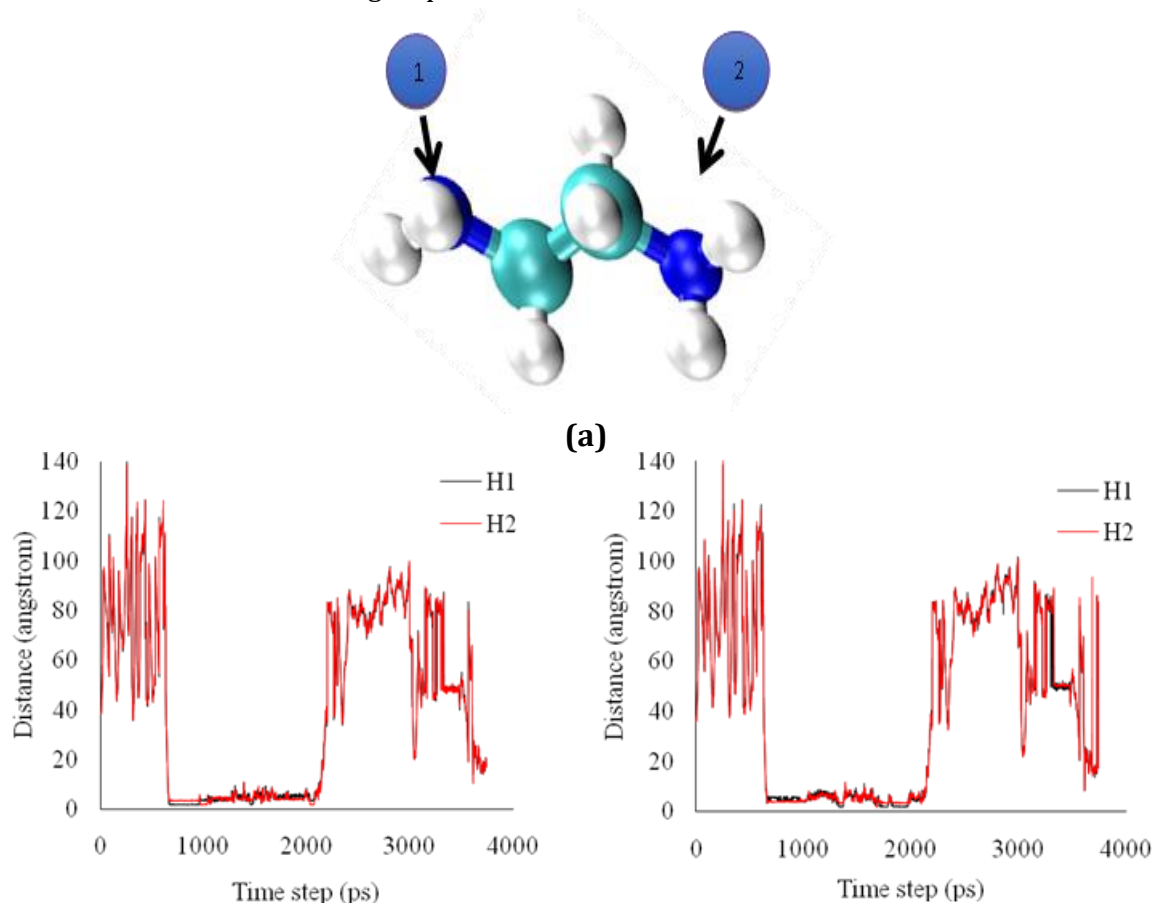
representing the strongest interaction between the components of H₂S and ethylenediamine molecules. The reason for

such strong interaction between N and H of H_2S can be found in Figure 2. Generally, the H_2S molecules interaction with amine group can occur in two forms: 1- amine nitrogen interaction with the hydrogen atom of H_2S ; and 2- the interaction of H in amine group with S atoms. Due to their smaller size, hydrogen atoms can penetrate into ethylenediamine molecules far better than S atoms. Comparing the location of the first peak in RDF of H-S (3.25 angstrom) and Ne-Hs RDF (in 1.8 Angstrom) indicates more penetration of hydrogen atoms of H_2S than ethylenediamine. As H atoms of the H_2S got closer to ethylenediamine (in comparison with S atoms), the electrostatic interaction between amine N and hydrogen sulfide H will be stronger.

Regarding the height of sharp peak in radial distribution function of amine N (Ne) and S, it seems that the second strongest interaction between components of ethylenediamine and H_2S is related to the interaction between amine group N and S.

However, it must be noted that, both these components are negatively charged, and the peak height cannot indicate the strong absorption between the two particles. The reason of the relatively high height of the Ne-S RDF peak is the height of strong interaction between amine groups N and H of H_2S . As sulfur is attached to H, its location remains close to the H atom involved in the interaction with N. That is why it has a sharp peak in a definite distance from the H.

As the strongest interaction is associated with H atom of H_2S and amine group N and H_2S molecules approached to ethylenediamine from its amine N site, the interaction between Ne and Hs will be discussed. For this task, the interaction between one ethylenediamine with one of the H_2S molecules was considered. Each ethylenediamine molecule has two nitrogen atoms. The variation of the distance between H of H_2S with each N in ethylenediamine was calculated.



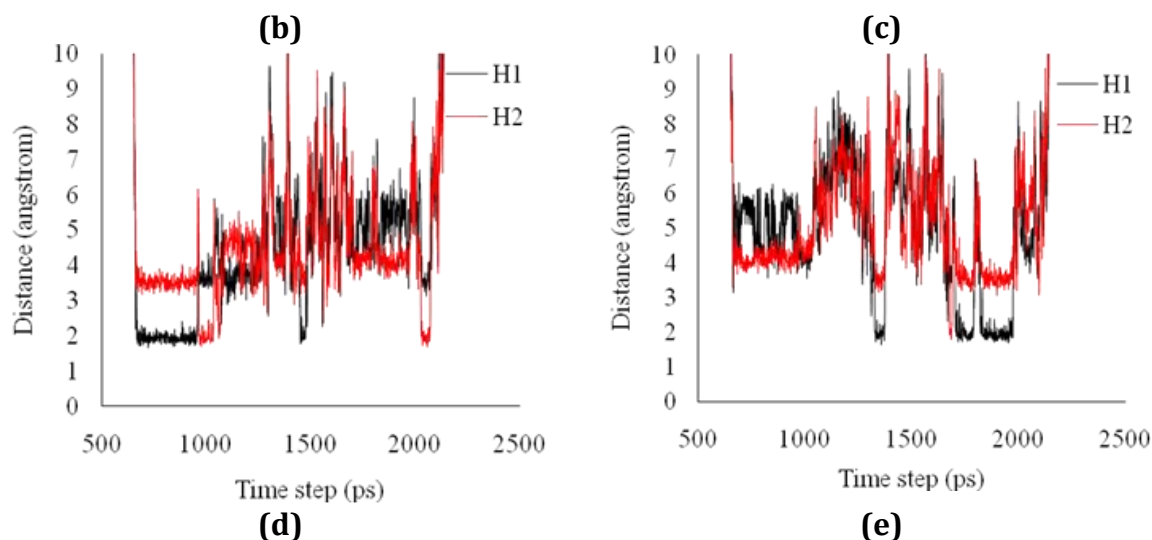


FIGURE 3 Variation of the distance between H atoms of H_2S with N atoms in ethylenediamine. H1 and H2 represent H atoms of hydrogen sulfide molecule whose distance with a) two N atoms of ethylenediamine are calculated. b) Distance variation between H atoms of H_2S and N1 atom throughout the simulation. c) Distance variation between H atoms of H_2S and N2 atom throughout the simulation d) Distance variation between H atoms of hydrogen sulfide and N1 atom at 500-2500 ps time interval of the simulation where absorption took place d) Distance variation between H atoms of hydrogen sulfide and N2 atom at 500-2500 ps time interval of the simulation where absorption took place e) Distance variation between H atoms of H_2S and N2 atom throughout the simulation.

Figure 3 depicts the variation of Hs distance from Ne. as Figures 3-b and 3-c suggest, H_2S molecule arrived at the distance <10 angstroms at about 500 Ps, which indicates the approach of H_2S molecule to ethylenediamine. There is a distinct difference between this time interval and the rest of time intervals: at some points of this interval, the curve associated with H atoms of H_2S separated from each other. This time interval lasted for about 2200 Ps and then tended to larger values, suddenly, which in fact indicated that H_2S was separated from ethylenediamine. For closer investigation of the time interval between 500 to 2500 ps, when H_2S approached to ethylenediamine, the curves in Figures 3-b and 3-c are investigated in smaller intervals in Figures 3-d and 3-e; one of the common points in Figures 3-d and 3-e is that when one of the H atoms is located in the distance shorter than 2 Angstrom, H atoms of H_2S would be separated and a gap would be created. What was happened is as follows: when one of the

H atoms of H_2S is located in the distance from N atoms smaller than 2 Angstrom, a strong interaction will be formed between them. In such a condition, one of the H atoms would be closer to N atoms rather than the other H atom of hydrogen sulfide. The result of such configuration was the creation of a gap in Figure 3 when one of the hydrogen atoms was located in the distance shorter than 2 Angstrom. As seen in Figures 3-d and 3-e, some gaps were created in different sections of the curves with different lifetimes. This observation demonstrated that, the hydrogen sulfide molecules were separated from the N at different times and then reattached to that. One of the other interesting observations of Figure 3-d and 3-e is that in the sections where gaps were created, the places of red and black colors were replaced. This shows that there are moments when the H_2S molecule absorbs nitrogen, which replaces the two H_2S hydrogen atoms. The reason for this and the mechanism behind it can be an interesting topic that has not been explored.

Also, as can be seen in Figures 3-d and 3-e revealed another aspect of the molecular mechanisms of the system. It is the comparison between the location of gap creation in 3-d and 3-e curves. Here, no typical time can be found in Figures 3-d and 3-e referring to the formation of one gap. In the other words, whenever Figure 3-d showed gap creation in the distance smaller than 2 Angstrom, no such gap can be seen in the 3-e curve and vice versa. Molecular interpretation of this event is that at some specific points, H₂S immigrated from one N atom of ethylenediamine to another N atom.

Regarding the explanations on the H₂S molecule by the passing of time, from t=0 to t=600 ps, H₂S has no interaction with ethylenediamine. In a time interval of 600-2200 ps, the hydrogen sulfide molecule got close to ethylenediamine. This interval is divided into several smaller intervals. In 650-950 ps interval, the H₂S molecule was absorbed into one of N atoms of ethylenediamine from its H₂ head (Figure 3-d). In continue, in t=950 ps to t=1050 ps, H₁ and H₂ changed their place, and H₂S would be absorbed to N by H₁ (figure 3d). At 150-13300 ps interval, the H₂S molecule is separated from N and moves around ethylenediamine, and at the time interval, od 1325-1375 ps H₂S molecule is absorbed by the second N from its H₂ head (Figure 3-e). Therefore, at this time interval H₂S molecule hopped from one N to another. A closer look at the curves in Figure 3 reveals the repetition of the above-mentioned processes, including absorption H atoms replacement and change of absorption site.

At the beginning of the result section, it was mentioned that the H₂S molecule only interacts with two N amine sites of ethylenediamine. This does not necessarily mean that each ethylenediamine can only absorb two H₂S molecules. Our simulation results showed that 2-7 hydrogen sulfide molecules could be found around each ethylenediamine molecule.

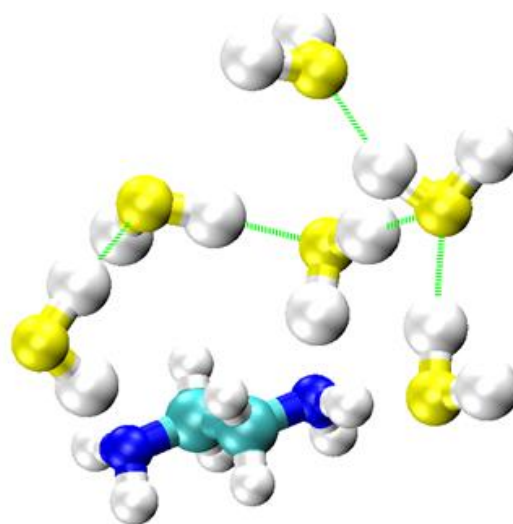


FIGURE 4 an instant image of ethylenediamine with its surrounding hydrogen sulfide molecules. Blue, yellow, turquoise, and white balls represent N, S, C, and H atoms, respectively. Green dashed lines show a hydrogen bond.

Figure 4 clearly shows that hydrogen sulfide molecules formed a hydrogen bonds with each other in the vicinity of ethylenediamine. In such a way that in Figure 4, 6 hydrogen sulfide molecules can be found in the vicinity of the ethylenediamine molecule. While only two N site of ethylenediamine were filled and the H-sites of ethylenediamine were empty. Indeed, this can be explained as follows: first, two H₂S molecules will be absorbed by N atoms of ethylenediamine and then form a bond with hydrogen sulfide molecules absorbed by N atoms.

Conclusion

In this work, by means of molecular dynamic (MD) simulation, it was observed that, the ethylenediamine could absorb the H₂S molecules and sweeten sour gas. It was also observed that, the hydrogen sulfide molecules only attached to nitrogen sites of ethylenediamine, which could be attributed to the small size of H in the H₂S molecule, facilitating its approach to ethylenediamine

more than S atom of H₂S molecule and provides the condition for interacting with ethylenediamine. RDF plots demonstrated that the H in H₂S could get closer to the ethylenediamine compared with that of the S atoms of H₂S. Examination of the distance variation between the H₂S and ethylenediamine showed that, after absorption of H₂S by ethylenediamine, at some time intervals, hydrogen sulfide immigrated from one N in ethylenediamine to another N. During the time when hydrogen sulfide is located on one N, its H atom interacting with N changed its place with the other H.

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Orcid:

Abolghasem Shameli: <https://orcid.org/0000-0003-0440-5286>

Mahnaz Qomi: <https://orcid.org/0000-0001-7264-871X>

Sara Hallajian: <https://orcid.org/0000-0002-5643-249X>

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