Eurasian Chemical Communications

SAMI

FULL PAPER

Molecular dynamics simulation of natural gas sweetening by monoethanolamine

Nima Novin[a] |Abolghasem Shameli[b],* |Ebrahim Balali[a]

[a]Department of Organic Chemistry, Faculty of Pharmaceutical Chemistry, Tehran Medical sciences, Islamic Azad university ,Tehran, Iran

[b]Department of Chemistry, Faculty of Science, Omidiyeh Branch, Islamic Azad University, Omidiyeh, Iran

The aim of the study is to investigate sweeting process of sour gas by dynamic simulation of monoethanolamine (MEA) molecule. In the present paper using molecular dynamic simulation, the interaction of sour gas mixture included methane, ethane and H_2S with MEA as absorption was also investigated the quantum method DFT B3LYP 6-311 (+) G** was used for electric charge calculation. The simulation results confirmed that the tendency of the H_2S molecule is to be absorbed to amine nitrogen and oxygen hydroxyl group in MEA. No tendency for strong interaction between sulfur atoms of H_2S molecule and hydrogen of amine or hydroxyl groups was observed. The investigation of changing distance between the hydrogen of H_2S and nitrogen/oxygen of MEA confirmed a stable between hydrogen atoms of H_2S and nitrogen/oxygen atoms in MEA. Also the investigation of distance changing show movement of hydrogen atoms of H_2S molecule which interacted with MEA molecule in the time frame of the simulation. This study was observed that after absorption of H_2S molecule by MEA molecules sour of them made the bridge for connection of MEA molecules with each other. Actually H_2S molecules after interact with MEA molecules used addition their free hydrogen forinteraction and Making Bridge. Finally a structure of some MEA molecules are joined together, which are stable up to end of the simulation.

*Corresponding Author:
Abolghasem Shameli
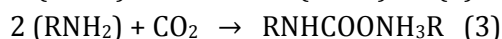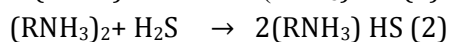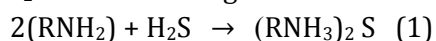Email: shameli678@gmail.com
Tel.: +98 (61) 52631034

Introduction

Conventional natural gas sweetening processes are mainly focused on H_2S removal and the bulk removal of CO_2. Natural gas with H_2S or other sulfur compounds is called sour gas, and gas with only CO_2 is called sweet gas. Sour gas can cause extensive damage to natural gas pipelines is not processed correctly. The combustion of sulfur compounds products serious air pollutants and eventually products acid rain when combined with water [1]. The acid gas removal is based on two type's processes: adsorption and absorption. Adsorption is a physical-chemical phenomenon in which the gas concentrated on the surface of a solid to remove impurities. Absorption differs from adsorption in 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 of the concentrations of CO_2 and H_2S; 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 consequences, many process re presently in use. In chemical processes, absorption of acid gases is achieved mainly by use of amines or alkaline salts of various weak acids such as sodium and potassium salts of carbonate [2]. Chemical solvents are specifically suitable

when contaminants at a relatively low partial pressure have to be removed to very low concentrations. In physical solvent processes, which use an organic solvent, no chemical reaction occurs, and acid gas/organic sulfur components removal depends entirely on physical absorption. In addition, physical solvent can usually be stripped of impurities by reducing the pressure without the addition of heat [3].

Monoethanolamine (MEA) is a primary amine and the strongest amine among others. MEA is a stable compound and in the absence of other chemicals, suffers no degradation or decomposition at temperature up to its normal boiling point. MEA reacts with H_2S and CO_2 as the following:

$$2(RNH_2) + H_2S \rightarrow (RNH_3)_2 S \quad (1)$$
$$(RNH_3)_2 + H_2S \rightarrow 2(RNH_3) HS \quad (2)$$
$$2 (RNH_2) + CO_2 \rightarrow RNHCOONH_3R \quad (3)$$

These reactions are reversible by changing the system temperature. MEA can remove both H_2S and CO_2 from the gas stream to meet sales gas specifications. In practice, however, acid gas loading and solution concentrations are limited because of corrosion problems. MEA also reacts irreversibly with carbonyl sulfide (COS) and carbon disulfide (CS_2), which can result in degradation of the solvent and buildup of heat-stable salt (HSS) that can't be regenerated. MEA has a higher vapor pressure than the other amines. This can result in significant solution losses through vaporization. The problem usually can be overcome by a simple water wash of the sweet gas stream.

The selectivity of methyl diethanolamine (MDEA) can be reduced by the addition of various amounts of primary or secondary amines as so-called promoters, which enhance CO_2 removal while retaining desirable characteristics of MDEA [4]. Promoters work by a shuttle mechanism and effect thermodynamics, but more importantly, they allow the reactivity of the mixture as a whole toward CO_2 to be closely controlled. Finding an optimum

concentration for mixed amines (also called blended amines) strongly depends on the H_2S and CO_2 content of the sour gas, operating pressures, and sale gas specifications. After the blend formula is established, normal control schemes will be used to ensure the H_2S specification. However, the treated gas CO_2 content will not be controllable, except by adjusting the blend composition from time to time [5]. Amine mixtures are particularly useful for low-pressure applications because MEDA becomes less capable of CO_2 pick up sufficient enough to meet pipeline specifications. At higher pressure, amine mixture appears to have little or no advantage over MDEA [6]. Among all amine solvent processes, mixed amines have been extensively used because they offer many advantages, such as their ability to meet the most stringent H_2S and CO_2 specifications. However, their performance as regards mercaptan/ COS removal is extremely limited. A series of chemical activators used with methyl diethanolamine offers the most cost-effective answer to complete or controlled removal of acid gases as well as bulk removal of mercaptans and COS from sour natural gas. The BASF-formulated MDEA solvent achieves a high degree of COS removal and retains appreciable selectivity for H_2S over CO_2. H_2S can be virtually completely removed while the COS removal level can be targeted to meet the overall sulfur removal regulations. This strategy would limit CO_2 Co absorptions and may preclude the need for a COS hydrolysis unit upstream of the amine unit [6]. The BASF a MEDA process is highly energy efficient due to the high acid gas loadings achievable with the solvent; this enables using low circulation rates and reduced energy consumption as well as reducing the required equipment size. Additional advantages include very low hydrocarbons co-absorptions, no degradation products, no corrosion (mainly carbon steel equipment can be used), and low foaming tendency; also, no reclaimer operation is

necessary, and the solvent is nontoxic and biodegradable.

H_2S reacts much faster with the amine than does the CO_2, because the reaction between a mine and H_2S appears gas film diffusion-rate limited, whereas the reaction between the amine and CO_2 is kinetically limited. Therefore, if the absorber is designed in such a manner to provide an adequate number of contact stages with sufficient contact time, the total absorption of H_2S and CO_2 can be achieved [7,1].

Modeling has been used for a very long time for the design and for improved operation of gas processing and transmission facilities [26-29]. The use of steady-state models is universally accepted in all stages of the design and operation of gas processing plants. Dynamic simulation has been used a long time, but The rigorous first principles of dynamic simulation have been confined to use by specialists and control engineers who were using models based on transfer functions that were incapable of representing the nonlinearities in systems and the discontinuities in start-up cases for example[1]. The areas of application have been divided into two large groups (plant design and plant operation) [8]. As an essential tool exploring.

The structure and properties of materials at a detailed atomistic level, the molecular dynamic (MD) simulation has been successfully applied to estimate the complicated interface properties of composites [9-19]. Although some relevant researches have been finished by computer simulations, further and much more information is still necessary, especially before applying core–shell microspheres in the oilfield. This study is focused on the absorption of H_2S from the natural gas By Monoethanoleamine.

Simulation details

Weemployed molecular dynamics simulations in the well-known large-scale atomic/molecular massively parallel simulator (LAMMPS) [20] and structures visualized using VMD package [21]. All simulations carried out in constant-volume and constant-temperature (NPT) ensemble and the NPT-ensemble at 300K and 15bar, using a Nose–Hoover thermostat [22] with a relaxation time of 100 fs for the temperature and 1ps for the pressure.

Time integration of Newton's equation of motion undertaken using a velocity Verlet algorithm with a time step of 0.5 fs. Non-bonded van der Waals interactions modeled in terms of 12-6Lennard-Jones famous potentials U_{LJ} (r_{ij}) [23]. We applied particle-particle particle-mesh (PPPM) method to minimize error in long-range terms in both Columbia and Lennard-Jones potentials. Lennard-Jones and Columbia 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 [24] SHAKE algorithm was used to keep S-H distance fixed at 1.336 Å and H-S-H angle at 92.070°. The initial size of the simulation box for was (80×80×80) Å^3 with Compound percentage: methane 16.5%, ethane 72.1%, sulfide hydrogen (with title atomic H_s and S) 8.8% and monoethanolamine (MEA with title atomic H_e amin, O_e and N_e) 2.6%.

We have performed density functional theory (DFT) calculations to optimize the structural models of MEA and the hydrogen disulfide with systems has been studied in the gas. All the structures were optimized B3LYP exchange–correlation functional and the 6-311 (+) G** standard basis set have been used to run all computations as implemented in the NWCHEM package [25].

Result and discussion

The general purpose of this study was to investigate the molecular absorption of H2S molecules by MEA molecules in gas mixtures included methane, ethane, MEA and H_2S. Actually H_2S molecules just absorb through a

hydrogen bond to amine nitrogen and alcoholic oxygen of MEA molecules.

System electrostatic properties are one of the most important and effective properties which effect on the interactions of molecular system components and usually it has an excellent effect on system behavior. For this purpose the study of charge distribution was considered firstly.
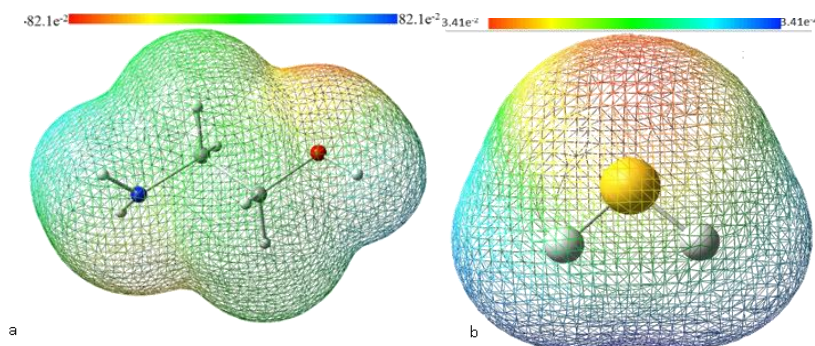

FIGURE 1 An electrical charge distribution around molecular (a) MEA (b) H_2S

Figure 1 shows the charge distribution on MEA and H_2S molecules. Blue, red, yellow, turquoise, white colors respectively indicated nitrogen, oxygen, sulfur, carbon and hydrogen atoms. Figure 1 shows that the charge distribution on MEA and H_2S molecules are different. In Figure 1 a, a positive electrical load accumulation on MEA molecule is observed in dense from on the both end sections closed to hydrogen atoms. While the negative electrical load distribution in MEA molecule was concentrated at the end of molecular on nitrogen and oxygen atoms. In the Figure 1b is observed the electrical load distribution around hydrogen sulfide made double pole electrics.

In the following, the interaction between H_2S and MEA molecule is studied. The graph of radial distribution functions (RDF) can show suitable information about the method of particle interactions. Figure 2 shows an RDF of nitrogen and oxygen atoms for MEA and hydrogen sulfide.
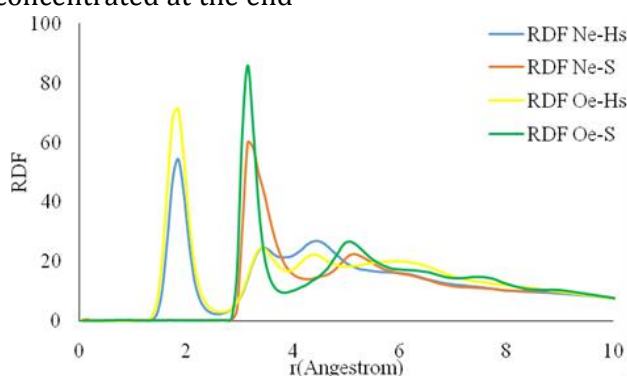

FIGURE 2 Radial distribution function graph of MEA and H_2S

H_2, S and Ne, Oe symbols indicate sulfur atom, hydrogen of H_2S, alcoholic oxygen and amine nitrogen in MEA. All graphs of radial distribution functions in Figure 2 have a significant peak. Among radial distribution function graphs, RDF Oe-Hs has a sharp peak in 1.85 distance with 71 height. That confirms the strong interaction between H2S with the oxygen of MEA after that in RDF Ne-Hs a sharp peak in 1.75 distance with 53 in observed, which indicates a strong interaction between hydrogen of H_2S and nitrogen of MEA.

The reason for the strong interaction between nitrogen and hydrogen of H_2S can be observed in Figure 2. H_2S molecules can

interact with amine and alcohol groups of MEA in two forms. Interaction of negative section of an amine group (nitrogen) or alcohol (oxygen) with H_2S hydrogen also interaction of positive section amine group (He) or alcohol (Ho) with H_2S sulfur.

Considering the small size of a hydrogen atom, it is penetrated better than sulfur and oxygen. Due to adsorption H2S hydrogen to the MEA in comparison to sulfur atom, stronger electrostatic interaction between alcohol, hydrogen and the amine nitrogen with H_2S hydrogen is done. Also in Figure 2 radial distribution function, RDF Ne-S and RDF Oe-S have a sharp peak in 3.15 distance with 86 heights and 3.35 distance with 40 height. Of course it is not strong interaction between Ne-S, O_e-S components in interaction of hydrogen sulfide and MEA molecules, it is clearly visible that Oe-Hs and Oe-S are the stronger bonds than Ne-Hs and Ne-S. The reason of the high peak height of radial distribution functions of RDF Ne-S and RDF

Oe-S is the strong interaction between nitrogen amine with H_2S hydrogen.

Since sulfur and oxygen in MEA molecule are connected to hydrogen, the position of them always remains close to hydrogen, which interacted with nitrogen and cause a sharp peak in specified distance of hydrogen. Since there is a strong interaction between H_2S hydrogen with alcohol oxygen and amine nitrogen, the interaction H_2S hydrogen with alcohol oxygen and amine nitrogen is reviewed each.

MEA molecule has one alcohol and one nitrogen amine. The distance changes are calculated between hydrogen atoms of hydrogen sulfide with alcohol oxygen and the amine nitrogen of MEA. Figure 3 graph shows the distance changes between hydrogens of H_2S molecule with alcohol oxygen and the amine nitrogen of MEA.
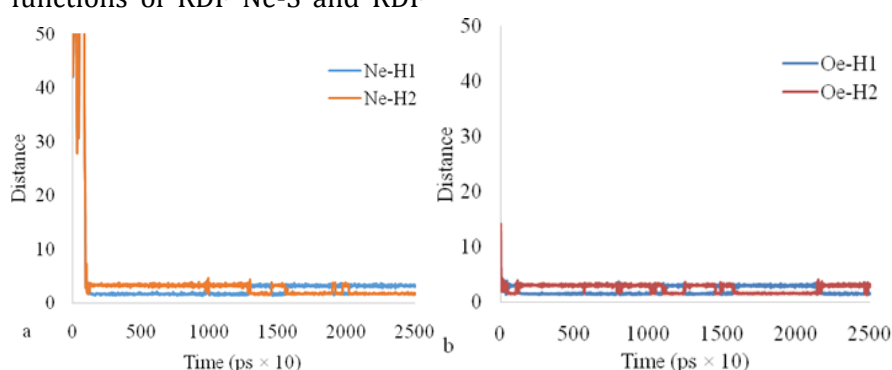

FIGURE 3 Distance changes between hydrogens of H2S molecules with nitrogen and oxygen atoms of MEA

The purpose of H1 & H2 are hydrogens of H_2S molecule which their distance to nitrogen and oxygen atoms of MEA is calculated. (a) Distance changes between hydrogen atoms of H_2S molecule and nitrogen atoms of amine molecular during total simulation time. (b) Distance changes between H_2S molecules and alcoholic oxygen atom during the total simulation time. As indicated in figure 3a & 3b H_2S molecules reach into the distance less than $6A^0$ at about 100-1000 ps which confirm

absorption and interaction between H2S and MEA molecules.

In Figure 3 a and 3b can observe that when one of the hydrogens place in less than 2 A^0, H_2S hydrogens are separated from each other and make a gap in space. Actually, when one of the hydrogens of H_2S molecule place in less than $2A^0$ to amine nitrogen or alcohol oxygen, the strong interaction is happening between atoms. In this situation, one of hydrogen place in the closed distance and second hydrogen stay further away.

The result of this structure, creating distance change in the graph of Figure 3. In the graph of Figure 3 is observed that in different parts of graph some gaps with different lifetime created. This observation confirms that hydrogens of H_2S molecule at various times separated from the relevant nitrogen and oxygen then reconnected. Another important observation in Figure 3 is that sometimes the place of the hydrogens of H_2S molecule is changed in the gap space of the graph and the color of the closed graph is changed. The movement of two hydrogens happens at first, the closed hydrogen atom more a little from equilibrium distance which had been created by the interaction between nitrogen and oxygen. In this time hydrogen further has closed to another hydrogen, and both hydrogen start the vibration compared to before. In finally one of the hydrogen atoms close to nitrogen or oxygen and the other goes away.

Figure 4 shows as mentioned H_2S molecules have just interacted with amine nitrogen and alcoholic oxygen (MEA) positions. After the interaction between H_2S and MEA molecules it can use its free hydrogen for interaction and bridge rule.
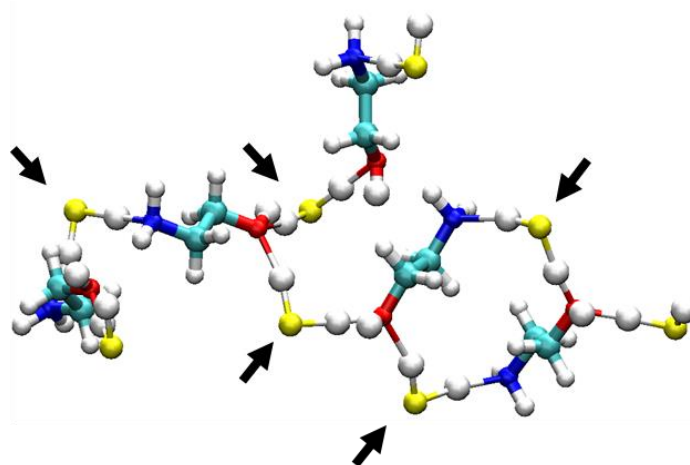

FIGURE 4 A relevant snapshot showing the attachment of H2S with MEA molecule

Blue, red, yellow, turquoise and white color are nitrogen, oxygen, sulfur, carbon and hydrogen atoms respectfully.

Some H_2S molecules which interact with MEA will have second interaction with other MEA molecules this phenomenon will create a complicated structure from H_2S/MEA interaction. This stable structure will continue until the end of the simulation.

the H_2S molecule are closer to the MEA molecule than a sulfur atom. A Review of distance changes between hydrogen in H_2S and nitrogen/oxygen in MEA showed that absorbed H_2S has interaction with the bond position of MEA to the end of the simulation. In the RDF diagram also showed that hydrogen in H_2S could be changed during the interaction.

Conclusion

In this study by molecular dynamic simulation, it was observed that adding MEA to sour gas causes H_2S removal and gas sweetening. H_2S molecules absorbed by amine nitrogen and alcoholic oxygen of MEA molecules from the hydrogen head. RDF diagram showed that the hydrogen atoms in

References

[1] S. Mokhatab, W.A. Poe, *Handbook of natural gas transmission and processing*. Gulf professional publishing, **2012**, 1-74.
[2] A.L. Kohl, R. Nielsen, *Gas purification*. Elsevier, **1997**, 6-31.
[3] W.A. Poe, S. Mokhatab, *Modeling, control, and optimization of natural gas processing*

plants. gulf professional publishing,, **2016**, 97-172.

[4] B. Mandal, M. Guha, A. Biswas, S. Bandyopadhyay, *Chem. Eng. Sci.,* **2001**, *56*, 6217-6224.

[5] L. Oshinowo, F. Said, Y. Bokhedaim, K. Suwailem, M. Paul, Methn A. Multiphase Flow Simulation to Estimate Erosion/Corrosion Potential in Gas Sweetening Process Piping. InInternational Petroleum Technology Conference **2020** Jan 13. International Petroleum Technology Conference.

[6] R. Hugo, R. Wagner, T.S. Holst, C. inventors; BASF SE, assignee. Method for removing mercaptans from fluid fluxes. United States patent US 6,740,230. **2004** May 25.

[7] J. C. Polasek, G. Inglesias-Silva, J. A. Bullin, Using mixed amine solutions for gas sweetening. In proceedings of the annual convention-gas processors association, **1992**, 58-58. Gas Processors Association.

[8] V. Raju, R.H. Krishna, R. Wegner, Ground Improvement Using Vibro Replacement in Asia 1994 to 2004. In5 th International Conference on Ground Improvement Techniques. Kuala Lumpur, Malaysia **2004**.

[9] W.D. Cornell, P. Cieplak, C.I. Bayly, I.R. Gould, K.M. Merz, D.M. Ferguson, D.C. Spellmeyer, T. Fox, J.W. Caldwell, P.A. Kollman, *J. Am. Che.m Soc.*, **1995**, *117*, 5179-97.

[10] S. Aparicio, M. Atilhan, *J. Physical Chem. C,* **2013**, *117*, 15061-15074.

[11] J.M. Vicent-Luna, A. Luna-Triguero, S. Calero, *J. Physical Chem. C*, **2016**, *120*, 23756-23762.

[12] A. Abedini, E. Crabtree, J.E. Bara, C.H. Turner, *Chemical Physics,* **2019**, *516*, 71-83.

[13] A. Mafi, D. Hu, K.C. Chou, *Surface Science,* **2016**, *648*, 366-370.

[14] M. Feng, X. Z. Jiang, K.H. Luo, *Proceedings of the Combustion Institute,* **2019**, *37*, 5473-5480.

[15] R. Jafarzadeh, J. Azamat, H. Erfan-Niya, *Petrol. Sci. Technol.,* **2019**, 1-6.

[16] M. Maurya, J.K. Singh, *J Physical Chem. C,* **2018**, *122*, 14654-14664.

[18] A. Santaniello, G. Golemme, *J. Ind. Eng. Chem.,* **2018**, *60*, 169-176.

[17] A. Santaniello, G. Golemme, *J. Ind. Eng. Chem.*, **2018**, *60*, 169-176.

[18] A.R. Shaikh, H. Karkhanechi, E. Kamio, T. Yoshioka, H. Matsuyama, *J. Phys. Chem. C,* **2016**, *120*, 27734-27745.

[19] S. Plimpton, *J. Comput. Phys.,* **1995**, *117*, 1-19.

[20] W. Humphrey, A. Dalke, K. Schulten, *J. Mol. Graph.*, **1996**, *14*, 33-38.

[21] W.G. Hoover, *Phys. Rev. A,* **1985**, *31*, 1695.

[22] J.E. Lennard-Jones, *Proc. Phys. Soc.,* **1931**, *43*, 461-482

[23] W.L. Jorgensen, D.S. Maxwell, J. Tirado-Rives, *J. Am. Chem. Soc.,* **1996**, *118*, 11225-11236.

[24] M. Valiev, E.J. Bylaska, N. Govind, K. Kowalski, T.P. Straatsma, H.J. Van Dam, D. Wang, J. Nieplocha, E. Apra, T.L. Windus, *Comput. Phys. Commun.,* **2010**, *181*, 1477-1489.

[25] E.A. Grubert, A.R. Brandt, *J. Clean. Prod.,* **2019**, *222*, 760-767.

[26] B. Wang, Q. Liao, J. Zheng, M. Yuan, H. Zhang, Y. Liang, International Petroleum Technology Conference, **2019**.

[27] J.M. Price, A.B. Nayak, B. Dai in Reverse design technique for optical processing elements, Vol. *Google Patents*, **2019**.

[28] M. Mikolajková-Alifov, F. Pettersson, M. Björklund-Sänkiaho, H. Saxén, *Energies,* **2019**, *12*, 351, 1-27.