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Evaluation of Diffusivity and solvent concentration effect on intermolecular interaction of secondary and tertiary amines for CO_2 absorption process

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ABSTRACT

Diffusion coefficient study gains an interest to know the mass transfer properties of molecules especially in the study of the absorption process. The main objective of the present study is to investigate the effect of temperature on the diffusivity of the MEA absorption process for CO_2 capture and to explore the effect of solvent concentration on intermolecular interactions of 2EAE (2-ethylamino ethanol) and 2DMAE (2-dimethylamino ethanol). The molecular dynamic simulation study is conducted for the calculation of diffusivity and intermolecular interaction of amines. Three different values of process temperature are chosen for calculation of diffusivity i.e. 298 K, 313 K and 318 K. Mean Square Displacement (MSD) analysis was done to compute the diffusion coefficient of molecules in secondary and tertiary amine system. Radial distribution function analysis was carried out for the calculation of intermolecular interactions. The results show that the rate of the diffusion coefficient is increased as temperature is increased and the CO_2 diffusivity on MEA is higher as compared to 2DMAE but lower than 2EAE. The diffusivity results obtained from the present work are in good agreement with theoretical results. The results of the main solvent concentration on intermolecular interaction show that by increasing the concentration of the solvent, the intermolecular interaction strength increases in both cases of secondary and tertiary amines. The 30% of 2EAE shows highest intermolecular interactions in CO_2 and 40% & 60% of 2DMAE show higher intermolecular interactions. Therefore, 30% of 2EAE and 40% & 60% of 2DMAE can be a good choice for CO_2 absorption process.

Keywords: CO_2 diffusion coefficient, Molecular dynamic simulation, mean square displacement, Primary & secondary amines, Radial Distribution Function

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1. INTRODUCTION

Emission of CO_2 from the coal-fired processes has incurred the greenhouse effect over the past decades, resulting in a severe climate change throughout the world [1], which force people to take measures to capture CO_2 from the central emission point source. However, the CO_2 emission mitigation target might be difficult due to the huge amount of energy consumption on CO_2 capture, using monoethanolamine (MEA) absorption method as state-of-the-art technology during the industrial process [2]. The energy requirement related to regeneration of monoethanolamine (MEA) solvent accounts for 60%–80% of the total energy consumption, which will increase the electricity cost by approximately 81% for a supercritical power plant [3]. Hence, developing the alternative to MEA with a high absorption rate and low heat duty is still a great challenge to depress global climate warming.

To address this issue, many researchers have focused on different alternatives to MEA such as MDEA tertiary amine and AMP hindered amine [4]. This study also aims to conduct to find an efficient absorbent for CO_2 capture application by calculating the diffusion coefficient as well as the intermolecular interaction strength of 2EAE and 2DMAE for CO_2 absorption process by taking the different solvent concentration as 30%, 40%, 50% and 60%, respectively.

Table.1.Comparrision of results from simulation & theoretical

System	Simulation	Theoritical (Versteeg & van Swaaij)	Theoritical(Wilke-Chang)
Temperature	298K		
MEA(m^2/s)	1.40E-09	1.4463E-09	1.28E-09
Temperature	313K		
MEA(m^2/s)	2.04E-09	2.0577E-09	1.83E-09
Temperature	318K		
MEA(m^2/s)	2.10E-09	2.2954E-09	1.96E-09

Table. 2 Intermolecular interactions of 2EAE at different concentrations

2EAE	N_{2EAE}-H_{water}	HO_{2EAE} O_{water}	O_{2EAE}-C_{CO2}	N_{2EAE}-C_{CO2}
30%	4.75,1.08	2.25,1.32	5.25,1.19	5.25,1.41
40%	4.75,1.14	3.25,1.40	5.25,1.16	4.75,1.28
50%	4.75,1.19	3.25,1.62	5.25,1.16	5.25,1.32
60%	4.75,1.24	3.25,1.79	5.25,1.15	5.25,1.37

$\boldsymbol{N_{2EAE}}$; Nitrogen in 2-Ethylamino ethanol ; $\boldsymbol{HO_{2EAE}}$; Hydrogen at Oxygen in 2EAE; $\boldsymbol{H_{WATER}}$; Hydrogen in water,$\boldsymbol{O_{2EAE}}$; Oxygen in 2EAE;$\boldsymbol{C_{CO2}}$; Carbon in CO_2

Table.3 Intermolecular interactions of 2DMAE at different concentrations

2DMAE	N_{2DMAE}-H_{water}	HO_{2DMAE} -O_{water}	O_{2DMAE}-C_{CO2}	N_{2DMAE}-C_{CO2}
30%	4.75,1.25	3.25,1.31	5.25,1.11	5.25,1.75
40%	4.75,1.37	3.25,1.41	5.25,1.19	5.25,1.80
50%	4.75,1.42	3.25,1.60	5.25,1.08	5.25,1.75
60%	4.75,1.47	3.25,1.77	5.25,1.17	5.25,1.81

$\boldsymbol{N_{DMAE}}$; Nitrogen in Dimethylamino ethanol $\boldsymbol{HO_{DMAE}}$; Hydrogen at Oxygen in DMAE $\boldsymbol{H_{WATER}}$; Hydrogen in water $\boldsymbol{O_{DMAE}}$; Oxygen in DMAE; $\boldsymbol{C_{CO2}}$; Carbon in CO2

Recently, computer-based simulation is widely used in all over the world in different research fields. The present study will adopt molecular dynamic simulation to analyze the intermolecular interaction during the process of absorption.

MATERIALS & METHODS

The simulation methodology is done in material studio software provided by Biovia [5]. While doing the simulation, selection of simulation parameters is most

important to get accurate and reliable results. In the material studio,the most important is the selection of forcefield and step length because their sizes influence the length of computer simulation time and accuracy of simulation results. In the present study, through a lot of trial and error, the step length of 1fs and COMPASS forcefield is chosen. Literature shows that COMPASS forcefield can predict the structure, conformation, vibration and thermal physical properties of various molecules within the isolated or condensed system in a large range of temperature and pressures [6]. The methodology contains two types of case studies, first is the calculation of diffusivity coefficient for MEA, 2EAE and 2DMAE and second is for the solvent concentration effect on intermolecular interactions of 2EAE & 2DMAE. So the methodology for the calculation of diffusion coefficient, it consists of the following steps, first of all, the structures are replicated from ChemSpider database by Royal society of chemistry [7]. Simulation methodology contains three types of phases in MD simulation, relaxing phase, equilibrium phase and the sampling phase [8]. The 2nd step is energy minimization, 3rd is amorphous cell construction, 4th steps is simulation box energy minimization and annealing. At 5th step, the dynamics at NVT ensemble, (a simulation protocol in which number of atoms (N), volume (V) and temperature (T) of the system retain constant) and NVE ensemble, (a simulation protocol in which number of atoms (N), volume (V) and Energy (E) of the system retain constant) was figure out. And at the end, the Mean square displacement analysis was carried out to calculate the diffusion coefficient. For calculating the intermolecular interaction strength, the dynamics at equilibrium and production phase is performed. After that, the Radial Distribution Function (RDF) analysis was executed to know the intermolecular interaction strength.

3. RESULTS & DISCUSSIONS

Molecular dynamic simulation study is used for two types of case studies. First, to calculate the CO_2 diffusivity in MEA, 2EAE and 2DMAE and 2nd to know the solvent concentration effect on intermolecular interaction of 2EAE and 2DMAE. For above two types of case studies, the results are described one by one.

3.1 Calculation of CO_2 Diffusivity in MEA, 2EAE & 2DMAE

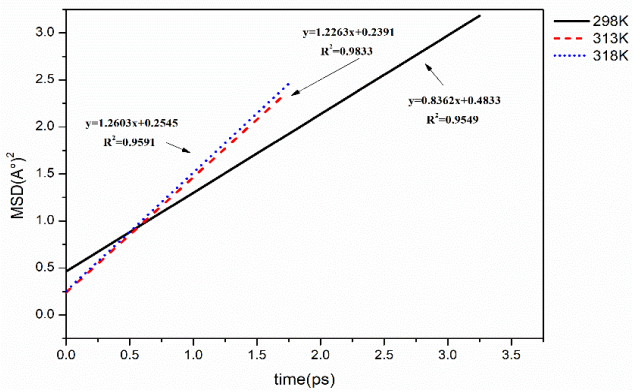

Figure 1.Mean square displacement analysis for the prediction of MEA diffusivity in MEA

In the simulation process, MEA, 2EAE and 2DMAE chemical solvents are selected to absorb CO_2 gas. CO_2 will diffuse from gaseous state to liquid phase and then dissolve in liquid phase and do interactions and reaction [9]. The CO_2 diffusivity is calculated for MEA. The purpose behind the diffusivity calculation of MEA is firstly, it is regarded as the standard solvent for CO_2 capture process, secondly the results of MEA diffusivity will help to validate the diffusivity results of 2EAE and 2DMAE, because as the best knowledge of author, no study is conducted for the diffusivity calculation of 2EAE and 2DMAE. Figure 1 shows the graphical representation of mean square displacement analysis for the prediction of MEA diffusivity in MEA at three different temperatures i.e., 298K, 313K and 318K.

Table 1 shows the diffusivity results of the simulation. To validate the methodology used in the present study, the results are compared with theoretical calculation [9]. There are two types of theoretical calculations, one is Wilke-Chang equation [10] and another is Versteeg and Van Swaaij (1988). The Wilke-Chang equation is based on the Versteeg and Van Swaaij (1988) study [11]. The comparison of results in Table 1 show that there is good agreement between simulation and theoretical results.

3.2. Effect of solvent concentration on intermolecular interaction of 2EAE and 2DMAE

3.2.1. Intermolecular interactions of 2EAE with CO_2 at different concentrations

2EAE (2-ethylamino ethanol) is a secondary amine and the intermolecular interaction strength of

2EAE with PZ (Piperazine) was examined by (Sharif et al., 2020) [12]. The present study aims to know the effect of main solvent concentration (pure solvent) on intermolecular interactions of selected amine. Different concentrations i.e. 30%, 40%, 50% and 60% of 2EAE and 2DMAE were taken to study the intermolecular interaction strength with CO_2 so that the solvent with higher intermolecular interaction can be selected for experimental studies.

Radial distribution function analysis was performed to explore the intermolecular interaction strength of selected amines i.e. 2EAE secondary and 2DMAE tertiary amine. RDF radial distribution function is a graphical representation of the relationship between r and g(r). Here 'r' is a distance of molecules to neighboring atoms, and g(r) shows the tendency of different atoms to interact with other atoms. Strong intermolecular interaction between atoms will be observed if a higher value of g(r) is obtained at a smaller distance of 'r' [9]. The higher intermolecular interaction will facilitate the absorption process. The summary of results is given in Table 2 for 2EAE. Figure 2a and Figure 2b show the graphical representation of RDF analysis for particular observed interactions. It can be seen that by increasing the solvent concentration, the intermolecular interaction strength increases. All the intermolecular interactions are higher at 30% of 2EAE. The results show that 30% of 2EAE can be a good choice for CO_2 absorption process as compared to 40%, 50% and 60%.

3.2.2 Intermolecular interactions of 2DMAE with CO_2 at different concentrations

2DMAE is a tertiary amine and it contains two methyl groups at the nitrogen atom. The literature shows that the hydroxyl group in amine is responsible for the solubility of amines in water whereas the amino group gives details about the reaction with an acidic gas [13]. Table 3 shows the intermolecular interactions of 2-dimethylamino ethanol with CO_2 and water. It can be seen from the Table 3 that for N_{2DMAE}-H_{WATER} & HO_{2DMAE}-O_{WATER} interaction, the intermolecular interaction strength increases by increasing the percentage of solvent. It shows that hydroxyl and amino group in water are more attracted towards CO_2. The other two interactions O_{2DMAE}-C_{CO2} & N_{2DMAE}-C_{CO2} show rise and fall in intermolecular interaction strength by increasing the concentrations. Therefore, it can be concluded that the reaction of CO_2 with 2DMAE is slow but with high solubility of 2DMAE in water.

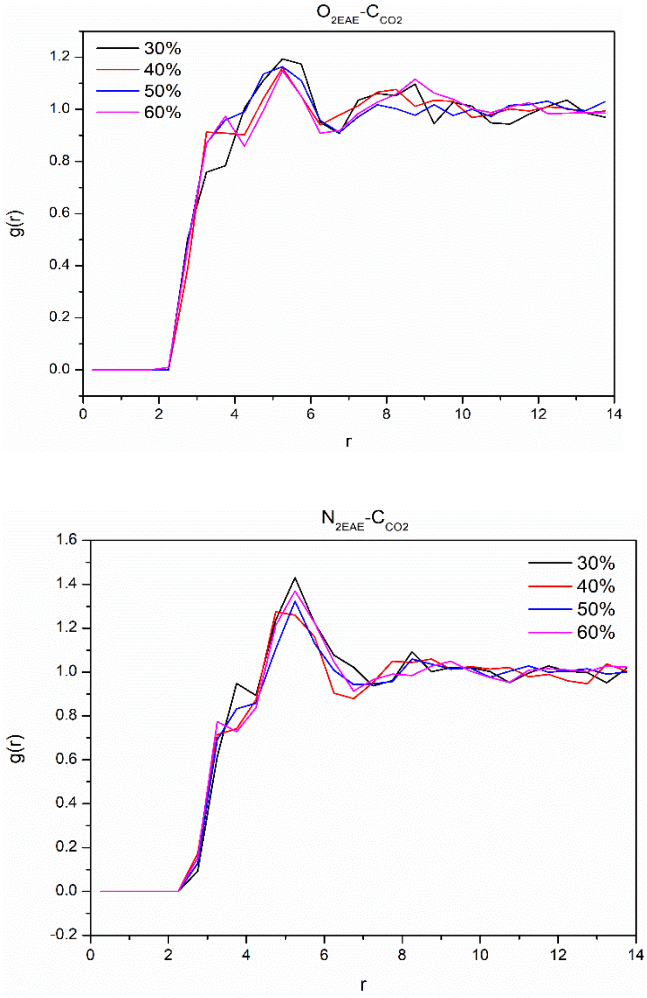

Figure 2b.RDF analysis of 2EAE at different concentrations

On the other hand the overall intermolecular interaction strength from Table 3 show that in 2DMAE (tertiary amine), for all types of interactions observed in the present study, the intermolecular interaction strength is higher in 40% and 60% of solvent concentration as compared to 30% of 2DMAE. Figure 3a & Figure 3b show the graphical representation of RDF plot for particular observed interactions. From the RDF analysis we can conclude that for tertiary amine which is 2-dimethylamino ethanol, 40% and 60% of solvent concentration is favorable for CO_2 absorption process because these two solvent concentrations show stronger intermolecular interaction towards CO_2. Therefore for

experimental studies, the priority can be given to 40% and 60% of solvent concentrations. The literature shows that 30% of amine solvent is regarded as a standard concentration for CO_2 absorption process but the intermolecular interaction strength results of present study show that 40% and 60% of solvent concentration can also be a good choice for CO_2 absorption process.

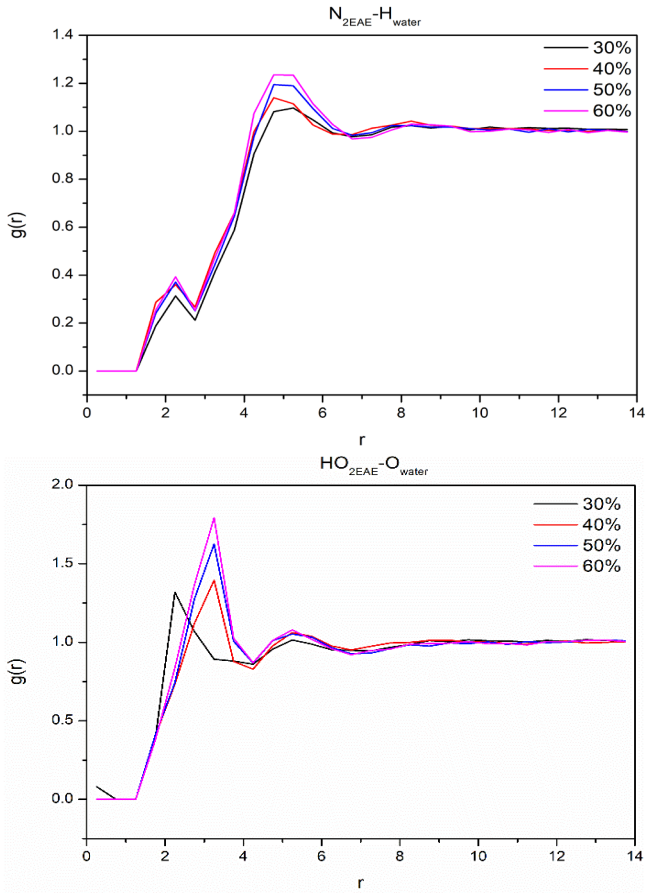

Figure 2a. RDF analysis of 2EAE at different concentrations

4. CONCLUSIONS

Based on mean square displacement analysis results for the calculation of diffusivity, it is concluded that the diffusivity of CO_2 in MEA is higher as compared 2DMAE but lower than that of MEA. The diffusivity of CO_2 in 2EAE is higher than that of MEA. Further important properties i.e. regeneration energy, degradation and loading capacity etc. are needed to study to use 2EAE as an alternative to MEA in industry. The effect of temperature on the diffusivity of selected solvents results show that by increasing the temperature, the diffusivity increases. This is due to the collision between particles, by increasing temperature, the movement of particles increases and as a result their collision increases, which is the cause of higher diffusivity coefficient. Theoretical calculation was done to check the reliability of results. The results of the present study are compared with the theoretical calculation. The diffusivity results obtained from the present work are in good agreement with theoretical results.

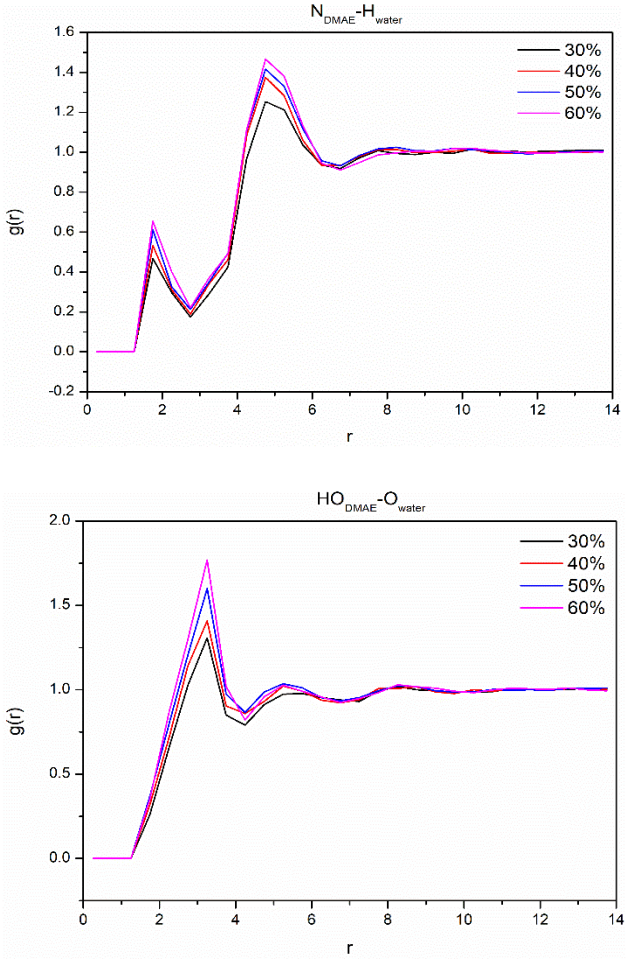

Figure 3a.RDF analysis of 2DMAE at different concentrations

The results of radial distribution function analysis of secondary and tertiary amines show that by increasing the main solvent concentration, the intermolecular interaction strength increases. In both cases of secondary and tertiary amines, there is a gradual increase in N_{amine}-H_{water} and HO_{amine} -O_{water} interactions and sharp peaks were observed. The other two interactions O_{amine}-C_{CO2} and N_{amine}-C_{CO2} peaks show rise and fall in 40%, 50% and 60% of solvent concentration. 2EAE (secondary amine) shows highest intermolecular interactions for all types of interactions observed at 30% of solvent concentration, which indicates that the 30% of solvent concentration can be favorable for CO_2 absorption process as compared to 40%, 50% and 60%.

For 2DMAE (tertiary amine), the intermolecular interaction strength is higher in 40% and 60% of solvent concentration as compared to 30% of 2DMAE. Therefore 40% and 60% of solvent concentration can also be a choice for CO_2 absorption process.

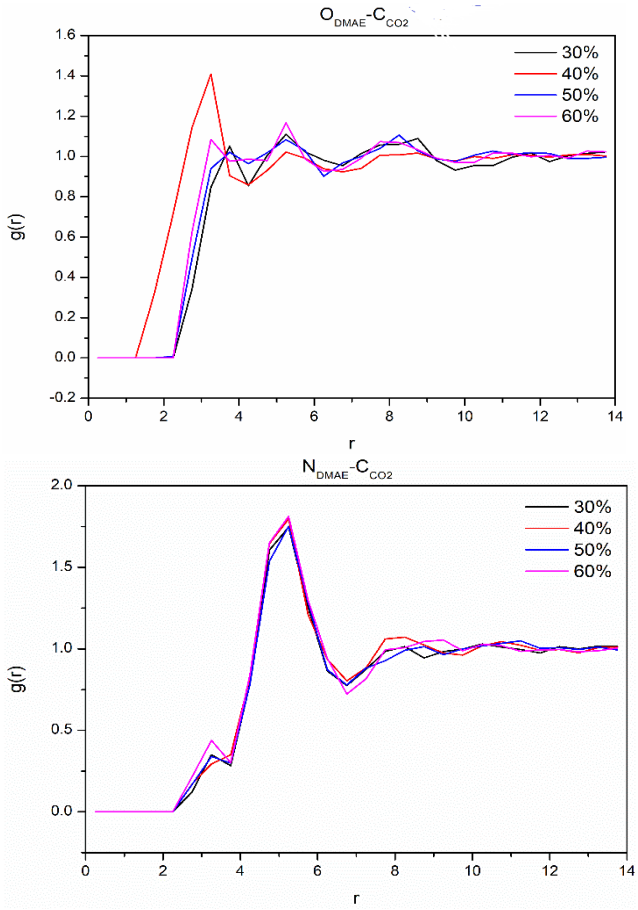

Figure 3b.RDF analysis of 2DMAE at different concentrations

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REFERENCES

[1] O. Geden, G.P. Peters, V. Scott, Targeting carbon dioxide removal in the European Union, Climate Policy, 19 (2019) 487-494.

[2] S. Zhang, M. Du, P. Shao, L. Wang, J. Ye, J. Chen, J. Chen, Carbonic anhydrase enzyme-MOFs composite with a superior catalytic performance to promote CO2 absorption into tertiary amine solution, Environmental science & technology, 52 (2018) 12708-12716.

[3] M. Xiao, H. Liu, H. Gao, W. Olson, Z. Liang, CO2 capture with hybrid absorbents of low viscosity imidazolium-based ionic liquids and amine, Applied Energy, 235 (2019) 311-319.

[4] P. Muchan, C. Saiwan, J. Narku-Tetteh, R. Idem, T. Supap, P. Tontiwachwuthikul, Screening tests of aqueous alkanolamine solutions based on primary, secondary, and tertiary structure for blended aqueous amine solution selection in post combustion CO2 capture, Chemical Engineering Science, 170 (2017) 574-582.

[5] Biovia, Material Studio,San Diego, USA, 2017 Version 8., 2020.

[6] S. Charati, S. Stern, Diffusion of gases in silicone polymers: molecular dynamics simulations, macromolecules, 31 (1998) 5529-5535.

[7] ChemSpider, ChemSpider Database, Royal Society of Chemistry, 2020. [Online], 2020.

[8] J. Wang, T. Hou, Application of molecular dynamics simulations in molecular property prediction II: diffusion coefficient, Journal of computational chemistry, 32 (2011) 3505-3519.

[9] E. Masiren, N. Harun, W. Ibrahim, F. Adam, Effect of temperature on diffusivity of monoethanolamine (MEA) on absorption process for CO2 capture, International Journal of Engineering Technology And Sciences (IJETS), 5 (2016) 43-51.

[10] C. Wilke, P. Chang, Correlation of diffuscoefficients in dilute solutions, AIChE Journal, 1 (1955) 264-270.

[11] E.D. Snijder, M.J. te Riele, G.F. Versteeg, W. Van Swaaij, Diffusion coefficients of several aqueous alkanolamine solutions, Journal of Chemical and Engineering data, 38 (1993) 475-480.

[12] Sharif, M., Zhang, T., Wu, X., Yu, Y. & Zhang, Z. Evaluation of CO2 absorption performance by molecular dynamic simulation for mixed secondary and tertiary amines. International Journal of Greenhouse Gas Control, 97(2020), 103059.

[13] A. Kohl, Nielsen, R., Gas Purification, 5th Edition. United States of America 5th Edition ed., Gulf Professional Publishing. Houston, Texas. 1997.