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Estimation of diffusivity and intermolecular interaction strength of secondary and tertiary amine for CO_2 absorption process by molecular dynamic simulation

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ABSTRACT

CO_2 capture by absorption method is a promising way to realise CO_2 reduction in the industrial process. To reduce the cost of the CO_2 absorption and desorption process, people are looking for efficient solvents. Mixed solvents are an attractive way to solve the problem. Thus evaluating the mass transfer features of molecules is critical for mixed solvents in the CO_2 absorption process, which requires knowledge of the diffusion coefficient. 2-ethylamino ethanol (2EAE) and 2-dimethylamino ethanol (2DMAE) are selected for current study. The key objective of the current study is to investigate the diffusivity of 2EAE and 2DMAE and to explore the effect of the solvent concentration on the intermolecular interactions of selected amines. A molecular dynamic simulation analysis is carried out to assess the diffusivity and intermolecular interaction strength. Three different process temperatures were selected, i.e. 298, 313, and 318 K. The results show that as temperature rises, the rate of the diffusion coefficient increases. The CO_2 diffusivity on MEA is higher compared to 2DMAE but lower than that of 2EAE. The intermolecular interaction strength increases by increasing the solvent concentration. The highest intermolecular interactions in CO_2 are shown by 30%wt of 2EAE and 40% wt of 2DMAE.

1. Introduction

As a result of technological advancement and significant population growth, the continuously growing global demand for energy has contributed to a rise in fossil fuel consumption. Fossil fuel combustion provides about 80% of the worldwide energy supply [1–3]. Significant greenhouse gas emissions are produced by the burning of fossil fuels such as coal, natural gas, and crude oil in industries, power plants, and other energy sectors [4,5]. This continuing release of greenhouse gas from coal-fired boilers has triggered global issues, such as global warming and extreme climate change, prompting individuals to take steps to trap CO_2 from the source of the central emission point [6,7]. Carbon capture and storage (CCS) technology, which is focused on collecting CO_2 from power plants and other industrial sources, compressing and then transporting it to underground storage sites, is one of the most promising approaches to addressing the high emission rate of carbon dioxide. There are several technical routes for power plant carbon capture; pre-combustion, post-combustion, oxy-combustion [8], and chemical looping. Post-combustion carbon dioxide capture through chemical absorption using alkanol amine is considered the state-of-the-art technology in all the approaches because of its benefits, such as retrofitting to existing plants and simple installation [9].

Numerous studies have shown that the most effective option for CO_2 separation from flue gas power plants is amine-based absorption systems [10]. However, there are major obstacles to the commercialisation of this technology:

excessive solvent regeneration energy, large absorption towers, high solvent losses, and degradation. Therefore, there is a need to develop a solvent system that is economical and efficient. To make the process energy efficient, the solvent should require low regeneration heat for the operation. A good solvent candidate should usually have elevated CO_2 loading with fast reaction kinetics to minimise plant size. Major research efforts are therefore aimed at creating better solvents for the commercialisation of chemical absorption technologies to capture carbon exhaust gases [11,12]. The CO_2 absorption by monoethanolamine (MEA) is considered the most advanced technology for carbon capture during the industrial phase. However, because of the high energy requirements for CO_2 capture by using the monoethanolamine absorption process, the goal to minimise CO_2 emissions from a point source remained a challenge [13,14]. The MEA solvent regeneration energy requirement accounts for 60-80% of overall energy consumption, which raises the electricity cost for a supercritical power plant by around 81% [15]. Consequently, introducing an alternative to MEA with a high absorption rate and low heat duty remains challenging to mitigate global climate change.

Currently, the selection of highly efficient absorbents by comprehensive properties comparison can be time-consuming and costly, especially the amine selection with various molecular structures toward better solvent design. The properties which can give the overall guidance for the absorbents in CO_2 capture include physical properties (like density, viscosity, and physical solubility) [16] and chemical properties

(like reaction kinetic constant, mass transfer coefficient, and regeneration heat, etc.). Therefore, as a preliminary step, a quick solvent evaluation process is required. The current approach of selecting amines by analysis of intermolecular interaction and diffusivity was created to estimate the performance of solvents for CO_2 capture.

Several investigations have concentrated on alternative solvents to MEA, such as MDEA tertiary amine and AMP hindered amine[17], but the problem of identifying the most promising solvent remains unsolved. The current study also attempts to investigate such an efficient absorbent for CO_2 capture purposes by using various solvent concentrations of 2EAE and 2DMAE, such as 30%, 40%, 50%, and 60%, and examining the diffusion coefficient and intermolecular interaction strength of 2EAE and 2DMAE for the CO_2 absorption process. Previous investigations have shown that 2EAE has a larger absorption potential and lower heat of absorption (68.59kJ/mol) than MEA (85.13kJ/mol) [18]. The desorption enthalpy of 2EAE (104.06kJ/mol) is comparable to that of MEA (97.43kJ/mol), and the reaction kinetics of 2EAE is likewise close to those of MEA [19]. Furthermore, because 2EAE has higher energy efficiency for CO_2 removal, it could be a suitable absorbent for industrial applications. The other selected amine is a tertiary amine, 2DMAE (2-dimethylamino ethanol). The literature indicates that it has lower heat of absorption ($\Delta H < 70$kJ/mol) and desorption (83.78kJ/mol) than MEA. Furthermore, compared to MDEA and TEA, the absorption rate of 2DMAE is satisfactory [20]. Therefore, it is vital to investigate the diffusivity of these solvents as many studies [18–20] have done to consider these solvents as prospective candidates for CO_2 absorption. However, there are a few restrictions in these studies, for example, the absorption capacity, the heat of absorption, reaction kinetics, and solubility are estimated, but the diffusion coefficient and intermolecular interaction intensity are not considered, so the current research is intended to bridge the gap in the existing literature by exploring the diffusion coefficient and intermolecular interaction intensity characteristics of 2EAE and 2DMAE for CO_2 absorption application. Intermolecular interaction strength and diffusivity analysis can help to know about the reaction kinetics and mass transfer coefficient.

Numerous studies have been performed to investigate the mechanism of primary, secondary, and tertiary amine reactions. Each of these amines has a different reaction rate for CO_2 absorption. In general, primary and secondary amines react faster with CO_2, producing zwitterions and transferring a proton to make carbamate [20]. On the other side, tertiary amines lack the N-H bonds that produce the carbamate ion and do not react directly with CO_2. However, tertiary amines stimulate CO_2 hydrolysis in an aqueous solution, resulting in bicarbonate and a protonated amine but at a far slower rate than primary and secondary amines. As a consequence, tertiary amines have low reactivity compared to primary and secondary amines but higher CO_2 loading [21,22].

An essential topic in the chemical engineering process is the assessment of gas diffusivity in the liquid system. In the open literature, the research on the diffusion coefficient by molecular dynamic (MD) is very limited; for example, the MD study was conducted by Makrodimitri et al. (2011) to calculate the diffusion coefficient of H_2, H_2O, and CO in various n-alkanes [23]. Chatterjee (2014) measured the diffusivity of pure water by MD simulation [24]. The MEA, DEA, MDEA & DIPA diffusivity estimation is done by an experimental analysis [25]. Derks et al. (2008) conducted a study to estimate the diffusivity of PZ and MDEA by the Taylor dispersion method [26]. These studies show the importance and role of diffusivity in the balanced equipment design of the CO_2 absorption process and the right and accurate analysis of many absorption rate experiments [27,28]. In optimising and correctly designing gas-liquid contractors, the diffusion coefficient is also fundamental as it makes the systems more efficient.

Recently, computer-based simulations are used all over the world due to their precision and speed [29–32]. The present research involves a Molecular Dynamic (MD) simulation study to estimate the diffusion coefficient and the intermolecular interaction strength of amines. This computational method of molecular dynamic simulation is an efficient way to examine the CO_2 absorption mechanism [33,34]. In addition, thermodynamic properties at the atomic level that cannot be studied by experimentation can also be studied by this computational approach. In comparison, this approach has many benefits over experimental research, including environmentally sustainable and cost-saving [35,36]. More than half is allocated to the absorbent regeneration section in the CO_2 capture process. Therefore, before operating the absorption process in the pilot plant, an analysis of the thermodynamic properties is very important and necessary.

The primary purpose of the current study is to explore the impact of temperature on MEA, 2EAE, and 2DMAE diffusivity and the influence of solvent concentration on the intermolecular interaction of 2EAE and 2DMAE. In that perspective, the three aspects of the current research make the most significant contribution to existing research; first, the present work includes molecular dynamic simulation (MD) to understand the diffusion coefficient better and explain the nature of molecules during the process of absorption. Secondly, to optimise the solvent concentration, the research examined the intermolecular interaction strength of secondary and tertiary amines. As for further (experimental) research, the higher intermolecular interaction strength of any solvent concentration will promote the absorption process and help to assign the solvent. Third, the current research has chosen unexplored solvents such as 2EAE and 2DMAE; to the authors' best knowledge, no molecular dynamic analysis is carried out for the diffusion coefficient of 2EAE & 2DMAE to optimise the solvent concentration. Finally, the current research results will help find an effective amine solvent for laboratory experiments and industrial use to protect the environment by reducing atmospheric carbon emissions.

In the following sections, the methodology for simulation is listed first. Next, in the results and discussion section, the simulation results, guiding calculations, and theoretical interpretation are discussed. The results are drawn at the end.

2. Materials and methods

The simulation is conducted using Biovia's material studio programme [37]. The specification of input parameters is

quite critical for consistent and accurate results while running the simulation. The essential thing in the material studio is to choose forcefield and step length because their sizes affect the period of computer simulation and the accuracy of performance. The step length of 1fs and COMPASS forcefield are selected through a lot of trial and error in the current analysis. Literature shows that the COMPASS force field estimates the configuration, structure, motion, and physical, thermal features of various compounds inside the discrete or simplified process in a broad range of temperatures and pressures [38]. The technique involves two types of case studies: the measurement of the diffusivity coefficient for MEA, 2EAE, and 2DMAE and evaluating the effect of solvent concentration on intermolecular interactions of 2EAE & 2DMAE. The technique of simulation comprises three types of MD simulation stages, the relaxation phase, equilibrium phase, and sampling phase [33]. The Royal Chemistry Society replicates the structures from the ChemSpider database [39]. Geometry optimisation was achieved after replicating the 3D structures of molecules to get the stable structure of the molecules. At the smart algorithm and fine convergence stage, geometry optimisation was carried out. Then the initial simulation model in Materials Studio Software via the Amorphous Cell module was created. The model's atoms initially do not share the cubic unit cell equally. Therefore geometry optimisation is done in the forcite module to minimise the overall energy of the simulation box. With three-dimensional periodic boundary conditions, the cell used the Ewald electrostatic summation method [40]. The energy minimisation is done at the smart minimisation method. MD simulations need to optimise the model to ensure that the minimum total energy of the simulation model remains consistent regarding the simulation time employed. Thus, with the NVT ensemble (a simulation protocol in which the number of atoms (N), volume (V), and temperature (T) of the process is assumed to be constant), the MD run of 200 ps was carried out for appropriate cell equilibration. The amorphous cell or simulation model must be annealed to produce a more realistic model. The simulated annealing procedure begins at 300 K and progresses to a maximum temperature of 500 K, heating every 50 K, then cooling down to the initial temperature every 50 K. The whole procedure is repeated once. The internal stress of the simulation model was reduced after the simulated annealing process, and the partial unreasonable structure generated in the construction was almost eliminated. Mean square displacement analysis is used in forcite of the material studio to simulate the diffusion coefficient of CO_2 in selected amines (MEA, 2EAE, and DMAE). The time step of 1fs was chosen to ensure that the number of molecules in the box does not overlap. To achieve an equilibrium density, pressure is kept constant at 1 atm. The simulation box includes 300 molecules of MEA, 2EAE, 2DMAE, CO_2 and 1000 molecules of H_2O. This model is simulated at three different temperatures at 298 K, 313 K and 318 K. The analysis of mean square displacement MSD is performed for the final trajectory in the material studio's forcite module. The simulation parameters for MEA, 2EAE, and 2DMAE, which reflect the absorption process, are shown in Tables 1 and 2.

Table 1. Simulation parameters for MEA diffusivity system.

System	Density(g/ml)	No. of Molecules	Box size A×B×C
H_2O	0.989	1000	43.6A° ×43.6A°×
CO_2		300	43.6A°
MEA		300	

In the molecular dynamic simulation, the mean square displacement analysis is characterised using the Einstein relation. In MD simulation, equation (1) determines the molecular diffusion coefficient D [41]. The slope of the MSD graph is used to estimate the diffusion coefficient D. Since the system is three-dimensional, the value is divided by six, and the unit conversion ($Å^2$/ps to m^2/s) is performed as shown in equation (1)

$$D_{i,self} = \frac{1}{6N_i} Lim_{m.\delta t} \frac{1}{m.\delta t} \sum_{l=1}^{Ni} [(r_{l,i}(t + m.\delta t) - r_{l,i}(t)]^2 \quad (1)$$

The important features used in the equation can be given as, 'N_i' is the number of molecules of components i, 'δt' is the time step used in simulation, 'm' is the total number of the time step, and $r_{l,i}(t)$ is the position of lth molecules of component i.

The Stokes-Einstein relation is used in MSD calculation. The Einstein equation over the time interval is represented by Equation (2) [42]

$$6Dt = < |r(t) - r(0)|^2 > = MSD(t) \quad (2)$$

$$D = 1/6 d/dt\, MSD(t) = \text{constant} \quad (3)$$

Eq. (3) is used to compute the diffusion coefficient as a function of MSD measurements, where r(t) = [x(t),y(t),z(t)] illustrate the coordinates of atoms at time t [43].

The amorphous cell was simulated for equilibrium and production phase at NVE and NVT ensembles for intermolecular interaction analysis. The final stage is Radial Distribution Function analysis (RDF) in Material Studio's forcite module. The procedure included in this study is based on previous studies and material studio tutorials [37,44–46].

Tables 3 and 4 show the input parameters for calculating the intermolecular interactions for 2EAE and 2DMAE, respectively.

3. Results & discussion

The present computational evaluation introduces a safer research model on the diffusivity and intermolecular interactions of amines with CO_2. Generally, the cost of experimental research analyzing the diffusion coefficient is high, and the experimental process is complicated; molecular dynamic

Table 2. Simulation parameters for 2EAE and 2DMAE diffusivity system.

System	Density(g/ml)	No. of Molecules	Box size A×B×C
2DMAE	1.07	400	48A° ×48A°× 48A°
CO_2		400	
H_2O		1000	
2EAE	1.06	400	47.9A° ×47.9A°×
CO_2		400	47.9A°
H_2O		1000	

Table 3. Simulation parameters for 2EAE/CO₂/H₂O system at different concentrations.

	2EAE	CO₂	H₂O
The density of mixture (g/ml)	0.98		
Wt.%	30%	10%	60%
No. of molecules	29	20	294
The density of the mixture (g/ml)	1.1		
	40%	10%	50%
	39	20	245
The density of the mixture (g/ml)	1.009		
	50%	10%	40%
	49	20	196
The density of the mixture (g/ml)	1.00		
	60%	10%	30%
	59	20	147

simulation (MD simulation) is, therefore, a viable option for studying the solvent diffusion coefficient without conducting experiments [47,48]. The diffusion coefficient is calculated using mean square displacement analysis (MSD). Three types of theories can be used to analyze the MSD process, i.e. Fick's laws [33], Einstein Smouluchowski's theory [49], and the theory of Maxwell Stefan [41]. In mean square displacement analysis, the Maxwell Stefan theory is used.

For two types of case studies, the molecular dynamic simulation analysis is used first to measure the CO₂ diffusivity in MEA, 2EAE, and 2DMAE, and second to analyze the influence of solvent concentration on the intermolecular interaction of 2EAE and 2DMAE. For the above two case studies, the findings are listed one by one.

3.1. Analysis of CO₂ diffusivity in MEA, 2EAE, and 2DMAE

In the simulation process, MEA, 2EAE, and 2DMAE chemical solvents are chosen to trap CO₂ gas. CO₂ will diffuse from the gaseous to the liquid phase and then be absorbed in the liquid phase, and do interaction and reaction [50]. The diffusivity of CO₂ is estimated for the MEA. The MEA diffusivity measurement serves two purposes: first, to establish the MEA as the standard solvent for the CO₂ capture process, and second, the MEA diffusivity measurements will support the validation of the current study's findings. To the best of the author's knowledge, in existing literature, neither research has been conducted to estimate the diffusivity of 2EAE and 2DMAE. Therefore the present research aims to estimate the diffusivity of 2EAE and 2DMAE by

Table 4. Simulation parameters for 2DMAE/CO2/H2O system at different concentrations.

	2DMAE	CO₂	H₂O
The density of the mixture (g/ml)	0.97		
Wt.%	30%	10%	60%
No. of molecules	44	30	441
The density of the mixture (g/ml)	1.1		
	40%	10%	50%
	59	30	367
The density of the mixture (g/ml)	1.009		
	50%	10%	40%
	74	30	294
The density of the mixture (g/ml)	1.00		
	60%	10%	30%
	89	30	220

using the Mean square displacement MSD analysis. Analysis of MSD (mean square displacement) is a technique that evaluates the mode of particle displacement followed over time. It will ultimately determine whether the particle is freely diffused, transported, or bound. In addition, an approximation of movement parameters such as the diffusion coefficient of freely diffusing particles can be driven by MSD analysis [37]. Figure 1((a) & (b)) displays the MSD plot versus time at three different temperatures, such as 298, 313, and 318 K for 2DMAE and 2EAE. MSD plot in Figure 1 shows a straight line with a constant slope in the diffusion coefficient, linearly increasing with time and temperature. The results of the diffusivity are shown in Table 5.

Due to the reaction between CO₂ and amines, the experimental determination of diffusivity is difficult; thus, the N₂O analogy is used in literature to assess the diffusivity of CO₂ in different alkanol amine solutions [25]. Two transport processes, diffusion, and reaction take place when CO₂ is absorbed into an amine solution. It is difficult to assess the diffusivity and solubility due to the reaction between CO₂ and amine molecules. Therefore, the diffusivity and solubility of CO₂ are evaluated in practice by replacing the reacting CO₂ with an inert gas of an identical composition like N₂O [51]. Previous studies validated the N₂O analogy [52–54]. Equation (5) denotes the N₂O analogy measurement of the CO₂ diffusivity in MEA. The CO₂ diffusivity is computed in MEA, 2EAE, and 2DMAE. It can be seen from Table 5 that MEA diffusivity is significantly greater at all the temperatures observed as opposed to 2DMAE. The MEA is known as a standard for the CO₂ capture application. Experimental studies of CO₂ diffusivity in MEA show that MEA has a higher diffusivity than di and tri-ethanol amines [27]. In addition, the experimental value of CO₂ diffusivity in MEA at 298 K is 1.15E-09 and at 313 K is 2.22E-09 [25,54], whereas the simulation results for diffusivity at 298 K and 313 K are 1.40E-09 and 2.11E-09. There is some difference between experimental and simulation results. As a consequence, additional theoretical analysis is performed to compare the simulation results.

3.1.1. Comparative analysis of diffusivity results with mathematical equations

The theoretical evaluation is carried out to verify the accuracy of the simulation results. There are two types of mathematical formulas, the Wilke-Chang equation (Wilke and Chang 1955) and the Versteeg and Van Swaaij equations (1988). The Wilke-Chang equation is based on the Versteeg and Van Swaaij (1988) findings [25].

Table 5. Simulation results of diffusivity estimation.

	Summary of results		
System/Temperature	298K	313K	318K
MEA in Aq.MEA(m²/s)	1.40E-09	2.04E-09	2.10E-09
CO₂ in MEA(m²/s)	1.40E-09	2.11E-09	2.41E-09
CO₂ in 2EAE(m²/s)	1.47E-09	3.26E-09	3.44E-09
CO₂ in 2DMAE(m²/s)	0.92E-09	1.47E-09	1.70E-09

Table 6. Comparison between simulation and theoretical results of diffusivity.

System	Simulation	Theoretical (Versteeg & Van swaaij)	Temperature
CO_2 in 2DMAE (m²/s)	0.92E-09	0.90E-09	298K
	1.47E-09	1.40E-09	313K
	1.70E-09	1.77E-09	318K
CO_2 in 2EAE (m²/s)	1.47E-09	1.48E-09	298K
	3.26E-09	3.74.E-09	313K
	3.44E-09	3.44E-09	318K

3.1.2. Mathematical evaluation of the Wilke-Chang diffusivity equation for liquids

The Wilke-Chang equation is used to evaluate MEA and H_2O diffusivity [55]. Equation (4) below demonstrates the equation of Wilke-Chang.

$$D_{AB} = 1.173 \times 10^{-16}(\emptyset M_A)^{1/2}\frac{T}{\mu_{B V_A^{0.6}}} \quad (4)$$

Here $\emptyset$ is the association parameter for solvent, M_A is the molecular weight of solvent B, T is the temperature of the system, μ_B is the viscosity of solvent B, and V_A is the molar volume of solute A.

Tables 6 and 7 describe the findings for CO_2 diffusivity in selected amines, as well as a comparison of the results to theoretical calculations. Table 6 shows that the current study's findings are consistent with theoretical results for CO_2 diffusivity in 2EAE and 2DMAE.

3.1.3. Theoretical calculation of diffusivity by Versteeg & Van Swaaij (1988)

The N_2O model is used in the literature to measure the diffusivity of CO_2 in MEA [25]. Versteeg and Van Swaaij's diffusivity is calculated in Equations (5) to (9),

$$D_{CO2} = (D_{CO2}/D_{N2O})\text{in water} \quad (5)$$

$$D_{CO2}(m^2 \cdot s^{-1}) = 2.35 \times 10^{-6}\{-2119/T(K)\} \quad (6)$$

$$D_{N2O}(m^2 \cdot s^{-1}) = 5.07 \times 10^{-6}exp\{-2371/T(K)\} \quad (7)$$

$$D_{N2O} = (5.07 + 0.86C_{MEA} + 0.278C_{MEA}^2)$$
$$\times 10^{-6}exp\{-2371 - 93.4C_{MEA}/T(K)\} \quad (8)$$

$$C_{MEA} = 10C_{\%W/W}d/M_W \quad (9)$$

where, %w/w = weight percentage, C = the concentration, D = the diffusivity.

Table 7 shows the comparison between simulation and theoretical results. Mean square displacement analysis is conducted for the calculation of diffusivity. Figures 1 and 2 show the results of MSD analysis for MEA, 2EAE, and 2DMAE.

Table 7. Comparison between simulation and theoretical results of diffusivity.

System	Simulation	Theoretical (Versteeg & Van swaaij)	Temperature
MEA in aq. MEA(m²/s)	1.40E-09	1.44E-09	298K
	2.04E-09	2.05E-09	313K
	2.10E-09	2.20E-09	318K
CO_2 in MEA(m²/s)	1.80E-09	1.42E-09	298K
	2.11E-09	2.11E-09	313K
	2.41E-09	2.42E-09	318K

The mean square displacement (MSD) analysis is the plot of MSD versus time. Three different values of process temperature were chosen, i.e. 298, 313, and 318 K. MSD slope is used to calculate the diffusion coefficient. The graph indicates a straight line, which increases linearly with time. It can be seen from Figures 1 and 2 that by increasing the temperature, the rate of diffusivity increases. The rate of diffusivity is higher at 318 K, followed by 298 K and 313 K for all amines studied. It shows that by increasing the temperature, the rate of diffusivity increases. A higher rate of diffusivity is due to the collision between particles in the boundary condition. When heat is provided to an atom, its vibrational motion increases, and it collides with a neighbouring atom, which is the cause of higher diffusivity. The plot of MSD contains the best fit line, slope, and R^2 value. Masiren et al., 2016 conducted a study to calculate the diffusivity of MEA; the findings of that study are significantly higher than theoretical and experimental studies [56]. But the results of the present study show that there is good agreement between simulation and theoretical results Tables 6 and 7, which proves the suitability of the used forcefield and methodology adopted in the present study.

The simulation results for CO_2 diffusivity in MEA are 1.40E-09m²/s, 2.11E-09 m²/s, and 2.41E-09 m²/s at 298, 313, and 318 K, respectively, as summarised in Table 5 and Figure 2(c). In contrast, the CO_2 diffusion coefficient for 2EAE at 298, 313, and 318 K is 1.47E-09 m²/s, 3.26E-09 m²/s, and 3.44E-09 m²/s, respectively, as given in Table 6. According to the findings, the CO_2 diffusivity of 2EAE (1.47E-09m²/s) is slightly higher than that of MEA (1.40E-09m²/s), at 298K and it increases significantly with temperature. Although knowledge of diffusivity can provide information about reaction kinetics, we can't conclude that MEA has slower reaction kinetics than 2EAE based on these findings because several other factors influence the rate of the reaction (i.e. concentration of reactants, physical state, surface area, temperature, catalyst, etc). However, it is clear that the results of 2EAE are comparable to MEA, as evidenced by previous studies in the literature, such as [57], who discovered that 2EAE has a very similar absorption rate (5.18kmolm^{-2}s^{-1}) to MEA (5.00kmolm^{-2}s^{-1}). Furthermore, the 2nd order reaction rate constant for 2EAE 4.17×10^3m³kmol^{-1}s^{-1} is higher than MEA 3.63×10^3m³kmol^{-1}s^{-1}. According to [58], the reaction rate constant for MEA at 298K is 5.52×10^0 m³mol^{-1}s^{-1}, whereas it is 8.00×10^0 m³mol^{-1}s^{-1} for 2EAE at the same temperature [59]. Based on the properties of 2EAE, it can be concluded that 2EAE can be a viable candidate for CO_2 capture applications.

To keep the plant size as small as possible, the solvent should have fast kinetics and higher CO_2 loading. The experimental studies show that 2EAE has higher loading 0.71 (mol CO_2/mol amine) than MEA 0.58 (mol CO_2/mol amine), and heat of absorption (68.59 KJ/mol) for 2EAE is lower than MEA (85.13KJ/mol). Additionally, because 2EAE has faster reaction kinetics than other secondary amines, kinetic and thermodynamic analyses show that it can be used as an alternative to the baseline molecule, MEA [18,19]. The higher diffusivity of 2EAE investigated in this work is also a step toward making it a potential absorbent for CO_2 capture applications.
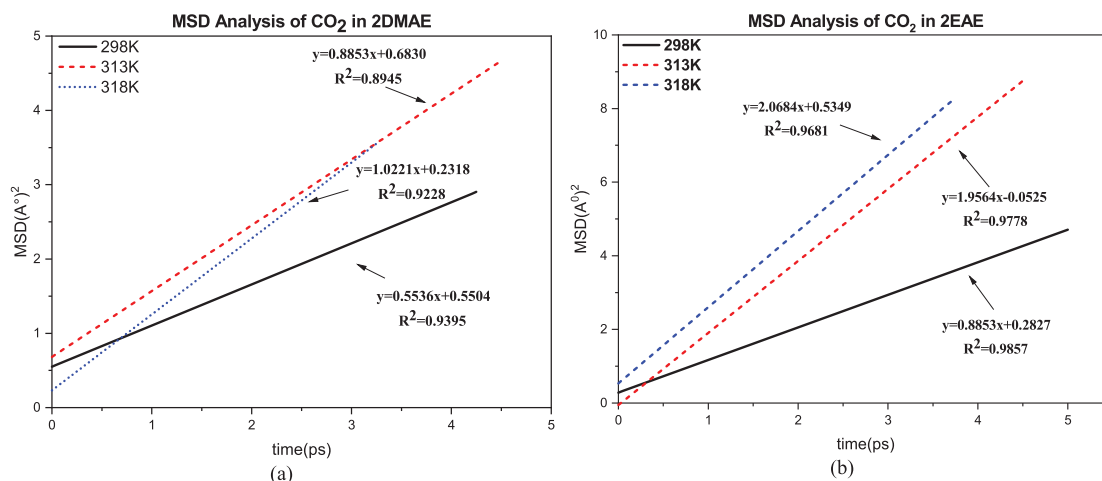
Figure 1. (Colour online) Prediction of Diffusivity of (a) CO_2 in 2DMAE and (b) CO_2 in 2EAE by MSD.

Figure 1 displays the MSD mean square displacement analysis plot for CO_2 diffusivity estimation in 2EAE and 2DMAE. At three different temperatures i.e. 298, 313, and 318 K, the CO_2 diffusivity of the tertiary amine 2DMAE is 0.92E-09m^2/s, 1.47E-09m^2/s, and 1.73E-09m^2/s, respectively. The comparison of simulation and theoretical calculations is provided in Table 6. Simulation findings demonstrate that 2DMAE has a lower diffusivity than that of MEA and 2EAE. The diffusion coefficient of MEA, 2EAE, and 2DMAE are 1.40E-09m^2/s for MEA, 1.47E-09m^2/s for 2EAE, and 0.92E-09m^2/s for 2DMAE respectively at 298 K. The lower diffusivity of 2DMAE can be justified by experimental studies [18,60] that indicate 2DMAE has lower reaction kinetics than MEA. The literature shows that the tertiary amines are less reactive and have a very slow reaction rate with CO_2 as compared to primary and secondary amines [46,61]. Because 2DMAE has a lower diffusivity value, its kinetics are more likely to be slower as compared to primary and secondary amines. The current study's simulation findings are consistent with previous research, as studies show that 2-Dimethylamino ethanol (2DMAE tertiary amine) has a high loading but with slow kinetics [21]. Therefore it is evident that simulation and theoretical findings are in strong agreement, indicating the validity of simulation methodology. Since the experimental diffusivity of 2EAE and 2DMAE has yet to be reported, these expected values could be useful in future research.

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

According to the literature, 30% of the main solvent concentration is considered a standard percentage for the CO_2 absorption process. In this analysis, various concentrations were used to optimise the concentration of solvents by measuring the strength of intermolecular interactions. A research was conducted by Sharif et al., 2020 to determine the intermolecular interaction intensity of pure 2EAE and 2EAE/PZ & pure 2DMAE and 2DMAE/PZ at 30% of the solvent concentration [46]. However, the objective of the present analysis is to determine the effect of the main solvent (pure solvent, without piperazine) concentration on the intermolecular interactions of 2EAE secondary and 2DMAE tertiary amines by choosing various solvent concentrations.
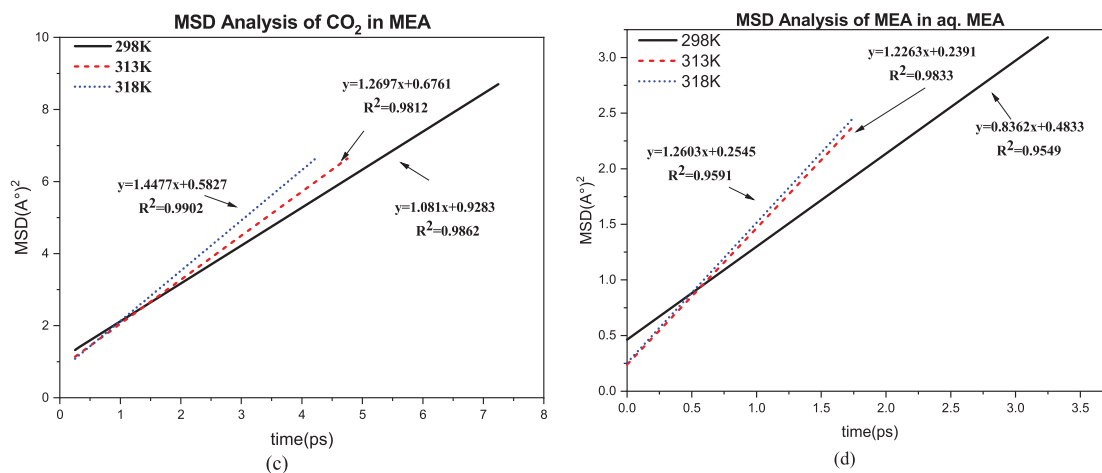

Figure 2. (Colour online) Prediction of diffusivity of (c) CO_2 in MEA and (d) MEA in aq. MEA by MSD analysis.

3.2.1. Intermolecular interactions of 2EAE with CO₂ at various concentrations

Analysis of the radial distribution function is performed to measure the intermolecular interaction of various amines, i.e. 2EAE secondary and 2DMAE tertiary amine. The RDF radial distribution function is a relationship between 'r' and $g(r)$ by graphical representation. Here, 'r' represents the distance between molecules and neighbouring atoms, while $g(r)$ represents the tendency of distinct atoms to interact with one another. Strong intermolecular interactions between atoms will be noticed if a stronger value of $g(r)$ is obtained at a smaller distance of 'r'. The greater the intermolecular interaction, the faster the absorption.

The peak value shows the highest potential to interact for a particular interaction in a graphical representation of RDF, enhancing the absorption process [46]. Various concentrations, i.e. 30%, 40%, 50%, and 60% of 2EAE and 2DMAE, were used to evaluate the strength of intermolecular interaction with CO₂ so that solvents with stronger intermolecular interactions could be chosen for experimental studies. Stronger intermolecular interaction will help in promoting the process of absorption.

Table 8 provides a description of the findings for 2EAE. The interactions after 15A° are supposed to be ignored. N_{2EAE}-C_{CO2}, HO_{2EAE}-C_{CO2}, HO_{2EAE}-O_{water}, N_{2EAE}-H_{water}, as shown in Table 8, are the specific interactions observed. For the 2EAE system, the intermolecular interaction between N_{2EAE}-H_{water} and HO_{2EAE}-O_{water} is 1.08 at a distance of 4.75A° for a solvent concentration of 30% and 1.23 at a distance of 2.25A°, respectively. Whereas in 40% of the solvent concentration, at the same distance of 4.75A°, it shifts to 1.14. Similarly, in 50% and 60% 2EAE concentrations, it changes to 1.19 and 1.24. Similar patterns are found in HO_{2EAE}-O_{water} and N_{2EAE}-H_{Water} interactions; by increasing the concentration, the intermolecular interaction strength increases (Figure 3(a) & (b)). Table 8 shows that the interaction between N_{2EAE}-H_{Water} and HO_{2EAE}-O_{Water} increases by increasing the concentration from 30% to 60% at the same distance of 4.75A°. The hydroxyl group in amines is

responsible for the solubility of amines in water, so stronger intermolecular interactions with the hydroxyl group suggest that 2EAE has high solubility. O_{2EAE}-C_{CO2} interaction intensity at 30% of concentration is 1.19 at a distance of 5.25A°. On the other side, at the same distance of 5.25A°, the intensity is 1.16, 1.16, and 1.15, respectively, for 40%, 50%, and 60% of 2EAE, as shown in Figure 4(d). This demonstrates that the intermolecular interaction strength for O_{2EAE}-C_{CO2} interactions decreases by increasing the solvent concentration. It is lowest at 60% of concentration, which implies that at 40%, 50%, and 60% concentration, the effect of O_{2EAE}-C_{CO2} interaction is very weak. For 30% concentration, at the distance of 5.25A°, the intermolecular interaction strength of N_{2EAE}-C_{CO2} is 1.41, whereas in 40% concentration, for the same interaction, the distance decreases to 4.75A°, and strength decreases to 1.28 as well Figure 4(c). Similarly, at a distance of 5.25A°, the N_{2EAE}-C_{CO2} interaction increases to 1.32 and 1.37 in 50% and 60% concentration, respectively. It can be seen that increasing the solvent concentration, increases the strength of the intermolecular interactions.

The focus of this research is to figure out which amines have a high intermolecular interaction with CO2 and water, and how that interaction affects the absorption process. Intermolecular interaction can reveal how physical interactions between molecules occur prior to the reaction. A high value of $g(r)$ at a small distance of r indicates a stronger interaction strength. As a consequence, we consider the higher interaction intensity for a specific observed interaction. On the other hand, some factors affect a liquid's viscosity. The presence of intermolecular forces in a liquid influences its viscosity. The greater the intermolecular forces, the greater the viscosity. The molecules of liquids are strongly bonded to each other when there is a strong intermolecular force. This creates a refusal to move. On the other contrary, Temperature is an important factor that influences viscosity. Since the operating temperature in the absorber is typically in the range of 313K-333 K [46,62–64], as a consequence, the current study chose a temperature range of 298 K to 318 K. When the temperature of the liquid rises, the kinetic energy of the molecules increases. The
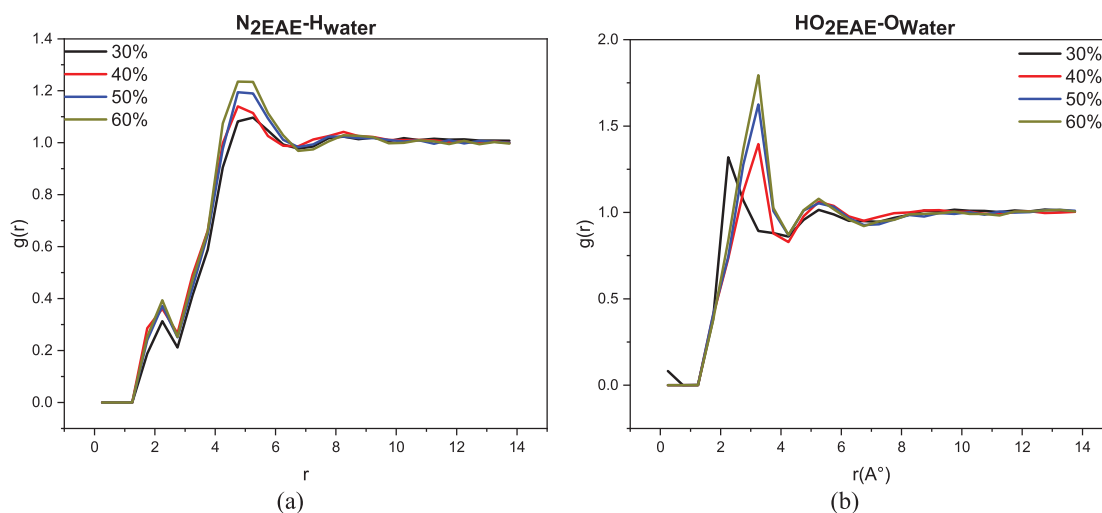

Figure 3. (Colour online) Graphical representation of RDF for Intermolecular interactions (a) N_{2EAE}–H_{water} and (b) HO_{2EAE}–O_{water} of 2EAE at different concentrations.
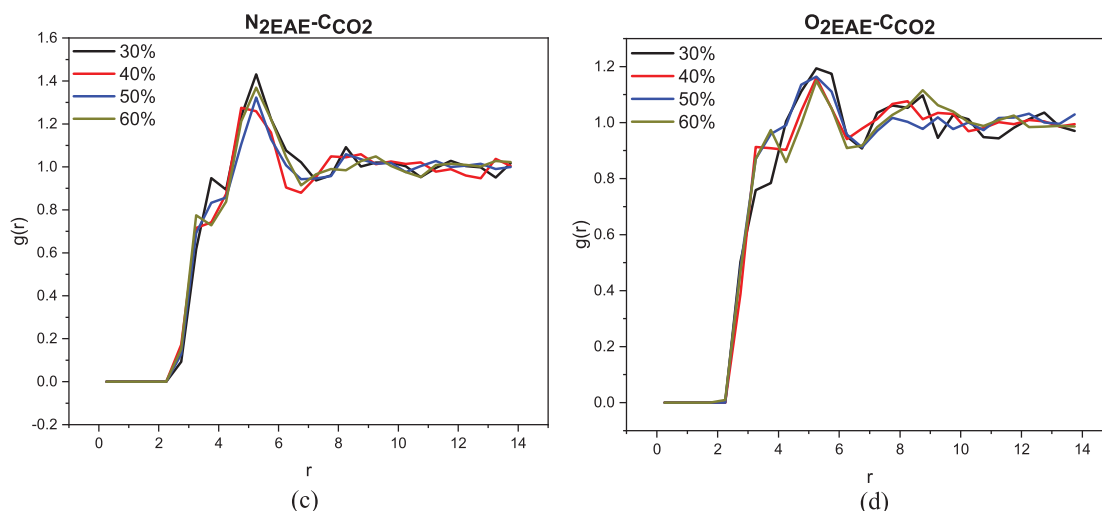
Figure 4. (Colour online) Graphical representation of RDF for Intermolecular interactions (c) N_{2EAE}–C_{CO2} and (d) O_{2EAE}–C_{CO2} of 2EAE at different concentrations.

Table 8. RDF results 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

H_{water} = Hydrogen of water, C_{CO2} = Carbon of CO2, N_{2EAE} = Nitrogen in 2-(ethylamino) ethanol, O_{2EAE} = Oxygen of 2EAE, HO_{2EAE} = Hydorgen at oxygen in 2EAE

molecules move faster, gaining enough energy to overcome the intermolecular force of attraction. As a result, the liquid's viscosity decreases. In the present scenario, the temperature range is high enough to overcome the intermolecular interaction forces, consequently, there is no increase in viscosity and no decrease in diffusivity.

3.2.2. Intermolecular interactions of 2DMAE with CO$_2$ at different concentration

To estimate the intermolecular interaction strength between amine molecules and CO$_2$, radial distribution function analysis is implemented. The summary of results for intermolecular interactions of 2-dimethylamino (2DMAE) ethanol with CO$_2$ and with water is shown in Table 9.

2-dimethyl amino ethanol (2DMAE) is a tertiary amine and comprises two methyl groups at the nitrogen atom. The literature indicates that the hydroxyl group in amine is responsible for the solubility of amines in water, while the amino group provides descriptions of the acid gas reaction [65].

Figure 5 represents the comparative analysis of interactions for different concentrations of solvent. It can be seen that by

increasing the solvent percentage, the intermolecular interaction strength increases for N_{2DMAE}–H_{Water} & HO_{2DMAE}–O_{Water} interactions (Figure 5(e) & (f)). The strength for particular interaction of N_{2DMAE}–H_{Water} is 1.25, 1.37, 1.42, and 1.47 for 30%, 40%, 50%, and 60% of solvent concentrations, respectively, at the distance of 4.75A°. For other interactions of 2DMAE with water HO_{2DMAE}–O_{Water}, the interaction intensity is 1.31, 1.41, 1.60, and 1.77 for 30%, 40%, 50%, and 60% of concentration respectively at the distance of 3.25Å. It indicates that both interactions are strongest at 60% of the solvent concentration, which implies that the hydroxyl and amino groups are more responsive to CO$_2$ in water. From Figure 6, it can be seen that for O_{2DMAE}–C_{CO2} interaction, at the distance of 5.25Å, the intermolecular interaction strength is 1.11 for 30% concentration of solvent, whereas, for 60% of solvent concentration, the strength is 1.17 at the same distance of 5.25Å. There is a 5.12% increment in intermolecular interaction strength for 60% concentration. It means the strength is increased by increasing the percentage of solvent. On the other hand, while observing the same interaction O_{2DMAE}–C_{CO2} in 50% of solvent concentration, the intensity of intermolecular interaction is reduced to 1.08 at the same distance of 5.25Å. The RDF study demonstrates that N_{2DMAE}–C_{CO2} intermolecular interaction strength increases and decreases, i.e. it is 1.75 and 1.80 at a distance of 5.25 Å, respectively, in 30% and 40% (Figure 6(g)). Even, again for 50% and 60%, it is 1.75 and 1.81 respectively at the distance of 5.25Å. This implies that the intermolecular interaction intensity of N_{2DMAE}–C_{CO2} & O_{2DMAE}–C_{CO2} for 50% and 60% of solvent concentrations do not increase (Figure 6(g) & (h)). But the other two interactions, like N_{2DMAE}–H_{water} and HO_{2DMAE}–H_{water} exhibit a higher tendency in 50% and 60% of 2DMAE concentrations, with comparable results in 40% of the concentration.

No noticeable improvement in the interactions between O_{2DMAE}–C_{CO2} and N_{2DMAE}–C_{CO2} means that the reaction of the amine to acid gas is slower, but the other two interactions show that 2DMAE, a tertiary amine, has higher water solubility (Figure 6). Literature confirms the effects of 2DMAE
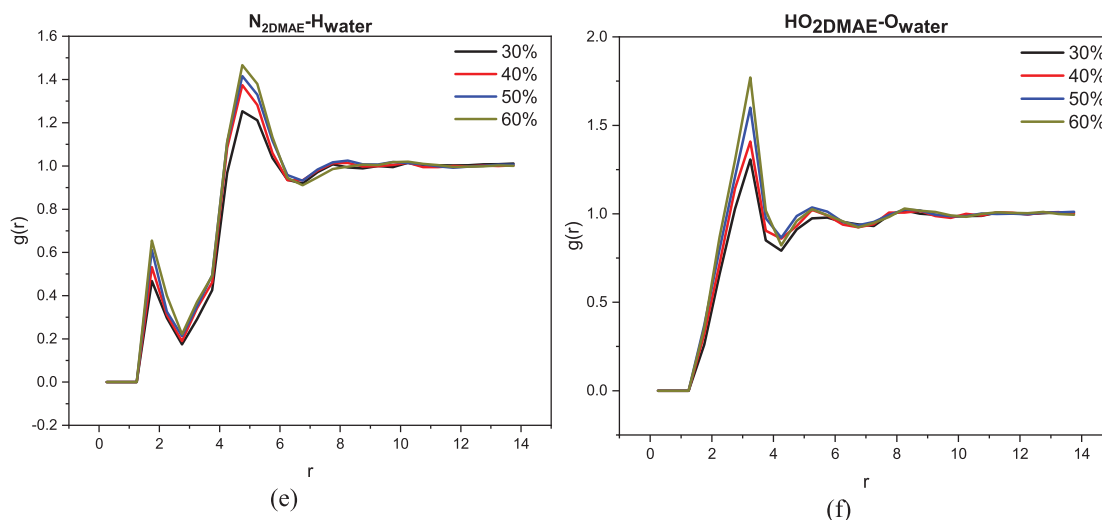
Table 9. RDF results of 2DMAE at different concentrations.

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

H_{water} = Hydrogen of water, C_{CO2} = Carbon of CO2, N_{2DMAE} = Nitrogen in 2-dimethylamino ethanol, O_{2DMAE} = Oxygen of 2DMAE, HO_{2DMAE} = Hydorgen at oxygen in 2DMAE

Figure 5. (Colour online) Graphical representation of RDF for Intermolecular interactions (e) $N_{2DMAE}-H_{H2O}$ and (f) $HO_{2DMAE}-O_{H2O}$ of 2DMAE at different concentrations.
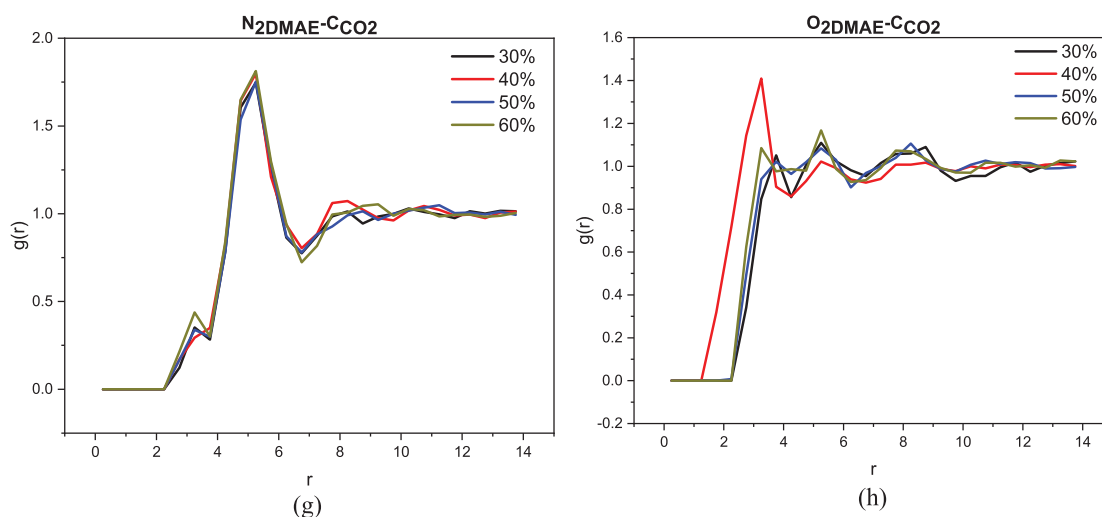

Figure 6. (Colour online) Comparative analysis of RDF at various concentrations for the intermolecular interactions (g) $N_{2DMAE}-C_{CO2}$ & (h) $O_{2DMAE}-C_{CO2}$ of 2DMAE.

intermolecular interactions as the tertiary amines are less reactive as compared to primary and secondary amines [60]. Table 9 shows that at 40% of solvent concentration, all the observed interactions indicate the maximum g(r). The 60% of 2DMAE, also yields comparable results to 40% concentrations, but the 60% concentration may not be suitable in terms of cost for a CO_2 capture plant. Therefore we can only consider 40% of 2DMAE for further studies. Because this concentration (40%) implies higher intermolecular interaction strength towards CO_2, the RDF study assumes that 40% of the solvent concentration is advantageous for the CO_2 absorption process for 2DMAE (2-dimethylamino ethanol). As a result, 40% of solvent concentration can be prioritised for experimental studies.

4. Conclusion

To optimise the solvent concentration for CO_2 capture application, a molecular dynamics simulation assessment was used. The effect of primary, secondary, and tertiary amines on CO_2 absorption is examined from a molecular perspective. For the

calculation of diffusivity and intermolecular interaction intensity for the CO_2 absorption process, three types of amines (MEA, 2EAE, and 2DMAE) were selected. Analysis of mean square displacement (MSD) and radial distribution function (RDF) is performed to measure diffusivity and intermolecular interaction strength, respectively.

Based on the mean square displacement analysis results of the diffusivity measurement, it is concluded that the diffusivity of CO_2 in MEA is greater than in 2DMAE but less than in 2EAE. 2EAE, a secondary amine, appears to be more prominent than MEA. According to the literature, 2EAE exhibits faster reaction kinetics than other secondary amines. When compared to MEA, 2EAE has a greater CO_2 loading. Because of its high loading potential and lower absorption heat than MEA, the results of thermodynamic and kinetic studies suggested 2EAE as an alternative to MEA. The influence of temperature on the diffusivity of the results of specified amine solvents shows that the diffusivity increases as the temperature increases. The higher diffusivity is due to the collision between the particles; the movement of the particles increases

as the temperature rises. Their collision increases as a result, which is the cause of the higher diffusivity coefficient. The diffusivity results obtained from the present investigation are consistent with the theoretical and experimental results of the MEA diffusivity and prove the validity of the research methods used in the present work. Even though no experimental studies for diffusivity of 2EAE and 2DMAE have been reported so far, the intended results of the present study may help in future research in this direction.

Analysis of the radial distribution function of secondary (2EAE) and tertiary amines (2DMAE) shows that the intensity of intermolecular interaction increases by increasing the main concentration of solvents. There is a steady rise in N_{amine}-H_{water} and HO_{amine}-O_{water} interactions in both secondary and tertiary amines, and sharp peaks have been observed. The other two interactions O_{amine}-C_{CO_2} and N_{amine}-C_{CO_2} peaks result in a rise and fall in 40%, 50%, and 60% of solvent concentrations. 2EAE (secondary amine) demonstrates the highest intermolecular interactions for all observed interactions at 30% of the solvent concentration, suggesting that 30% of the solvent concentration is favourable for the CO_2 absorption process compared to 40%, 50%, and 60%. The intermolecular interaction strength of 2DMAE (tertiary amine) is highest for all observed interactions in 40% and 60% of solvent concentrations compared to 30% of 2DMAE. Even though 60% of 2DMAE also exhibits higher intermolecular interactions strength, but the expense of the capture process using 60% 2DMAE solvent should be taken into consideration. Therefore we can only consider 40% 2DMAE for further studies rather than a 60% concentration of 2DMAE. Moreover, future recommendations could investigate the relationship between amine structure and diffusivity for CO_2 capture applications using a broader range of amines.

Disclosure statement

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