Investigation of Rational Design of Amine Solvents for CO_2 Capture: A Computational Approach

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A B S T R A C T

Solvent selection and design are critical in the CO_2 capture process as the choice of solvent directly impacts the cost of the process, capture efficiency, equipment size, and regeneration energy. In the present study, 1MPZ-PZ, PZ, PIP, DEEA and MEA-DEEA are analyzed in terms of interaction intensity (attractive and repulsive) and diffusivity by molecular dynamic simulation. A high intermolecular interaction intensity promotes CO_2 absorption, while intra-molecular interaction intensity affects CO_2 desorption during the regeneration process. Diffusivity is also an important factor for a fast CO_2 uptake rate, which is desirable for efficient CO_2 capture. The interpretation of diffusivity and intermolecular interaction intensity findings is conducted through mean square displacement and radial distribution function analysis, respectively. The order of interaction intensity in various amines is DEEA>MEA-DEEA>PIP>1MPZ-PZ. It shows that DEEA can increase the CO_2 absorption rate as it shows the highest interaction intensity in pure and blended amine systems. The results of the intramolecular interaction intensity show that it is easier to regenerate DEEA, PIP, PZ, and 1MPZ than MEA. The temperature effect on the interaction intensity is revealed at higher temperatures, where the molecular structure becomes unstable due to higher thermal motion, which is the cause of lower interaction intensity. On the other hand, the mean square displacement analysis for the diffusivity rate shows that PZ shows the highest diffusivity rate compared to other selected solvents. The order of diffusivity rate in various pure and blended amine systems is PZ>PIP>1-MPZ-PZ>MEA-DEEA. The diffusivity of various amine solvent systems increases with temperature. As examined in this current research, assessing solvent characteristics holds significant importance in optimizing the most effective solvent system.

1. Introduction

Modern industrialization has been a driving force behind economic growth and technological advancement over the past century (Zhao et al., 2023). However, a significant drawback of this industrialization model has been its heavy reliance on the combustion of fossil fuels, including coal, petroleum, and natural gas, to meet energy demands (Wang et al., 2024; Zhang et al., 2023). These fossil fuels have served as the primary sources of energy for various industrial processes, electricity generation, transportation, and heating (Dong et al., 2022). CO_2 is the most abundant anthropogenic greenhouse gas. It results primarily from the burning of fossil fuels for energy and industrial processes. It accounts for a staggering 93% of total anthropogenic greenhouse gas emissions. The accumulation of CO_2 in the atmosphere is the primary driver of global warming and climate change (EV, 2011; Zhang et al., 2021).

Carbon capture and sequestration (CCS) stands as one of the viable options to enable the continued use of fossil fuels while reducing CO_2 emissions (Yi et al., 2022). Among the various technologies for carbon dioxide (CO_2) capture, chemical absorption is the method that has made significant progress and is closest to commercialization (Fang et al., 2020). Several alternative solvents have been identified for application in CO_2 chemical absorption (Liu et al., 2021a; Li et al., 2021). The current study focuses on developing a consistent framework for better solvent systems through computational processes like molecular dynamic simulation.

Numerous research studies employing computational methods have explored amine-based absorption processes. For example, the study conducted by (Masiren et al., 2014) explored the impact of temperature

on the intermolecular interaction of primary amine and CO_2 in the absorption process through Molecular Dynamics (MD) simulations, focusing on (MEA+H_2O+CO_2) system at three different temperatures (298 K, 313 K, and 318 K). The analysis utilizes the radial distribution function (RDF). Results indicate stronger interactions at 318 K compared to 298 K and 313 K (Masiren et al., 2014). Hwang et al., (2015). conducted a quantum chemical and molecular dynamics study to investigate the reaction mechanisms of aqueous monoethanolamine (MEA) with carbon dioxide (Hwang et al., 2015). The analysis reveals a zwitterion-mediated two-step mechanism for both CO_2 absorption by MEA and solvent regeneration (Hwang et al., 2015). A study conducted by Harun and Masiren 2017a, and Harun and Masiren 2017b investigated the amine absorption processes by focusing on the mixture of blended amines MDEA/PZ. This study employs MD simulations to gain insights into the intermolecular interactions by RDF analysis within this blended system. The findings indicate that the hydroxyl group (-OH) of MDEA exhibits a stronger attraction to water molecules compared to the amino group (-NH), and the intermolecular interaction probability between -OH and -NH groups of MDEA with CO_2 is enhanced in the presence of PZ. This implies that PZ acts as an activator, promoting intermolecular interactions between MDEA and CO_2, potentially leading to increased CO_2 absorption rates and reduced heat regeneration requirements (Harun and Masiren, 2017a, 2017b; Masiren et al., 2016a). Similar results were obtained for the MDEA-PZ blend by Farmahini et al. (2011) which contributes to the understanding of the interactions between piperazine-activated MDEA and CO_2, which is crucial for designing efficient capture processes (Farmahini et al., 2011).

The study conducted by (Narimani et al., 2017) employed molecular dynamics (MD) simulation to calculate the physical and chemical properties of (amine/H_2O/CO_2) systems, including density, solubility, radial distribution function, and diffusivity (Narimani et al., 2017). The MD results demonstrated a consistent trend with reported experimental and quantum mechanical (QM) data, providing valuable insights into the absorption mechanism for CO_2 capture by tertiary amine compounds. A study conducted by (Masiren and Harun, 2017) employs molecular dynamics (MD) simulation to investigate the effects of different carbamate molecules, specifically monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP), and piperazine (PZ), in water during the regeneration process. The simulation reveals that during the stripping process, AMP and PZ facilitate easier CO_2 removal compared to MEA carbamate. The findings highlight MEA's limitations in the stripping process due to its weaker repulsive interaction strength in the carbamate (Masiren and Harun, 2017).

Furthermore, molecular simulations provide a virtual platform to investigate the influence of different solvent compositions, temperatures, and pressures on the transport properties of CO_2 (Yu et al., 2018) and interpret structure-property relationships (Malhotra et al., 2017; Firaha and Kirchner, 2016; Liu et al., 2019; Gao et al., 2023; Xie et al., 2023). Diffusion coefficients are crucial in understanding mass transfer properties in absorption processes. The research (Masiren et al., 2016b) estimated the diffusivity of various types of amines and the effect of temperature on the diffusivity of monoethanolamine (MEA) absorption for CO_2 capture. MD simulations at varying temperatures demonstrate that as temperature increases, the diffusion coefficient also increases, with the highest diffusion coefficient observed at 318 K (Masiren et al., 2016b). These findings align with the principle that higher temperatures enhance molecular movement, facilitating CO_2 capture in MEA solutions. Masy's research focuses on predicting the diffusivity of CO_2 in substituted amines. Diffusivity is a critical parameter in the context of CO_2 capture, as it influences mass transfer rates (Masy, 2013). This work contributes to a fundamental understanding of the transport phenomena involved in CO_2 capture and can aid in the selection and design of capture solvents. These computational approaches have proven successful in enhancing comprehension of experimental outcomes and have played a pivotal role in the development of innovative solvent systems.

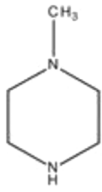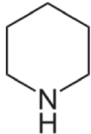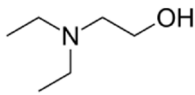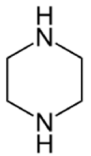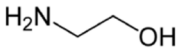Since the solvent plays a significant role in the chemical absorption process, careful selection of a solvent system coupled with ongoing research and development, is crucial for advancing the science and engineering of CO_2 capture techniques. Among other crucial characteristics, the reversibility of the absorbent and its liquid structural attributes, including diffusion coefficients and viscosities, hold substantial influence over the entire CO_2 absorption process. In addition to a high absorption rate with CO_2 and a low energy requirement, there are other properties to consider while searching for an appropriate solvent. For example, the solvent should be the least corrosive and should have a low volatility and a high selectivity. It should also not be prone to temperature and contaminant degradation (Zhao et al., 2024). Additionally, economic considerations play a crucial role, with cost reduction being a paramount objective. To achieve cost minimization, researchers concentrate their endeavours on improving absorption efficiency, necessitating the utilization of absorbents with robust absorption characteristics.

Many researchers have recently investigated several novel individual amine candidates such as diethylenetriamine (DETA), triethylenetetramine (TETA), piperazine (PZ), 1-methylpiperazine (1MPZ), 2-amino-2-methyl-1-propanol (AMP) and 3-dimethylamino-1-propanol (3DMA1P) with the comparison of existing absorbents for CO_2 removal (Dubois et al., 2010; Rayer et al., 2014). Recent studies have predominantly emphasized the absorption of CO_2 into sterically hindered polyamines and tertiary amines, which have been identified as promising alternatives to traditional MEA (Monoethanolamine) systems. This is why the present study selected several amine systems like 1-methylpiperazine (1MPZ), Piperidine (PIP), Piperazine (PZ), and Diethyl ethanol amine DEEA (as presented in Table 1) (Chowdhury et al., 2013). estimated the characteristics of MDEA against that of 24 different tertiary amine absorbents. The results of a comparative analysis show that DEEA has a larger CO_2 loading capacity, a greater cycle capacity, and superior chemical stability. Furthermore, the heat of the reaction of DEEA is lower (Chowdhury et al., 2013). Because it has significant potential for removing CO_2 from gaseous streams, DEEA is a good substitute for conventional tertiary alkanol amines like MDEA (Vaidya and Kenig, 2012). Kruszczak and Kierzkowska-Pawlak (2017) measured the rate of CO_2 absorption in aqueous N, N-diethylethanolamine (DEEA) solutions and examined the reaction kinetics of CO_2 with DEEA. The results of this study indicated that DEEA can be a good potential candidate with a second-order reaction rate constant (Kruszczak and Kierzkowska-Pawlak, 2017). Dubois and Thomas measured the absorption and regeneration characteristics of piperidine (PIP), Piperazine PZ, piperazinyl-1,2-ethylamine (PZEA), and various individual/blended amines. In their study, AMP, MDEA/PZ, and PIP were identified as possible solvent candidates for CO_2 absorption (Dubois and Thomas, 2012).

The use of blended amine solvents in carbon dioxide (CO_2) capture processes has gained significant attention due to their potential advantages over monoethanolamine (MEA), for example, the fast absorption kinetics of primary and secondary amines and the lower regeneration energy penalty associated with tertiary amines, makes them promising candidates for CO_2 capture (Wang et al., 2021). In line with this, Muchan et al. (2017) conducted a study aimed at selecting the most suitable amine solvents for CO_2 capture, taking into account the position of hydroxyl groups within the amine structure. Their findings highlight that primary, secondary, and tertiary amines with a single hydroxyl group attached to the amine structure, such as AMP, 2EAE, and 2DMAE, demonstrate superior CO_2 capture performance (Muchan et al., 2017). A study conducted by Sharif et al. (2023a) revealed that primary and secondary amines mixed with tertiary amines show greater potential as compared to single amines (Sharif et al., 2023a).

These findings emphasize the potential of unconventional amines in CO_2 capture applications, which forms the basis for the current study's exploration of these alternative amines. Table 1 provides essential molecular information about the selected solvents in this study, laying the foundation for further investigation into their CO_2 capture capabilities.

Table 1
Chemical Solvents Selected in the Present Study.

Name of Solvents	Molecular Structure	Molecular Weight (g/mol)	Density (g/ml)	CAS No.
1-Methylpiperazine (1-MPZ)		100	0.903	109–01–3
Piperidine		85	0.861	110–89–4
N, N-Diethyl ethanol amine (DEEA)		117	0.885	100–37–8
Piperazine PZ		86	1.1	110–85–0
Monoethanolamine MEA		61	1.01	141–43–5

This study is primarily concerned with two fundamental metrics: the rate of CO_2 diffusion and the intensity for intermolecular interactions within carbamate molecules. The primary goal of this research is to determine the best solvent candidate for the absorption and stripping operations. This is accomplished through a detailed examination of the intermolecular and intramolecular interaction strengths of selected amines, as well as a thorough investigation of the diffusion coefficients within various blend compositions. The solvent system under consideration includes 1-MPZ, PIP, PZ, DEEA, 1MPZ-PZ, and MEA-DEEA. While previous research has focused on individual pure solvents as well as amine blends, there is a considerable gap in the literature regarding the complete analysis of diffusivity and interaction intensities (both intra- and inter-molecular), within these specific combinations. As a result, the present study fills the gap in the literature by exploring diffusivity and interaction intensity. The current study's three components offer the most contribution to existing research in this area. Beginning with an analysis of molecular behaviour throughout the absorption process, the current study used a computer technique called molecular dynamic (MD) simulation. Second, in this investigation, various types of amines were employed to identify which solvent system have the best intermolecular and intramolecular interaction intensity. The solvent system characterized by the most robust intermolecular interactions plays a pivotal role in facilitating absorption, whereas the solvent system with the lowest intra-molecular interaction can lead the amine-CO_2 system through the regeneration or stripping process. Third, the current study established a simulation-based approach for estimating the diffusivity of the previously unexplored solvent system. Finally, the investigation will ultimately contribute to the identification of the most promising amines for laboratory-scale implementation to protect the environment by lowering atmospheric carbon emissions.

2. Model design and framework

Molecular dynamics simulation is employed to replicate particle motion by solving the fundamental equations of motion within the context of CO_2 capture (Biovia, 2017). In this current study, the computational tool utilized for the simulation is Material Studio. There are two types of case studies, i.e., the first is to calculate the interaction intensity (intermolecular and intra-molecular) and the second one is to estimate the diffusivity of the various solvent systems. The precise specification of input parameters is of paramount importance for ensuring both the consistency and accuracy of results during the simulation process. The structural foundations are drawn from the Royal Society of Chemistry's comprehensive database (Chemspider, 2020). The simulation methodology encompasses a sequence of distinct phases: initial structure replication, energy minimization, construction of an amorphous simulation environment, progressive relaxation of the model to reduce pressure and energy, subsequent equilibrium and production stages conducted under NVE (constant number of particles, volume, and energy) and NVT (constant number of particles, volume, and temperature) ensemble (Sharif et al., 2020) as presented in Fig. 1. Boundary conditions are critical to the accuracy and dependability of the results produced by the material studio. Another important aspect of the technique is selecting the forcefield and step duration, as both have a direct impact on the timing and reliability of the result (Sharif et al., 2022). The current step length is 1fs, and the force field is COMPASS. According to the literature, the COMPASS force field evaluates the configuration, structure, motion, and thermal physical properties of numerous compounds at a wide temperature and pressure range (Charati and Stern, 1998). The simulation commences with a 200-pico-second equilibration phase under a fixed ensemble of particles, volume, and energy (NVE), along with randomized initial velocities. This phase aims to establish a stable system configuration while conserving energy. Subsequent progression into dynamic mode, with constant particles, volume, and temperature (NVT), facilitates the evaluation of diffusion behaviour. The chosen forcefield and summation approach are derived from the COMPASS and Ewald models, respectively, ensuring an accurate representation of intermolecular forces. To estimate the interaction intensity, the atoms are selected which take part in the reaction process. This is conducted by doing the RDF analysis in the forcite module of the
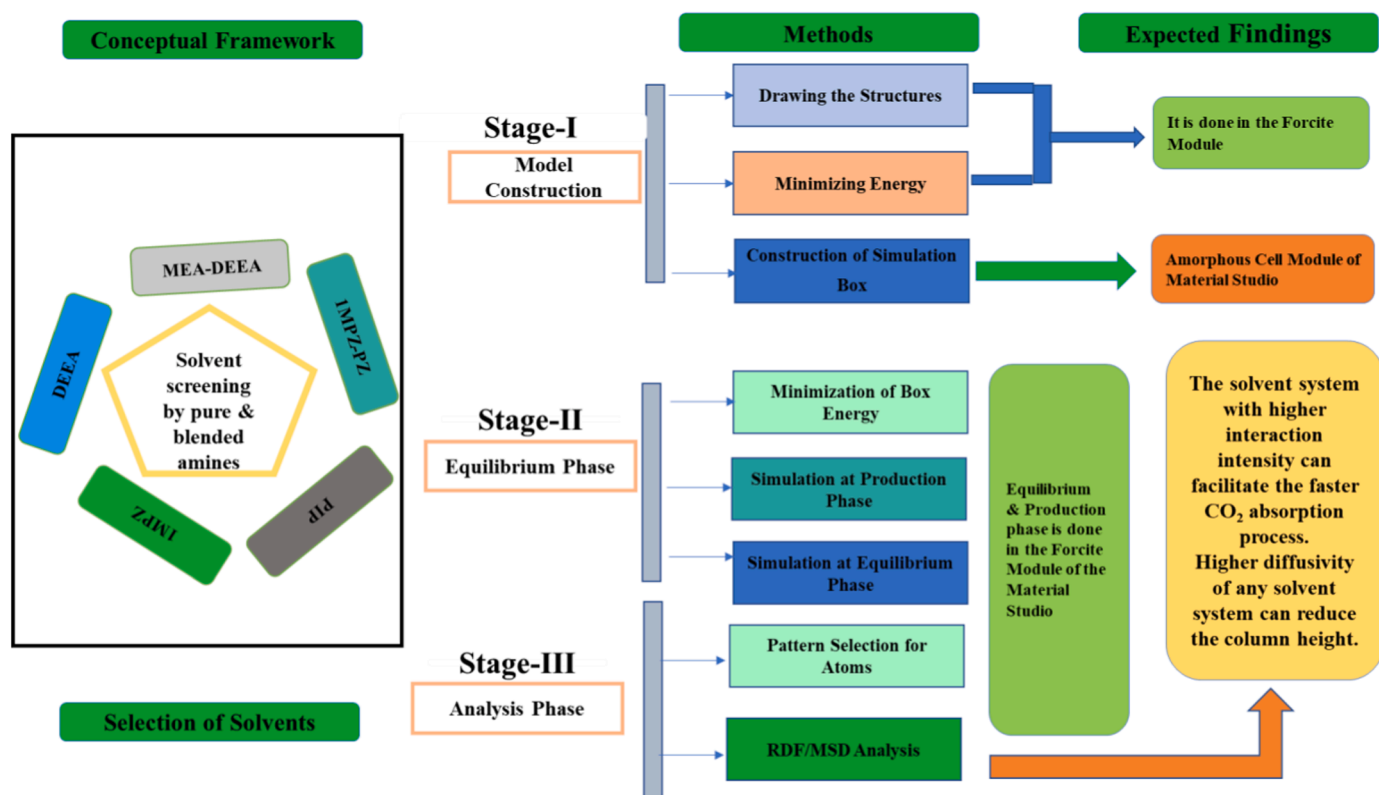
Fig. 1. Steps of Model Development in Material Studio.

material studio. To calculate RDF, we analyze the trajectories generated during molecular dynamics (MD) simulations. The RDF, often represented as g(r), quantifies the likelihood of atom pairs being at a distance of r ± Δr from one another. Eq. (1) involves parameters like the number of atoms around a given atom in a shell within the distance r ± Δr (nij), the total number of atoms (N), and the volume of the simulation box (V).

$$g_{(i,j)}(r) = \frac{v}{N_i N_j} \sum_i n_{i,j} \frac{(r)}{4 \Pi r^2 \Delta r} \tag{1}$$

To compute the diffusivity of the selected solvent system, the next step after the construction of the amorphous cell is the dynamics at the production and equilibrium phase. To enhance the authenticity of the simulation model, the amorphous cell or simulation construct undergoes an annealing process. Depending on the desired adjustments to density and external pressure, the choice between the NPT (constant number of atoms, pressure, and temperature) ensemble and NVT (constant number of atoms, volume, and temperature) ensemble is crucial. For instances where the initially chosen density aligns with practical considerations, NVT can be adopted, aiming to stabilize the system's pressure at an average of 1 atm or 0.0001 GPa. This entire process is repeated once. The simulated annealing procedure effectively mitigates internal stress within the simulation model, substantially rectifying less plausible structures introduced during construction. This phase is executed with random initial velocities and a time step of 1 femtosecond (1 fs), as certain thermostats may potentially interfere with system dynamics and the diffusion coefficient. To evaluate the diffusion coefficient of CO_2 in selected amines, the forcite module of Material Studio employs mean square displacement analysis, providing insights into the diffusion dynamics. Table 2 provides the simulation parameters for developing the model in the material studio. The amorphous cell structure of the model constructed in the present study is given in supplementary material Fig. S3.

Table 2
Calculation of the simulation model parameters for the selected solvent system.

Solvent System	Description	I-MPZ	PZ	CO_2	H_2O
1-MPZ-PZ	Density of mixture (g/ml)	1.031			
	wt%	30%	10%	10%	50%
	Number of molecules	103	40	78	955

System	Description	PZ	CO_2		H_2O
PZ	Density of mixture (g/ml)	1.08			
	wt%	30%	10%		60%
	Number of molecules	46	30		442

System	Description	MEA	DEEA	CO_2	H_2O
MEA-DEEA	Density of mixture (g/ml)	1.04			
	wt%	30%	10%	10%	50%
	Number of molecules	172	30	79	975

System	Description	MPZ	CO_2		H_2O
MPZ	Density of mixture (g/ml)	1.02			
	wt%	30%	10%		60%
	Number of molecules	26	20		293

System	Description	PIP		CO_2	H_2O
PIP	Density of mixture (g/ml)	1.008			
	wt%	30%		10%	60%
	Number of molecules	46		30	440

3. Model validation

The study employs the COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field for molecular simulations, accounting for both intermolecular and

intramolecular forces. COMPASS is a versatile third-generation force field suitable for various systems, including organic molecules, inorganic gases, and polymers. It demonstrates high simulation accuracy comparable to industrial processes (Cash, 1999; Balbuena and Seminario, 1999). The studies show that COMPASS forcefield provides a balanced representation of intermolecular interactions, encompassing van der Waals forces, electrostatic interactions, and hydrogen bonding, ensuring accurate descriptions of molecular properties like solvation, solubility, and conformational behaviour. Furthermore, the COMPASS force field, a versatile all-atom force field for molecular dynamic simulation, was developed through a combination of state-of-the-art ab initio methods and empirical parameterization techniques (Qiang et al., 2013).

In molecular dynamics (MD) simulations, assessing the density of amines plays a pivotal role in evaluating the suitability of the applied force field. This computational approach utilizes the COMPASS force field to calculate the density of amines within the simulated system, allowing for an understanding of their molecular packing. To validate the accuracy of these simulations, it's common practice to compare the obtained density values with experimental data. In this context, Table 3 presents the densities of selected amines at standard conditions of 298 K and 1 atm, serving as a benchmark for validating the MD results. The simulations were conducted using the NPT ensemble over a 2 ns timescale, with data recorded at regular intervals of 5000 steps. The resulting average density profiles, depicted in Fig. 2, offer graphical representations of how the densities of specific amines, including MEA, 1MPZ, PIP, PZ, and DEEA, vary across different regions within the simulation cell, shedding light on their intermolecular interactions and behavior under these conditions.

While examining the experimental densities provided in Table 3, it can be seen that the densities of the selected amines follow the order: PZ>MEA>1MPZ>DEEA>PIP. This density information is vital for initializing the MD simulation, and ensuring the construction of a stable configuration within the simulation cell. The process of cell construction and geometry optimization takes place within the amorphous cell module of the material studio. Fig. 2 visually illustrates the density variations of the selected solvents throughout the simulation process. Remarkably, the results from Table 3 and Fig. 2 exhibit strong alignment with experimental data at the designated temperature. Consequently, this congruence affirms the validity and appropriateness of the COMPASS force field and model employed in this study, providing authentication for the simulation outcomes. This is according to the literature which show that COMPASS forcefield is compatible with molecular dynamics simulations, facilitating a robust framework for capturing essential molecular interactions and dynamics, particularly in the context of CO_2 capture processes (Narimani et al., 2017; Harun and Masiren, 2017b).

4. Results and discussion

Molecular dynamics (MD) modelling is a powerful computational technique employed in various scientific disciplines, including chemistry and materials science, to simulate and analyze the behaviour of molecules and atoms over time. In the context of carbamate synthesis,

Table 3
The calculation of Densities of Pure amines in Amorphous cell module of Material Studio.

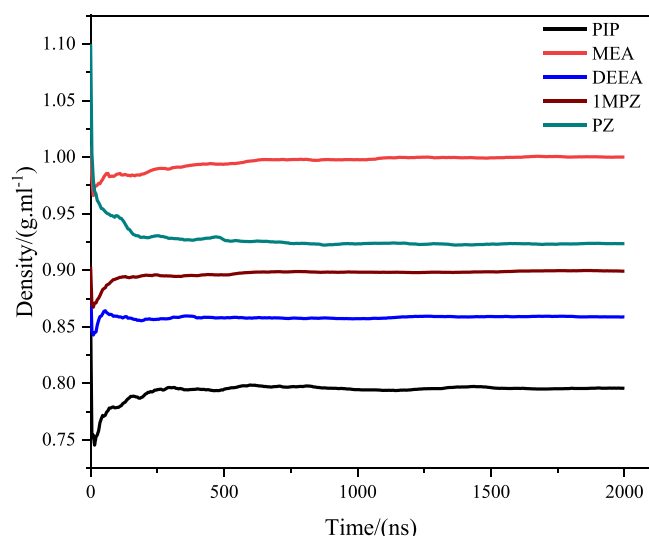| Name of Solvent	Experimental Density Chemspider (2020)	Simulation Density	Deviation (%)
MEA	1.01	1.00	0.99
1-MPZ	0.90	0.91	1.01
PIP	0.86	0.84	2.32
PZ	1.10	1.09	0.90
DEEA	0.88	0.86	2.32

Fig. 2. Density/(g.ml^{-1}) calculation of various selected amines.

MD modelling plays a pivotal role in understanding both inter and intramolecular interactions of amines, which are critical in the reaction mechanism. Another important key parameter studied in MD simulations is the diffusion coefficient of amines. Mean square displacement (MSD) analysis is a widely used method to calculate this coefficient. It provides insights into the mobility of amine molecules within a given system. A higher diffusion coefficient signifies faster movement of molecules, which can be indicative of the efficiency of the reaction process. The radial distribution function (RDF) analysis is an essential aspect of MD simulations in this context. RDF analysis allows us to evaluate the intensity of intermolecular interactions among amines. It provides a quantitative measure of how likely two molecules are to be found at a certain distance from each other. A stronger value of g(r) at smaller distances (short-range interactions) indicates strong intermolecular interactions. These interactions are crucial for the formation and stability of reaction intermediates (Sharif et al., 2020).

The stripping or regeneration step in the CO_2 capture process is indeed a critical and often expensive phase. It involves breaking the amine-CO_2 link, which typically requires extremely high temperatures. This step is necessary to separate the absorbed carbon dioxide from the rich solvent, allowing for the regeneration of the solvent for further use in the absorption process. The high temperature is needed to release the captured CO_2 from the amine solution, therefore the temperature effect on interaction intensity is also analysed in the current study. To better understand the molecular-level interactions and temperature effect involved in this process, simulations are employed. These simulations investigate how carbon dioxide combines with water to form bicarbonate ions, primarily by examining the attractive forces between carbamate molecules of various amines (MEA, PIP, PZ, DEEA, and 1MPZ) and water molecules. These attractive forces play a crucial role in the formation and stability of bicarbonate ions and can provide insights into the efficiency of the stripping process. Additionally, intramolecular interactions, particularly those involving $N_{Carbamate}$-$C_{Carbamate}$, are explored in different amine solvents like MEA, PIP, PZ, DEEA, and 1MPZ. The outcomes of these case studies are provided in the following sections. Fig. 3

4.1. Intermolecular interaction intensity of selected solvents for CO_2 absorption process

The CO_2 absorption and desorption process is a crucial step in mitigating the negative impact of CO_2 emissions on the environment. This process involves capturing CO_2 from flue gas or other sources, followed by its separation and storage. The efficiency of the CO_2 capture
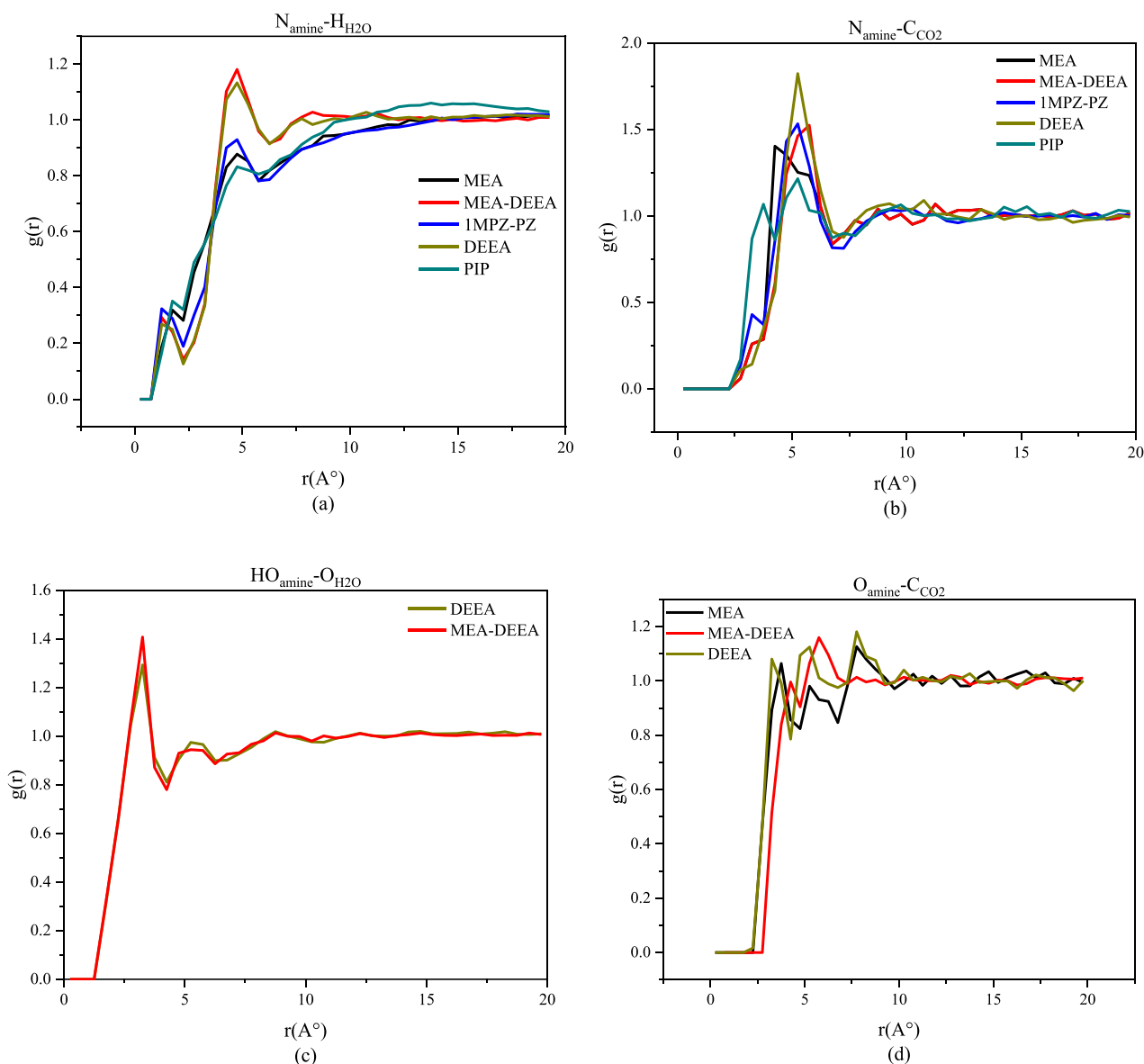
Fig. 3. Comparative RDF Analysis of Various Solvent Systems (a) N_{amine}-H_{H2O} (b) N_{amine}-C_{CO2} (c) HO_{amine}-O_{H2O} (d) O_{amine}-C_{CO2} at 313 K in MEA-DEEA, DEEA, 1MPZ-PZ and PIP.

process is largely determined by the interaction between the CO_2 and the solvent used in the process. The strength of this interaction is influenced by both inter-molecular and intra-molecular interactions.

Inter-molecular interactions refer to the forces between two or more solvent molecules that determine the physical properties of the solvent, such as its viscosity, density, and solubility. In the CO_2 absorption process, inter-molecular interactions play a crucial role in determining the ability of the solvent to dissolve CO_2. Solvents with strong inter-molecular interactions are typically more effective at absorbing CO_2 because they can more easily dissolve the gas. These forces can be broadly classified into several categories, including ionic, covalent, metallic, and van der Waals forces. The present study analyses inter and intra-molecular interaction intensity for various solvent systems by Radial Distribution Function analysis. This analysis considers the interactions of C, N, O and H atoms involved in the reaction pathway. Table 4 shows the summary of interaction intensity findings, and Fig. 4 shows the comparative analysis of interaction intensity for all selected solvents in the present study. We discuss the reaction mechanism and RDF finding one by one.

4.1.1. Interaction intensity and reaction mechanism in DEEA and MEA-DEEA system

There are two main pathways for primary, secondary and tertiary amines that contribute to CO_2 capture. Primary and secondary amines react with CO_2 to form carbamate ions. In this reaction, the amino group (-NH_2) of the amine molecule reacts with CO_2 to create a stable carbamate ion. The carbamate ion can later release CO_2 during the regeneration phase, allowing for the separation and capture of CO_2. Tertiary amines react with CO_2 to form bicarbonate ions (Liu et al., 2021b). This reaction involves the amine group accepting a proton (H^+) from CO_2, leading to the formation of bicarbonate ions. Bicarbonate ions are soluble in the amine solution and play a key role in capturing and converting CO_2 into a soluble form. During regeneration, bicarbonate ions can release CO_2 for subsequent capture or utilization (Xiao et al., 2018). Eq. (2) and Eq. (3) below show the general reaction mechanism for tertiary amine (refer to DEEA in the present study).
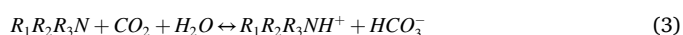
$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \tag{2}$$

$$R_1R_2R_3N + CO_2 + H_2O \leftrightarrow R_1R_2R_3NH^+ + HCO_3^- \tag{3}$$

Table 4
Interaction Intensity of Various Solvent Systems at 313 K, 323 K and 333 K.

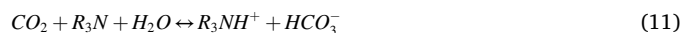| DEEA	N_{DEEA}-H_{2O}	O_{DEEA}-C_{CO2}	HO_{DEEA}-O_{H2O}	N_{DEEA}-C_{CO2}
313 K	5.25, 1.13	3.25,1.08	3.25, 1.29	5.25, 1.82
323 K	5.25, 1.12	3.25,1.04	3.25, 1.34	5.25, 1.74
333 K	5.25, 1.12	3.25,0.84	3.25, 1.29	5.75, 1.53
1MPZ-PZ	N_{MPZ}-H_{2O}	N_{MPZ}-C_{CO2}	N_{PZ}-C_{CO2}	N_{PZ}-H_{2O}
313 K	4.75, 0.90	4.75,1.43	5.75,1.27	4.75,0.87
323 K	4.75, 0.94	4.75,1.50	5.75,1.20	4.75,0.84
333 K	4.75, 0.91	4.75,1.49	5.75,1.29	4.75,0.81
MEA-DEEA	N_{DEEA}-H_{2O}	O_{DEEA}-C_{CO2}	HO_{DEEA}-O_{H2O}	N_{DEEA}-C_{CO2}
313 K	5.25, 1.18	3.25, 0.89	3.25,1.41	5.75,1.52
323 K	5.25, 1.17	3.25, 0.89	3.25,1.33	5.25,1.53
333 K	5.25, 1.18	4.25, 1.16	3.25,1.31	5.25,1.68
MEA-DEEA	N_{MEA}-H_{2O}	O_{MEA}-C_{CO2}	HO_{MEA}-O_{H2O}	N_{MEA}-C_{CO2}
313 K	4.25, 1.11	5.25,1.16	3.25,1.33	3.75,1.42
323 K	4.25, 1.11	5.25,1.14	3.25,1.31	3.75,1.36
333 K	4.25, 1.11	5.25, 1.12	3.25,1.30	3.75,1.39
PIP	N_{PIP}-H_{2O}	O_{PIP}-C_{CO2}	HO_{PIP}-O_{H2O}	N_{PIP}-C_{CO2}
313 K	5.25, 0.83	-	-	3.75,1.07
323 K	5.25, 0.76	-	-	5.25,1.23
333 K	5.75, 0.85	-	-	5.25,1.31
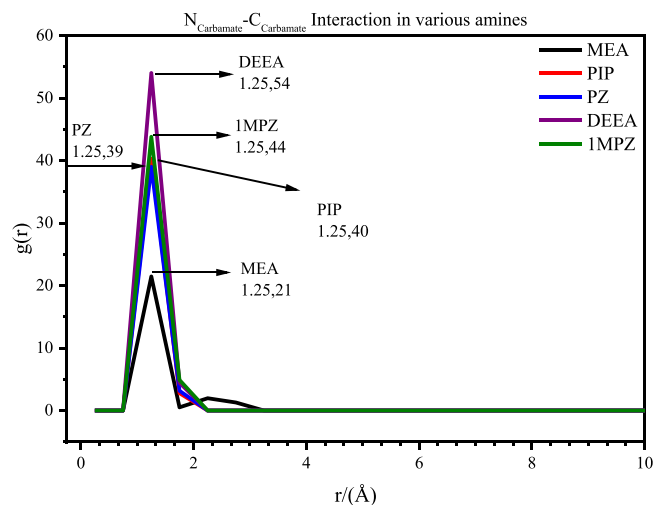
Fig. 4. RDF Analysis of Repulsive Interaction in Various Amines at 313 K.

The most important interactions are O-C and N-C. For the tertiary amine DEEA under investigation, a prominent peak appears around r = 5.25 Å for (N_{DEEA}-C_{CO2}) nitrogen in DEEA and carbon of CO_2 in the RDF plots (b). This peak signifies a common distance at which interactions occur between the carbon atom of CO_2 and the nitrogen atom of the tertiary amines. The reaction mechanism in Eq. (3) shows that the protonation of tertiary amines takes place in the presence of H_2O and CO_2 molecules. The RDF analysis shows its highest peak at 5.25 Å (N_{DEEA}-C_{CO2}), (5.25,1.82) for all three temperatures observed in the present work in the DEEA system (Table 3). It means that the carbon atom of CO_2 and the nitrogen atom of DEEA are approximately 5.25 Å apart at three different temperatures. Interestingly, tertiary amines lack the N-H group necessary for direct interaction with CO_2 to form carbamate ions. Consequently, the electrostatic attraction between the tertiary amines and CO_2 is weaker and we observe the first peak at a larger distance like 5.25 Å. This weaker interaction results in a probability of finding CO_2 molecules at further distances from the tertiary amines (Fig. 3). These results can be justified by Narmani et al., 2017, where similar results are obtained from a molecular dynamic simulation study of tertiary amines (Narimani et al., 2017), the reaction rate in tertiary

amines is slower than primary and secondary amines (which is the cause of observing interaction at a higher distance of 5.25 Å) (Chowdhury et al., 2013). These results are reflected in the RDF plots in Fig. 3, where the probability of finding CO_2 molecules around different amine molecules in all the studied solvents is provided in a specific order.s

The chemical reactions occurring between CO_2 and blended DEEA-MEA solutions are controlled by the Eqs. (4)-(12) (Jiang et al., 2018). Monoethanolamine (MEA) is well-known for its ability to react with CO_2, forming a carbamate intermediate, a key step in the CO_2 capture process. This reaction is facilitated by the N-C interaction, where the nitrogen atom in MEA reacts with CO_2 to form the carbamate species as given in Eq. (8). Diethylethanolamine (DEEA), on the other hand, does not participate in carbamate formation due to its tertiary amine structure. Tertiary amines lack the hydrogen atom necessary for forming the N-H.O=C hydrogen bond, which is crucial in the carbamate formation process. When MEA and DEEA are blended, the CO_2 absorption process involves multiple pathways, not limited to carbamate formation. While DEEA does not form carbamate, it can still react with CO_2 and water to form bicarbonate and a protonated amine. This reaction enhances the overall CO_2 loading capacity of the blend without directly participating in carbamate formation Eq. (10).
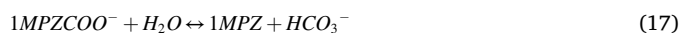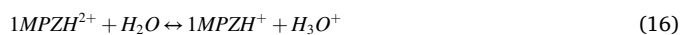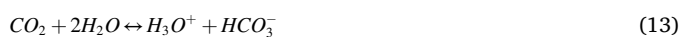
$$H_2O \leftrightarrow H^+ + OH^- \tag{4}$$

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \tag{5}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \tag{6}$$

$$MEA + H^+ \leftrightarrow MEAH^+ \tag{7}$$

$$CO_2 + MEA \leftrightarrow MEACOO^- + H^+ \tag{8}$$

$$MEACOO^- + H_2O \leftrightarrow MEA + HCO_3^- \tag{9}$$

$$R_3N + MEAH^+ \leftrightarrow R_3NH^+ + MEA \tag{10}$$

$$CO_2 + R_3N + H_2O \leftrightarrow R_3NH^+ + HCO_3^- \tag{11}$$

$$R_3N + H^+ \leftrightarrow R_3NH^+ \tag{12}$$

While analyzing the MEA-DEEA system, it can be seen from Table 4 that N_{MEA}-C_{CO2} is observed at 3.75 Å (3.75, 1.42) at 313 K, whereas the same interaction for DEEA shifts to 5.75 Å (5.75, 1.52), as the distance increased for DEEA. It indicates that MEA is more reactive to CO_2 than that of DEEA. Other studies in the literature also support these findings, for example, a study conducted by Chowdhury et al. (2013) demonstrates that primary amines are more reactive to CO_2 than tertiary amines (Chowdhury et al., 2013). On the other side, the protonation of DEEA takes place in the presence of CO_2 and H_2O as given in Eq. (11). As a result, it is obvious from Eq. (11) that the interaction HO_{DEEA}-O_{H2O} must be higher than HO_{MEA}-O_{H2O} which is reflected in Table 4 (HO_{DEEA}-O_{H2O}, 3.25,1.41), (HO_{MEA}-O_{H2O}, 3.25,1.33). The existing literature underscores that the presence of the hydroxyl group in amines primarily governs their solubility in water, whereas the amino group plays a crucial role in describing their reactivity in acid gas reactions (Kohl and Nielsen, 1997). Therefore, the higher interaction intensity for the hydroxyl group in MEA-DEEA indicates that it has a high solubility in water as compared to other studied systems. Fig. 3(a), and (c) demonstrated the comparative RDF analysis of N_{amine}-H_{2O} and HO_{amine}-O_{H2O} in the whole solvent system analysed.

The blend MEA-DEEA creates a synergistic effect, where MEA facilitates rapid CO_2 capture through carbamate formation, and DEEA contributes to the CO_2 loading capacity through bicarbonate formation. This synergy enhances the overall efficiency of the blend, even in the absence of direct N-C interactions involving DEEA in carbamate formation. The efficiency of the MEA-DEEA blend in CO_2 absorption is thus not solely dependent on the formation of carbamate by MEA but also the

complementary roles played by both amines. The presence of DEEA can influence the solution's physicochemical properties, such as viscosity and thermal stability, potentially affecting the kinetics of CO_2 absorption and desorption in the blend. The absence of direct N-C interaction related to carbamate formation by DEEA in the MEA-DEEA blend does not detract from the blend's CO_2 absorption capabilities. Instead, the blend leverages the strengths of both amines to achieve enhanced CO_2 capture efficiency through complementary mechanisms. As a result, we observe higher interaction intensity in the MEA-DEEA blend than in 1MPZ-PZ.

4.1.2. Reaction mechanism and interactions in 1MPZ-PZ and piperidine

1-methyl piperazine (1MPZ) is a derivative of Piperazine (PZ), containing a methyl group attached to one of the nitrogen atoms in PZ. It is classified as both a cyclic and a diamine and possesses dual amine characteristics, functioning as both a primary and secondary amine. During the interaction with CO_2, 1MPZ transforms, yielding formations such as carbamate ions, zwitterion ions, and protonated carbamates. The reaction pathway elucidating the MPZ interaction with CO_2 is outlined in Eq. (13) to Eq. (17) (Li et al., 2015).

$$CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3^- \tag{13}$$

$$HCO_3 + H_2O \leftrightarrow H_3O^+ + CO_3^{2-} \tag{14}$$

$$IMPZH^+ + H_2O \leftrightarrow 1MPZ + H_3O^+ \tag{15}$$

$$1MPZH^{2+} + H_2O \leftrightarrow 1MPZH^+ + H_3O^+ \tag{16}$$

$$1MPZCOO^- + H_2O \leftrightarrow 1MPZ + HCO_3^- \tag{17}$$

The intermolecular interactions in 1MPZ-PZ indicate that MPZ interaction with CO_2 (N_{MPZ}-C_{CO2}) is higher than the interaction of PZ with CO_2 N_{PZ}-C_{CO2}. Similarly, N_{MPZ}-H_{H2O} is also higher than N_{PZ}-H_{H2O}. This indicates that in the blend of 1MPZ-PZ, 1MPZ is more reactive to CO_2 than PZ. In addition, the solubility of 1MPZ is greater in H_2O than PZ. This is because of the methyl group attached to nitrogen in 1MPZ. On the other side, the reaction mechanism of PZ demonstrates that it also produces protonated carbamate. Hence the higher interaction intensity in the MPZ-PZ blend can be because of both MPZ and PZ. These findings can be supported by literature showing that PZ and its derivatives are good activators for amines (Dubois and Thomas, 2012). Farmahini et al. (2011) highlighted that the combination of MDEA and PZ in a blend demonstrated favourable properties for the CO_2 absorption process. Within this blend, the PZ molecule transforms protonated piperazine (PZH^+) and piperazine carbamate ($PZCOO^-$), contributing to increased solubility in water. Notably, the formation of $PZCOO^-$ was found to enhance the absorption rate, emphasizing the significance of this combination in CO_2 capture applications (Farmahini et al., 2011). While analyzing the Intra-molecular interaction intensity of PZ, the N-C bond is easy to break and for the carbamate breakdown, the intensity is 39 A$^\circ$, which is 46% less than MEA (whose strength is 21 A$^\circ$). Consequently, it is suggested to blend piperazine with other solvents to enhance the rate of the CO_2 absorption process.

Piperidine is a cyclic amine containing a hydrogen atom on nitrogen. The interaction intensity results of PIP indicate that it is more reactive to CO_2 as compared to DEEA and 1MPZ as presented in Fig. 3(b). The observed interactions in PIP are N_{PIP}-C_{CO2} and N_{PIP}-H_{H2O} as presented in Fig. 3 shows that Piperidine does not contain the -OH group, therefore it lacks O_{PIP}-C_{CO2}, HO_{PIP}-O_{H2O} interactions and we can only observe two interactions in it like N_{PIP}-C_{CO2}, and N_{PIP}-H_{H2O}. N_{PIP}-C_{CO2} interaction is higher than N_{PIP}-H_{H2O}, which indicates that PIP is more reactive to CO_2. These RDF results of interaction intensity show that it can be a good promoter for tertiary or secondary amines to increase the CO_2 absorption rate in solvent system. These findings are according to the literature, for example, a study conducted by Dubois and Thomas (2012) shows that PIP has better absorption-regeneration performance than

MDEA (Dubois and Thomas, 2012).

The RDF results of interaction intensity for various amines selected in the present study show that the aqueous system of DEEA possesses the highest interaction intensity than that of MEA-DEEA, PIP, and 1MPZ-PZ. The order of interaction strength for various systems from higher to lower is DEEA>MEA-DEEA>PIP>1MPZ-PZ. It shows that DEEA can help to increase the CO_2 absorption rate either in a single form or blended with other amines like MEA.

4.1.3. Temperature effect on interaction intensity of selected amines in the present study

To analyze the influence of temperature on intermolecular interactions, three different temperatures were selected: 313 K, 323 K, and 333 K. Intermolecular interactions are crucial in many chemical and physical processes, such as solubility and reactions. The strength of these interactions is influenced by various factors, including temperature. Understanding the effect of temperature on intermolecular interactions is essential for designing and optimizing chemical processes.

The RDF analysis is conducted at three different temperatures 313 K, 323 K and 333 K. The graphical representation of RDF at various temperatures is presented in supplementary materials Figs. S4-S7. The intensity results at various temperatures demonstrate that increasing temperature does not have a significant impact on the interaction intensity of DEEA, MEA-DEEA, PIP and 1MPZ-PZ. This is because, at low temperatures, intermolecular interactions tend to be stronger. After all, the molecules are more closely packed together due to reduced thermal energy (Sharif et al., 2023a). With the temperature rise, the molecules have more thermal energy as a result of which, the intermolecular distances increase. Therefore, the strength of intermolecular interactions typically decreases with increasing temperature for example in DEEA (N_{DEEA}-H_{H2O}) and MEA-DEEA (N_{DEEA}-H_{H2O}), the strength of the interaction decreases with increasing temperature Fig. S4. However, in some cases, the opposite trend is observed. For example, in the case of hydrogen bonding, the strength of the interaction increases with an increase in temperature up to a certain point (HO_{DEEA}-O_{H2O}) in aqueous DEEA and then decreases at 333 K (Supplementary material Fig. S5). This is because thermal energy can facilitate the breaking of hydrogen bonds and the formation of new ones, leading to an overall increase in the strength of the interaction. However, beyond a certain temperature, the thermal energy becomes too high, and the hydrogen bonds become too weak to maintain their strength. In addition to hydrogen bonding, other types of intermolecular interactions, such as van der Waals forces and dipole-dipole interactions, can also be affected by temperature. For example, in the case of van der Waals forces, the strength of the interaction decreases with increasing temperature due to the reduction in molecular packing and increased thermal motion, this is the reason that the interaction strength decreases at 333 K as given in supporting information Figs. S4 and S5. The temperature shows anomalous behaviour for all the types of amines selected in the present study and this effect is not substantial. In other words, temperature has no positive effect on the strength of interaction and there is no significant increase or decrease in intensity of various types of amines observed by RDF at various temperatures.

4.2. Intra-molecular interaction intensity of selected solvents in the present work for CO_2 desorption

The interaction intensity is investigated using two methods to assess carbamate stability. The first is the attractive interaction of $C_{carbamte}$-O_{Water} and $N_{Carbamate}$-H_{Water}, and the second is the repulsive interaction of $N_{Carbamate}$-$C_{Carbamate}$. The pictorial representation of attractive and repulsive interactions in primary and tertiary amines is given in the supporting information file (Fig. S1). The results of these two interactions are shown below.

Intramolecular interactions refer to the forces within a solvent molecule that determine its shape and stability. In the CO_2 desorption

process, intramolecular interactions are crucial in determining the ease with which the solvent can release the CO_2. Solvents with weak intramolecular interactions are typically more effective at desorbing CO_2 because they can release the gas more easily. Intramolecular interactions are crucial in determining the thermodynamic behaviour of molecules and their ability to absorb or desorb gases such as CO_2. In the context of carbamate molecules, the nature and strength of intramolecular interactions play a crucial role in the efficiency of the desorption process. Table 5 shows the results of repulsive interaction in various selected amines.

In computational methods, the strength of the repulsive interaction can be estimated by analyzing the radial distribution function (RDF) of the carbamate molecules. The RDF is a graph that shows the distribution of the distance between pairs of molecules in a solution. The RDF can be used to identify the strength of the repulsive interaction, as well as other interactions such as hydrogen bonding, van der Waals forces, and electrostatic forces. It is important to note that the repulsive interaction in carbamate molecules is not the only factor that affects the desorption process. Other factors, such as the size and shape of the carbamate molecules, the solvent used, and the temperature and pressure conditions, can also play a role in determining the efficiency of the desorption process.

Table 5 presents the summary of findings for attractive and repulsive interactions in various types of amines selected in the present study. The peak observed in the repulsive interaction in Fig. 4 is due to the strong repulsive force between the molecules, which pushes them apart and prevents them from coming too close to each other. This peak is distinct from the attractive interaction, which is responsible for holding the molecules together. The attractive interaction ($C_{carbamate}$-O_{H2O}) in MEA is the highest of all of the studied amines, which means that MEA is more reactive than all other amines. On the other side, the repulsive interaction ($N_{carbamate}$-$C_{carbamate}$) in MEA is lowest (1.25 Å, 21 Å) as compared to other solvents selected in the present study. Because it is a repulsive interaction, therefore its lower value of N-C in carbamate shows that it needs the highest energy to separate the solvent molecules (Fig. 4), which is the highest drawback of using MEA. After MEA, Piperazine (PZ), Piperidine (PIP), 1-methylpiperazine (1-MPZ) and DEEA show lower energy in the repulsive interaction of bicarbonate. One important factor that affects the strength of the repulsive interaction is temperature. As temperature increases, the molecules in a carbamate solution become more energetic and more likely to experience a strong repulsive interaction. This can result in a higher peak in the repulsive interaction and, in turn, a more efficient desorption process. This is the reason that desorption is often done at higher temperatures (Zhang et al., 2014). Another important factor that affects the strength of the repulsive interaction in the desorption process, is the nature of the solvent and the substituent attached to the nitrogen atom. Different solvents have different properties, such as viscosity and polarity, that can affect the strength of the repulsive interaction. For example, polar solvents tend to have a higher repulsive interaction than non-polar solvents due to the presence of hydrogen bonding between the solvent and the solute. This is the reason that different types of amines vary the strength. Table 5 shows that 1MPZ shows higher intensity for

the N-H bond which concludes that it can form strong hydrogen bonding. Recently a study revealed that the solvent with higher hydrogen bond capacity facilitates zwitterion (Wang et al., 2020), which provides information about the reaction mechanism of 1MPZ.

Hence, from Table 5, the order of intramolecular interaction intensity from higher to lower energy requirement is MEA>PZ>PIP>1MPZ>DEEA. It shows that DEEA postures the lowest interaction parameter (1.25,54) among selected solvents, while MEA has the highest. DEEA's classification as a tertiary amine, characterized by the presence of two hydroxyethyl groups on each nitrogen atom, is pivotal to its chemical behaviour. Our findings reveal that DEEA exhibits favourable ease of regeneration, a crucial factor in determining the economic feasibility of such processes. This observation aligns with established literature, such as Xiao et al. (2018); Wu et al. (2019), has consistently reported that tertiary amines, including DEEA, demonstrate lower desorption energies compared to primary and secondary amines. This is attributed to the steric hindrance created by the bulky alkyl groups, reducing the interaction with captured gases and facilitating their release during regeneration.

4.3. Mean square displacement analysis of CO_2 diffusivity estimation in MEA-DEEA, PIP, 1MPZ-PZ, and PZ at various temperatures

The mean square displacement MSD is defined as the average displacement of a given particle in a system and is a powerful means for determining the average molecular motion in solids, liquids and gases. The MSD can be expressed as Eqs. (18) and (19) given below.

$$MSD = \langle r^2(t) \rangle = \left\langle \frac{1}{N} \sum_{i=0}^{N} (r_i(t) - r_i(0))^2 \right\rangle \tag{18}$$

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt}(MSD) \tag{19}$$

Diffusivity is an important factor to consider in the design of a CO_2 absorption column because it affects the rate of CO_2 transfer from the gas phase to the solvent. High diffusivity ensures fast and efficient CO_2 absorption and reduces the size of the absorption column, thus reducing capital and operational costs. Furthermore, the absorption column's design, including column height, diameter, and flow rate, should take the solvent's diffusivity into account to ensure that CO_2 is absorbed efficiently. Therefore, the choice of solvent for the CO_2 absorption process should also be based on its diffusivity properties and its ability to absorb CO_2 effectively at the desired operating conditions.

Table 6 shows the CO_2 diffusivity estimation in various amine systems by MSD analysis. The blend of MEA-DEEA shows the diffusivity 0.48E-09 m^2s^{-1} at 298 K and this value gradually increases with temperature. For example, it is 0.70E-09 m^2s^{-1} at 313 K and 0.97 m^2s^{-1} at 323 K as presented in. A similar pattern is observed in PIP, 1MPZ-PZ and PZ. The CO_2 diffusivity of pure PZ is highest from all the blends as well as pure amines analyzed in the present study. Here MEA is taken as a reference solvent. The diffusivity rate in PZ is 1.52E-09 m^2s^{-1} at 298 K, 1.75 m^2s^{-1} at 313 K and 2.15E-09 m^2s^{-1} at 313 K. It can be seen from Table 6 that the diffusivity of a solvent generally increases with temperature. This is because of the increase in the thermal energy of the solvent molecules with temperature. At higher temperatures, the solvent molecules have higher kinetic energy, which increases the rate of molecular diffusion and hence the diffusivity of the solvent (Masy, 2013). Fig. 6 elaborates on the effect of temperature on the diffusivity of various amine systems.

Another significant physical parameter for CO_2-capture effectiveness is amine viscosity. Table 7 shows the viscosity of aqueous amines while the boiling point of pure amines. Diffusivity is related to viscosity. The well-known Stokes-Einstein relation provides the relationship between viscosity and diffusivity as presented in Eq. (20).

$$D \propto T \mu^{-1} \tag{20}$$

Table 5
RDF results of Attractive and Repulsive Interactions in Various Amines at 313 K.

System	$C_{Carbamate}$-O_{H2O} (r, g(r))	$N_{Carbamate}$-H_{H2O} (r, g(r))	$N_{Carbamate}$-$C_{Carbamate}$/ $H_{bicarbonate}$-$C_{bicarbonate}$ (r, g(r))
Interactions	Attractive interactions		Repulsive Interaction
MEA	3.75,1.41	4.25,1.09	1.25,21
PIP	3.75,0.92	5.25,0.83	1.25,40
PZ	3.75,0.60	5.75,0.92	1.25,39
DEEA	3.75,0.90	5.25,1.15	1.25,54
1MPZ	3.75,1.28	5.25,1.03	1.25,44

Table 6
Simulation Findings for CO$_2$ Diffusivity Estimation in Various Amines.

Solvent System/ Temperature	Simulation Results D(CO$_2$)/ m^2.s^{-1}			References
MEA-DEEA	**298 K**	**313 K**	**323 K**	
	0.48E-09	0.70E-09	0.97E-09	
MEA	**298 K**	**313 K**	**318 K**	
	1.42E-09	2.11	2.42	Sharif et al. (2023b); Yusof et al. (2021)
	1.39E-09			
DEEA	**313 K**	**323 K**	**333 K**	
	0.76E-09	0.98E-09	1.16E-09	Present work
1MPZ	**313 K**	**323 K**	**333 K**	
	0.66E-09	0.97E-09	1.09E-09	Present work
PIP	**303 K**	**313 K**	**323 K**	
	0.80E-09	0.96E-09	1.28E-09	Present work
1MPZ-PZ	**303 K**	**313 K**	**323 K**	
	0.56E-09	0.63E-09	0.84E-09	Present work
PZ	**298 K**	**303 K**	**313 K**	
	1.52E-09	1.75E-09	2.15E-09	Present work
		1.77E-09		Sun et al. (2005)
		1.73E-09		Derks et al. (2006)

Table 7
Viscosities* and Boiling Points of Various Selected Amines.

Solvent	Molecular Weight/(g. mol^{-1})	Boiling Point (°C)	Viscosity/ (cP)	References
DEEA	117	164	4.07	(Maham et al., 2002; Karunarathne et al., 2020)
PZ	86	149	1.87	(Freeman and Rochelle, 2011)
1-MPZ	100.162	138	0.894	(Rayer et al., 2011)
MEA	61.06	171	24.1	(Nakao et al., 2019)

*Viscosites are given for aqueous solvents

In Eq. (20) 'μ' is the viscosity of the solvent and 'T' is the absolute temperature. Viscosity is a measure of a fluid's resistance to flow. At higher temperatures, the kinetic energy of molecules increases, leading to reduced viscosity. This means that the amine solvent becomes less viscous and flows more easily. According to Eq. (20), the higher the amine viscosity, the slower the diffusion of CO$_2$ in the amine solvent. This indicates that low-viscosity amines benefit from fast kinetics and lower viscosity can facilitate the mass transfer of CO$_2$ molecules within the solvent, promoting efficient absorption and regeneration processes (Nakao et al., 2019).

Table 7 shows that the order of viscosity of aqueous amines chosen for this study is MEA>DEEA>PZ >1MPZ. It indicates that aqueous MEA has the highest viscosity so it should have the lowest reaction kinetics but the studies show that the reaction kinetics and diffusivity of MEA are faster than other conventional amines (Sharif et al., 2023b;. This can be because of the size of MEA. Table 7 demonstrates that the molecular weight of MEA is the smallest among all the amines. The larger the size of the solvent, the slower will be the diffusivity and vice versa. Another important aspect is the temperature. Temperature has a significant impact on the diffusivity and viscosity of the amine system. Higher temperatures tend to reduce viscosity, making the solvent less resistant to flow. This could, in turn, enhance diffusivity. However, viscosity reduction might not be linear and can vary with the nature of the solvent

and its components. This aspect can be seen in 1MPZ, PZ. 1MPZ has a lower viscosity than DEEA and PZ. However, the diffusivity estimation of PZ indicates that it should have higher kinetics. These results can be justified by other studies in the literature, which show that Piperazine is often used as a rate promoter in various types of amines (Derks et al., 2006).Fig. 5

Another reason for the lower CO$_2$ diffusivity in 1MPZ and DEEA is the structural variation due to the presence of different functional groups and the large size of amines. On the other hand, the boiling point of amine is a critical physical characteristic for CO$_2$-capture applications. Low-boiling-point amines, in particular, are harmful to the environment and the economy because they are prone to volatilization. In general, the higher the molecular weight, the greater the boiling point. The other important aspect is the intermolecular forces, such as hydrogen bonding, dipole-dipole interactions, and van der Waals forces. Temperature directly impacts these forces. As temperature rises, molecules vibrate more vigorously, leading to a greater number of collisions and increased chances for these forces to come into play which in turn cause increased diffusivity at higher temperatures. This can intensify the strength of attractive interactions,

particularly for hydrogen bonding where molecules with hydrogen atoms (such as NH or OH groups) can form stronger bonds. Therefore, in the present scenario, the temperature has positive effect on the CO$_2$ diffusivity in the selected amine. Fig. 6

Hence, efficient capture requires a delicate balance: strong interaction intensity to facilitate absorption, optimal diffusivity to enable fast CO$_2$ movement, and manageable viscosity to ensure reasonable flow behavior. Temperature's impact serves as a tuning knob, offering opportunities for enhancement while navigating complexities in solvent behavior.

5. Conclusion

The proposed molecular dynamic simulation method was used to investigate the influence of temperature on intermolecular interaction as well as the diffusivity of various types of amines. The study's findings can be utilized as a guideline to select a solvent based on properties that substantially impact the absorption process. This study's findings can be used to improve the efficiency of current solvents while also providing useful insights for the future development of blended amine solvents. The findings are described below.

(a) While examining the intermolecular interaction intensity of selected solvents, it was observed that the intensity is higher in
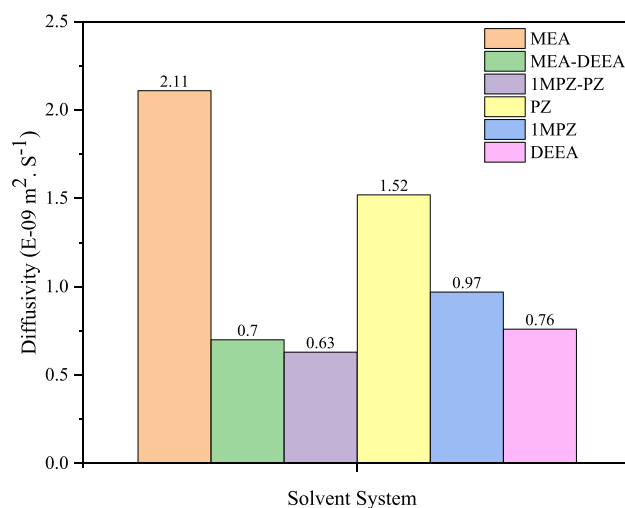
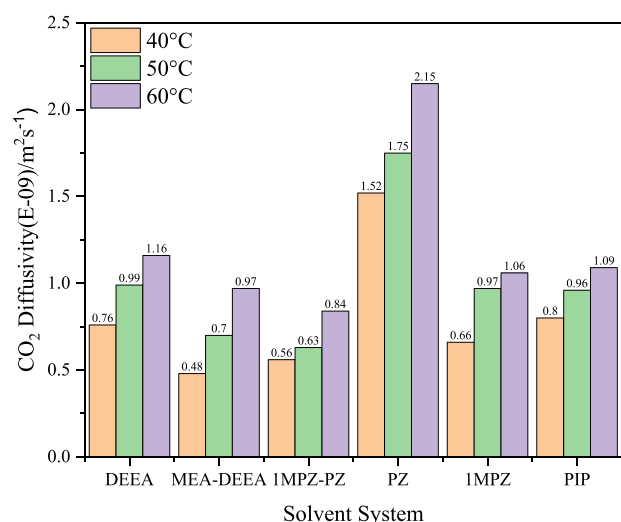**Fig. 5.** Diffusivity Estimation in Various Solvent System at 313 K.

Fig. 6. Temperature Effect on Diffusivity of Various Solvent Systems.

the blended amine system than in pure amines. The order of interaction intensity in various amine systems is DEEA>MEA-DEEA>PIP>1MPZ-PZ. It shows that pure MEA and a blend of MEA with DEEA show higher interaction intensity out of all studied amines. Consequently, MEA-DEEA blend can increase the CO_2 absorption rate. The degree of intensity in 1MPZ-PZ and PIP is also significant. It is suggested that PIP be combined with other amines as an activator.

(b) The intra-molecular interaction intensity finding revealed that PIP, PZ and 1MPZ required less energy to regenerate the solvent than MEA. The attractive interactions of N-H in DEEA for the desorption process are higher than C-O interactions because DEEA does not form carbamate during the reaction mechanism.

(c) There is anomalous behaviour in the temperature effect on interaction intensity. In certain circumstances, the intensity rises from 313 K to 323 K before dropping off again at 333 K. This is because molecules are more tightly packed together due to lower thermal energy at low temperatures, which tends to make inter-molecular interactions stronger. As the temperature rises, the molecules gain more thermal energy which causes higher distances between molecules. Since the molecular packing is reduced due to higher thermal motion, as a results intermolecular interactions become weaker and we observe lower interaction intensity.

(d) Diffusivity is a crucial factor in the design and operation of a CO_2 absorption column. The findings of the diffusivity estimation indicated that out of all the solvent system examined in the present study, PZ shows highest diffusivity rate in pure system. This is the reason that PZ is often used as a rate promoter in the various solvent system. The diffusivity estimation in blended amine system show that MEA-DEEA has higher diffusivity than 1MPZ-PZ. The order of diffusivity in various blended system is PZ>1MPZ>DEEA>MEA-DEEA>1MPZ-PZ. A higher diffusivity leads to a higher mass transfer rate, which can result in a smaller absorber unit size and reduced energy requirements.

(e) The temperature effect on diffusivity shows that as the temperature rises, the viscosity of the molecules decreases and the kinetic energy of the system increases, as a result, the diffusivity of the system increases. All the solvent system under consideration shows the highest diffusivity at 333 K than that of 313 K.

Declaration of Competing Interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cherd.2024.03.005.

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