SELECTION OF EFFICIENT ABSORBENT FOR CO_2 CAPTURE FROM GASES CONTAINING LOW CO_2

ABSTRACT

Amine-based absorption processes are widely used in the natural gas processing but recently it has been considered for CO_2 capture from flue gas emitted from the thermal power plant. The main issue of amine used in the CO_2 capture process is its high cost of solvent regeneration. So, this issue can be solved by using efficient amine absorbent. The amine type absorbents employed in the experimentation were an aqueous blend of 2-(Diethylamino)ethanol (DEEA) with different types of diamine activators such as piperazine (PZ), 2-(2-aminoethylamine)ethanol (AEEA), 1,6-Hexamethyldiamine (HMDA), ethylenediamine (EDA), and 3-(Dimethylamino)-1-propylamine (DMAPA). The absorption experiment was performed to evaluate the CO_2 absorption performance in terms of CO_2 loading, absorption capacity, and absorption rate. The desorption experiment was performed to assess the CO_2 desorption performance in terms of desorption capacity, desorption rate, cyclic capacity, and regeneration efficiency. From the results of absorption-desorption and comparison with benchmark amine absorbent MEA, the aqueous blend of DEEA and HMDA indicated the best performance for CO_2 capture applications among all the tested amine blends.

3.1 INTRODUCTION

The global energy demand has been increasing due to rapid industrialization and urbanization, which led to create various environmental problems. The significant environmental problems as global warming and climate change have taken place due to the continuous release of prime greenhouse gas CO_2 into the atmosphere by various industries in the world. The CO_2 present in the gas stream has been released from industries like fossil-fuel based thermal power plants for electricity generation, iron and steel industry, cement production, natural gas processing, oil refinery, chemical, and petrochemical manufacturing units. In which, the fossil-fuel based thermal power plants industries are mainly responsible for CO_2 emissions as it contributes approximately 40% of total CO_2 emission in the world. Among fossil-fuel based power plants, the coal-fired thermal power plants have a significant role in the global CO_2 emission of approximately 31% (IEA, 2016). The coal-fired thermal power plants release a large amount of exhaust gas, which contains 12-16 % CO_2 (Zaman and Lee, 2013). However, the global CO_2 emission has increased up to 70 % from 1971 to 2002, and also the energy-related CO_2 emissions in the world are increasing at a rapid rate of about 2.1 % per year which has made the emphasis on the reduction of CO_2 emission at the global scale (Xu et al., 2010). Currently, carbon capture and sequestration (CCS) is the best option to remove CO_2 from a different gas stream such as flue gas, natural gas, refinery gas, blast furnace gas, etc. Several types of separation technologies such as absorption, adsorption, cryogenic, membrane separation, and chemical looping have been used for the CO_2 removal from different gas streams. Among these, absorption technology using amine-based solvent has been widely used because it possesses good absorption efficiency, capable of removing CO_2 up to level present in the gas stream, a large volume of exhaust gas conditioning capacity retrofitting option, cost-effectiveness, and solvent regeneration option (Ciferno et al., 2009; Rao and Rubin, 2002; Xu et al., 2016). Therefore, the amine based absorbents such as alkanolamine and polyamine have been used in the removal of CO_2 from a gas stream. The different types of amine absorbents such as primary amine monoethanolamine (MEA), secondary amine diethanolamine (DEA), tertiary amine N-methyl diethanolamine (MDEA), sterically-hindered amine 2-amino-2-methyl-1-propanol (AMP), and polyamine piperazine (PZ) are widely used in the removal of CO_2 from gas streams (Kohl and Nielsen 1997). Several researchers measured the CO_2 capture performance of different tertiary amine such as 2-(Dimethylamino)ethanol (DMEA) (Xiao et al., 2018; Ling et al., 2019), 2-(Diethylamino)ethanol (DEEA) (Xiao et al., 2018) , 3-dimethylamino-1-propanol (DMAP-31) (Xiao et al., 2018; Nouacer et al., 2014), 2-(2-(dimethylamino) ethoxy) ethanol (DMAEOE) (Nouacer et al., 2014), 1,2-bis (dimethylamino) ethane (TEMED) (Nouacer et al., 2014), methyl-4-morpholine (Nouacer et al., 2014), pyridine (Nouacer et al., 2014), ethyldiethanolamine (EDEA) (Narku-Tetteh et al., 2017) and butyldiethanolamine (BDEA) (Narku-Tetteh et al., 2017) in terms of CO_2 loading, overall mass transfer coefficient, physical solubility, absorption rate, desorption rate, and cyclic capacity at various operating conditions at laboratory scale. Also, various researchers measured the performance of different single polyamine such as ethylenediamine (EDA) (Yu et al., 2017), 1, 3-diaminopropane (DAP) (Wilk et al., 2017; Yu et al., 2017), N-methylethylenediamine (MEDA) (Yu et al., 2017), N-methylpropane-1, 3-diamine (MAPA) (Yu et al., 2017), 2-Dimethylaminoethylamine (DMAEA) (Yu et al., 2017), 3-Dimethylaminopropylamine (DMAPA) (Yu et al., 2017), diethylenetriamine (DETA) (Muchan et al., 2017), triethylenetetramine (TETA) (Muchan et al., 2017), tetraethylenepentamine (TEPA) (Muchan et al., 2017) and 1-(2-aminoethyl)piperazine (AEP) (Choi et al. 2016) for CO_2 capture. The polyamine performance was measured in terms of CO_2 loading, absorption capacity, absorption rate, desorption rate, apparent absorption rate, overall mass transfer coefficient, ions species concentration and cyclic capacity at various operating conditions by using different experimental apparatus. Recently, Liu et al., 2019 studied the eleven different single amine using novel screening method and they selected secondary amine 2-(methylamino) ethanol and (MAE) 2-(ethylamino) ethanol (EAE) as a potential solvent for CO_2 capture. Among these single amine absorbents, MEA has been widely used in the industries for CO_2 removal from a several gas stream (Rochelle 2009), but its major drawacks include low absorption capacity, high regeneration energy required, high thermal degradation, and shows corrosive behavior at higher concentrations more than 30 wt. % (Ma'mun et al., 2007; Dawodu and Meisen, 2010; Vega et al., 2014)**.** The drawback of secondary amine is limited CO_2 absorption capacity. Also, the tertiary amine is a low CO_2 absorption rate as the main drawback. Sterically hindered amine such as AMP precipitated at higher concentration (above 3M), resulting from clogging in a pipe used in the CO_2 capture process (Gao et al., 2017). To overcome these drawbacks of single amine absorbent, researchers have been attracted to the development of amine blend absorbent to improve the existing single amine performance for CO_2 capture. The first researcher (Chakravarty et al., 1985) suggested alternative absorbent as an amine blend of tertiary amine or sterically-hindered amine with primary or secondary amine for the improvement of CO_2 capture from a gas stream. Consequently, significant efforts have been made by different researchers (Ramachandran et al., 2006; Sema et al., 2012; Benamor, and Al-Marri 2014; Mandal and Bandyopadhyay 2006; Xiao et al., 2000; Mandal et al., 2003; Fu et al., 2013) for improving the CO_2 absorption performance and they showed that blend of amines of MDEA and/ or AMP and MEA or DEA have better absorption performance than single amine MEA, DEA, MDEA, and, AMP. But recently, the aqueous blend of tertiary amine DEEA and polyamine have attracted more for CO_2 capture because DEEA has better absorption performance than conventional tertiary amine MDEA as well as it can be prepared from renewable sources like agricultural residue or waste products (Chowdhury et al., 2013; Vaidya and Kenig 2007). Also, polyamines show better CO_2 absorption performance than primary and secondary monoamines due to the presence of multiple reaction sites available to absorb a large amount of CO_2 in the solvent (Choi et al. 2016). However, a single polyamine solvent used at high concentration showed degradation behavior and also has a high material cost so it may not be preferred for CO_2 capture at industrial scale (Vaidya and Kenig 2009; Aronu et al., 2009). Therefore, researchers used different laboratory scale apparatus for testing the potential of individual DEEA based aqueous amine blend for CO_2 capture by adding different diamines such as Piperazine (Fu et al., 2016), N-Methyl-1,3-diaminopropane (Kim and Svendsen 2011; Liebenthal et al., 2013), 1,4-Butanediamine (Xu et al., 2013), and capture performance has been evaluated in terms of CO_2 loading, absorption capacity, absorption/desorption rate, cyclic capacity, absorption heat, mass transfer coefficient, and reaction rate constant of CO_2, etc. Furthermore, the researchers (Gao et al., 2016) selected an efficient solvent among together various DEEA based amine blends by using different types of additives as a primary amine (MEA), secondary amine (DEA), sterically-hindered amine (AMP, EAE), diamine (PZ, AEEA), triamine (DETA), tetramine (TETA) with the help of the absorption-desorption screening experiments. Furthers, several researchers developed advanced solvent system such as liquid biphasic solvents (Shen et al., 2018; Zhang et al., 2018a) and catalyzed solvent system using carbonic anhydrase enzyme (Zhang et al., 2018b; Ye et al., 2019) for CO_2 capture process to reduce the regeneration heat duty and improve capture performances. Consequently, Zhang et al. studied the different liquid biphasic solvent (Zhang et al., 2019) for CO_2 capture and they reported comprehensive list of absorbent in this paper. But, liquid biphasic solvent required unconventional handling cost and catalyzed solvent system required temperature limitation for CO_2 capture process (Budzianowski, 2015). Also, a little information is available on an amine blend of DEEA with diamine absorbent promising for the CO_2 capture (Sutar et al., 2013). So, due to drawacks of liquid biphasic solvent, catalyzed solvent system and limited information on DEEA+diamine solvent, the present work is focused on the selection of the efficient absorbent for CO_2 capture among various DEEA based amine blend using five different types of diamines such as PZ, AEEA, HMDA, EDA, and DMAPA. Because, a potential absorbent has a significant role in the design and selection of absorption-desorption column, heat exchanger, and pump applied in the CO_2 capture process.

In this work, five amine blends such as DEEA+PZ, DEEA+AEEA, DEEA+HMDA, DEEA+EDA, and DEEA+DMAPA have been proposed for selecting efficient absorbent for CO_2 capture. The CO_2 absorption-desorption experiments have been performed at atmospheric pressure. The absorption experiment has been conducted at temperature 313.15 K and CO_2 partial pressure 20.26 kPa to evaluate the absorption performance parameters. The desorption experiment has been conducted at 363.15K to evaluate desorption performance parameters. Among the proposed amine blends, the best amine blend has been selected based on evaluation of performance parameters concerning CO_2 loading, absorption rate, desorption rate, cyclic capacity, and regeneration efficiency. The performances of amine blends have also been compared with the performance of benchmark absorbent MEA as well as DEEA to see the potential of different diamine blended in DEEA solution.

3.2 EXPERIMENTAL

3.2.1 Chemicals and materials

The analytical grade chemicals 2-(Diethylamino)ethanol (SD-Fine Chem. Ltd, Mumbai), hexamethylenediamine (Tokyo Chemical Industries Co. Ltd., Japan), 2-(2-Aminoethylamino) ethanol (SD-Fine Chem. Ltd., Mumbai), Ethylenediamine (Sisco Research Laboratories Pvt. Ltd, Mumbai), 3-(Dimethylamino)-1-propylamine (Sigma-Aldrich Chemicals Pvt. Ltd., Bangalore) and anhydrous piperazine (SD-Fine Chem. Ltd, Mumbai) with minimum mass purity of 98% were used in the present work without any further purification. Monoethanolamine (SD-Fine Chem. Ltd, Mumbai) with purity greater than 99% was used as a reference amine for validation and comparison with all proposed amine blends studied in the present work. Hydrochloric acid with 37% mass purity without any further purification was used in the measurement of amine solution concentration and determination of CO_2 loading in all amine solutions. The required concentration of amine blend solution for the experiment was prepared by dissolving in double distilled water. The total concentration of final prepared amine blend solution was analyzed by titrating with 1M HCl solution to check the accuracy of solution concentration. The pH of prepared amine solutions was measured by microprocessor-based pH meter (Elico, accuracy: ±0.02). The commercial grade two gas cylinders, first containing the composition of 20% CO_2 balanced with N_2 gas and second containing 99.99% N_2 were supplied by Narayan Gas Company, India. The CO_2 simulated gas stream of desired concentration was prepared with the help of simulating gas chamber made of stainless steel and gas flow rotameter (Alicat, range: 0-3 LPM) to set at a fixed flow rate. The portable infrared flue gas analyzer (Gasboard-3800P, CO_2 range: 0-100 % by volume) with an accuracy of ±0.2% was used for the analysis of CO_2 in the gas phase.

Thermometers with temperature subdivisions of 0.1 K were used to measure the water and oil bath temperature as well as solutions placed in the bubble column and flask. The temperature programmed hot-plate magnetic stirrer (range: 0-473.15 K, accuracy: ±0.01 K) was used to heat solutions present in the flask.

3.2.2. Experimental set-up and procedure

3.2.2.1. CO_2 absorption experiment

A schematic diagram of the experimental set-up for absorption studies is shown in figure 3.1. This experimental set-up operating at atmospheric pressure was used for determination of absorption performance parameters such as CO_2 loading, absorption capacity, and absorption rate. In this set-up, a borosilicate glass bubble column having a liquid holding capacity of 250 ml was kept inside temperature-maintained water circulating bath. Then, the desired concentration of amine blend of 150 ml solution was loaded in the column. After that, nitrogen gas was passed at a low flow rate of approximately 15 min throughout the whole gas-liquid system to remove previously present trace gases with the starting of each experiment. Then, CO_2 simulated gas stream fixed concentration of 20 % v/v and flow rate of 250 ml/min. was passed through water saturation column to bubble column for the absorption of CO_2 in the amine solution. After the gas-liquid contact, bubbles were formed in the liquid bed of the column during the continuous flow of CO_2 gas stream and outlet gas stream emitted from the column was passed through silica bed column to absorb moisture present in the gas stream. Then, the concentration of the dried gas stream was measured by using a portable flue gas analyzer at a regular time interval of 5 min.

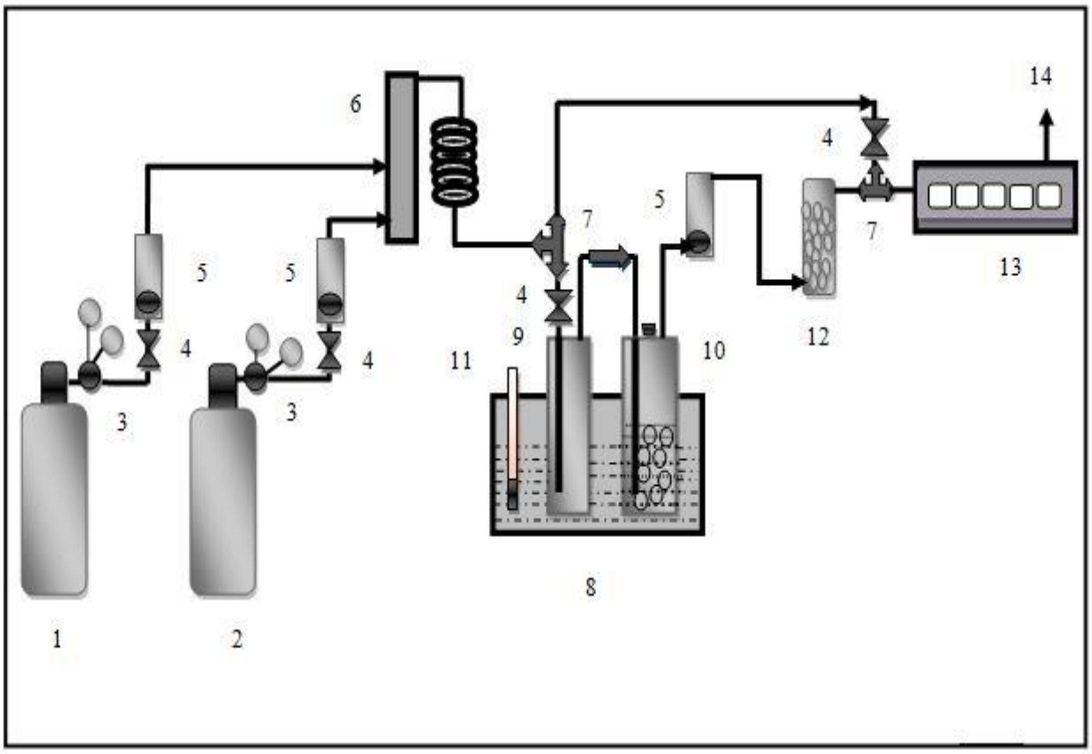

Figure 3.1 Schematic diagram of absorption set-up**:** 1. CO_2 cylinder; 2. N_2 cylinder; 3.pressure regulator; 4. stainless steel valve 5. gas-flow rotameter; 6. gas simulation chamber; 7. glass tee 8. constant temperature water bath; 9. water saturator; 10. bubble column fitted with septum; 11. thermometer; 12. silica bed column; 13. portable multi-flue gas analyzer; 14. exhaust

The gas flow was continued until the CO_2 concentration in outlet gas stream became equal to the inlet gas stream, and this phenomenon is also known as gas-liquid equilibrium. However, for evaluating the absorption performance parameters, partially absorbed CO_2 solution sample was collected at a regular time of interval of 10 min up to 60 min during the experiment for measuring the absorption rate. Finally, for evaluating the CO_2 loading and absorption capacity with time, a fixed volume (1ml) of saturated and partial CO_2 absorbed solutions, respectively were titrated with 1M HCl solution and volume of evolved CO_2 was measured using water-displacement column and its details were mentioned in the previously studied work (Horwitz 1980)**.**

3.2.2.2. CO_2 desorption experiment

The schematic diagram of the experimental set-up for desorption studies has also been shown in figure 3.2. The desorption setup operating at atmospheric pressure was used for determination of performance parameters such as desorption capacity, desorption rate, and cyclic capacity of CO_2. The four-necked round bottom flask made up of a borosilicate glass, having a liquid holding capacity of 250 ml was used in the desorption process. The flask fitted with a condenser, septum, and thermometer dipped in an oil bath was placed on the temperature programmed hot plate magnetic stirrer heater. The previous CO_2 saturated amine solution was further used for desorbing CO_2. The carbonated amine blend solution of 100 ml was filled in the flask and before starting the experiment N_2 gas with a flow rate of 1000 ml/min was continuously purged in an entire gas-liquid system to remove the trace gases present in the system. After that, the heater was started and maintained the temperature required for the desorption process. The dissolved CO_2 gas was released continuously after heating, and the outlet vapor stream was passed through a condenser to prevent losses of amine solution. Further, the discharged vapor stream was passed through a silica bed column for absorbing moisture present in the stream. The final outlet gas stream was passed through portable flue gas analyzer for measuring the concentration of CO_2 at a regular time interval of 5 min. Also, a fixed amount of partial desorbed solution was collected with the help of syringe at a regular time interval of 5 min up to 60 min, and it was required for the evaluation of the desorption rate. The desorption process was stopped when the outlet concentration of CO_2 achieved to be less than 1% by volume. After desorption of CO_2, a fixed amount (1ml) of the desorbed solution was titrated with 1M HCl solution to calculate the desorption capacity as well as desorption rate as described in the earlier section. Finally, at the room temperature and pressure, three successive analyses of the entire absorbed and desorbed samples were performed to calculate the CO_2 loading at rich and lean conditions and the results were found to be reproducible within 1.0% error.

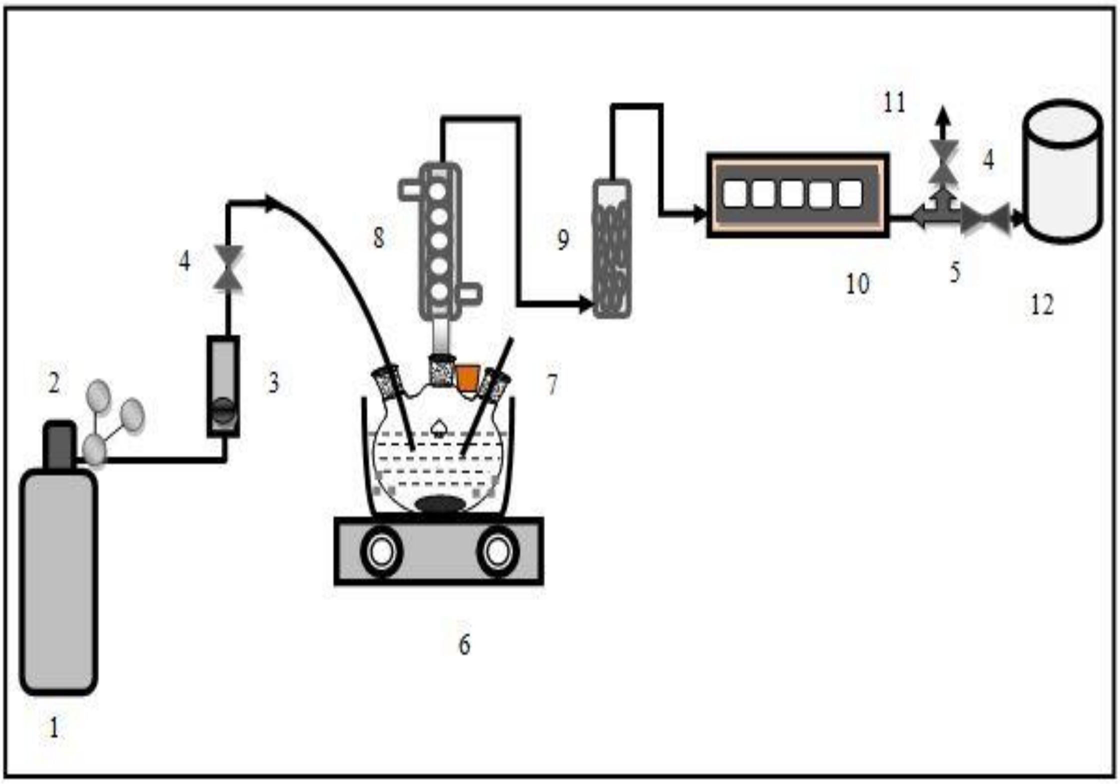

Figure 3.2 Schematic diagram of desorption set-up: 1. N_2 cylinder, 2. pressure regulator, 3. gas flow meter, 4. stainless steel valve, 5. glass tee, 6. heating and magnetic stirrer, 7. four necked round bottom flask placed in silicon oil bath and fitted with septum and thermometer, 8. condenser, 9. silica bed column, 10. portable multi-flue gas analyzer, 11. exhaust, 12. gas storage tank

3.3 CALCULATIONS OF PERFORMANCE PARAMETERS

The performance of amine blends for CO_2 capture were evaluated in terms of CO_2 loading, absorption rate, desorption rate, cyclic capacity and regeneration efficiency. These are as follows:

3.3.1 CO_2 loading

The amount of CO_2 absorbed in amine solution at equilibrium is called CO_2 loading. It has expressed as the ratio of a mole of CO_2 to the mole of amine. The CO_2 loading is determined by direct-titration methods (Gao et al., 2017). Mathematically, it follows as:

$$CO_2 loading(\alpha_{CO_2}) = \frac{V_{CO_2} - V_{HCl}}{22.4 \times M_{sample} \times V_{sample}} \times \frac{273.15}{(273.15 + T_{RT})} \qquad (3.1)$$

Where, α_{CO_2} is the CO_2 loading in mol CO_2/ mol amine, V_{CO_2} is the volume of CO_2 evolved in ml, V_{HCl} is the volume of HCl in ml, M_{sample} is the concentration of amine sample in M, V_{sample} is the volume of amine sample in ml, T_{RT} is the room temperature in K.

3.3.2 Absorption and desorption rate

It may be determined by the linear slope of plot drawn by CO_2 loading versus absorption or desorption time (Muchan et al., 2017). It is also called apparent absorbent or desorption rate. It is expressed as the ratio of mole of CO_2 to the product of volume of amine as well as absorption or desorption time. The unit of absorption or desorption rate is mole of CO_2/ litre of amine solution.sec.

3.3.3 Cyclic capacity and regeneration efficiency

Regeneration performance of amine blend solution is evaluated in terms of CO_2 cyclic capacity. It is defined as the difference between absorption capacity and desorption capacity. Here, absorption capacity, desorption capacity, and cyclic capacity have expressed as the ratio of mol of CO_2 per litre of amine solution. Also, regeneration efficiency is represented as the percentage ratio of the cyclic capacity of CO_2 to the absorption capacity or CO_2 loading at absorption condition.

Mathematically, it follows as:

Cyclic capacity = absorption capacity-desorption capacity (3.2)

Regeneration efficiency = (cyclic capacity/absorption capacity)* 100 (3.3

3.4 RESULTS AND DISCUSSION

3.4.1 Validation of experimental setup and procedures

In this work, the concentration of the amine solution was taken in molarity (M) unit, because chemical reaction occurred on a mole basis. The concentration of all the proposed amine blend solution was taken as 2.5 M along with 2M concentration of DEEA and 0.5M concentration of each diamine (PZ, AEEA, HMDA, EDA, and DMAPA) because the aqueous solution of DEEA blend concentration more than 3 M showed worst performance in terms of CO_2 loading at a low concentration of CO_2 (20 %v/v) in the gas stream corresponding to 20.27 kPa CO_2 partial pressure (Kumar and Mondal, 2018a). Also, the total concentrations of all amine blend solutions have lain between 27.5 wt. % and 30.52 wt. % and we know that the 30 wt. % concentration is favorable for the industrial point of view in the CO_2 capture applications (Kohl and Nielsen, 1997). The chemical structures of base absorbent (DEEA), benchmark absorbent (MEA) and diamine activators (PZ, AEEA, HMDA, EDA, and DMAPA) have been shown in figure 3.3 to see the effect of diamine activator after blending with DEEA solution.

Before measuring the aqueous amine blend potential for CO_2 capture, the reliability of the experimental apparatus was validated by measuring the CO_2 loading in MEA solution at temperature 313.15 K. The present and previous data of several authors (Lee et al., 1976; Shen and Li 1992; Song et al., 1996) on CO_2 loading have represented in figure 3.4. After the comparison, it can be seen that the measurement techniques used in this work are reliable and acceptable for the further measurement of CO_2 loading in proposed amine blend solution.

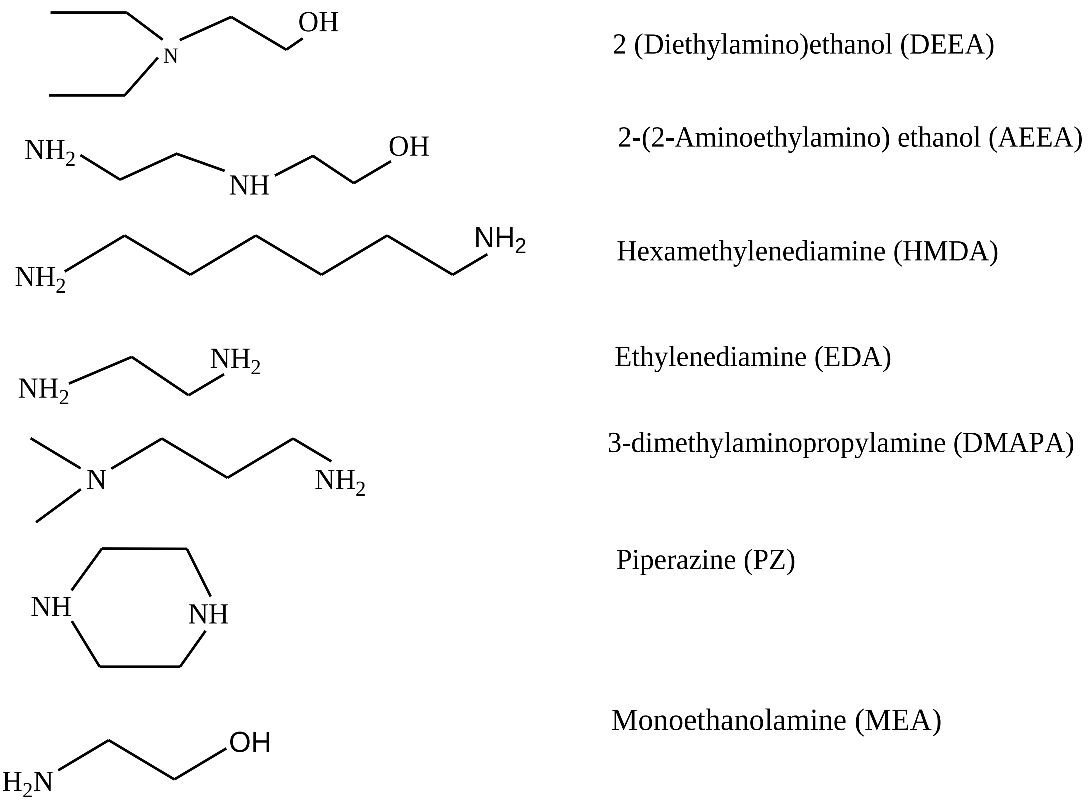

Figure 3.3 Chemical structure of alkanolamines and diamines

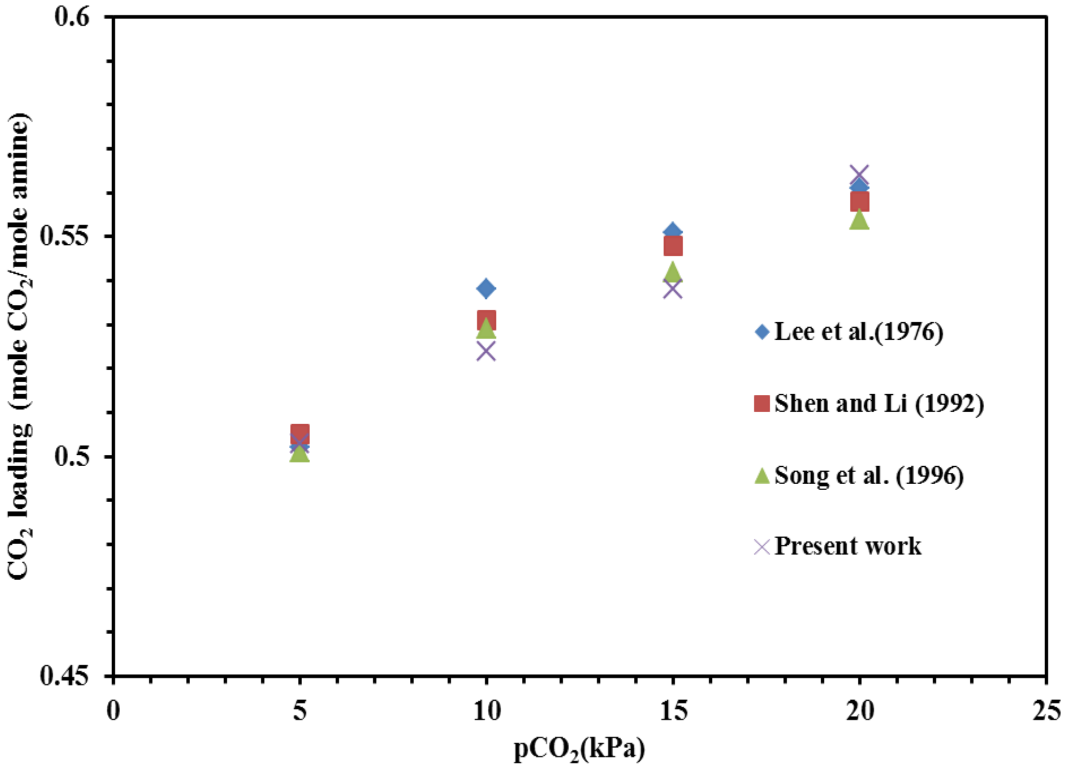

Figure 3.4 CO_2 loading in 2.5 M MEA solution at temperature 313.15 K

3.4.2 CO_2 loading

The CO_2 loading is the most significant absorption performance parameter because the CO_2 loading data are used in the development of empirical model which further applied for the design of absorption-desorption column used in CO_2 capture process (Shen et al., 2015). The absorbent having higher CO_2 loading required the smaller size of a column for the same amount of CO_2 absorption, which can reduce the capital cost of the absorption column. The CO_2 loading is the maximum absorption capacity of CO_2 in an absorbent which is expressed in terms of a mole of CO_2 absorbed per mole of the absorbent. Therefore, for measuring the CO_2 loading in various amine solutions, the absorption experiment was performed at a 313.15 K and 20.26 kPa of CO_2 partial pressure.

The results of CO_2 loading in MEA, DEEA, and five amine blends DEEA+PZ, DEEA+AEEA, DEEA+EDA, DEEA+HMDA, DEEA+DMAPA solution were shown in figure 3.5.

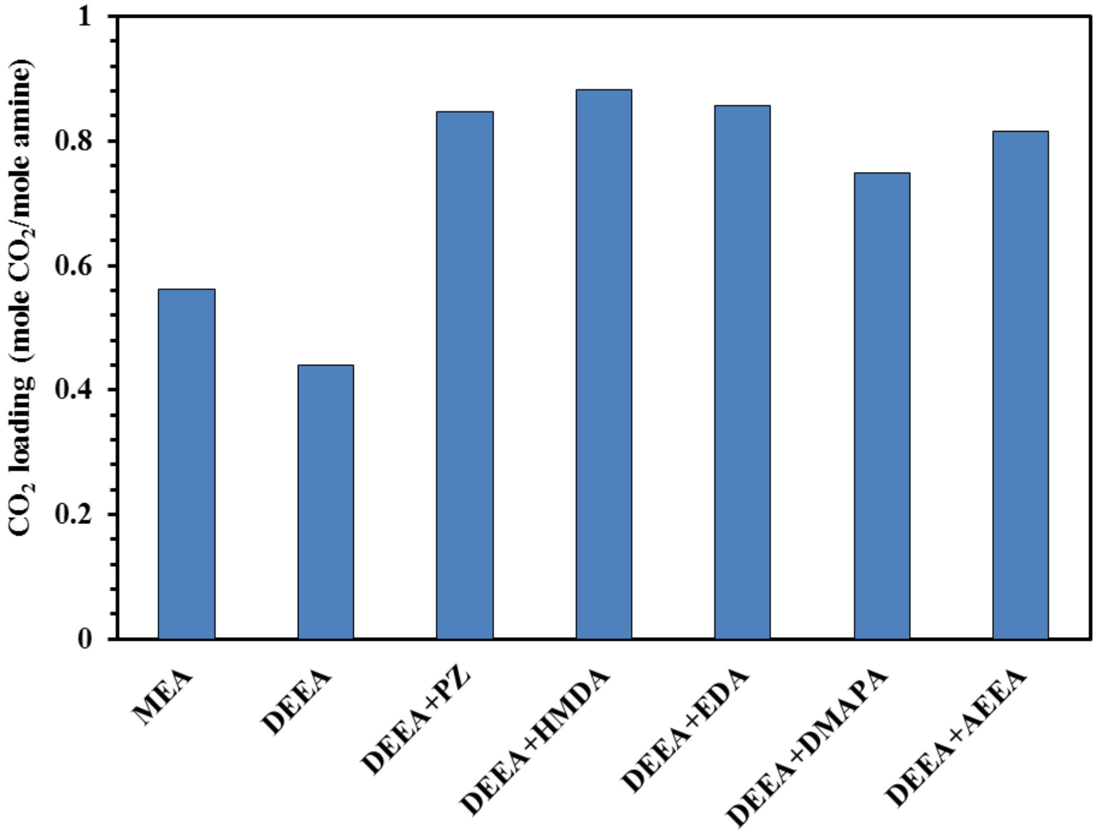

Figure 3.5 CO_2 loading in various amine solutions of total concentration of 2.5 M

From figure 3.5, it can be seen that the CO_2 loading in single amine solution and blend solution follows the order as DEEA+HMDA > DEEA+EDA ≈ DEEA+PZ > DEEA+AEEA > DEEA+DMAPA > MEA > DEEA. The results showed that the entire proposed amine blends had better absorption performance than DEEA and the benchmark absorbent MEA. Interestingly, a drastic increased in the CO_2 loading in the entire blends was observed because the activators present in DEEA blend solutions providing multiple reaction sites leading to absorb more CO_2 in blends solutions. However, a significant enhancement of CO_2 absorption in amine blends was found by HMDA, EDA, PZ, and AEEA activator but little enhancement by DMAPA. Mainly, DEEA+HMDA blend showed the best absorption performance in term of CO_2 loading among the entire blends because HMDA has two primary amines as well as long linear carbon chain in the structure, so it provides extra reactive sites than other diamines (Wilk et al., 2017). But, the amine blends DEEA+ EDA, and DEEA+ PZ showed similar absorption performance because EDA has an only primary amine group in the chemical structure and PZ has only secondary amine groups in the chemical structure, as known fact that reactivity of primary amine is more than the secondary amine. In the case of DEEA+AEEA blend, AEEA diamine contains a primary amine, a secondary amine, and a hydroxyl group in the chemical structure but the hydroxyl group reduces the absorption capacity of diamine. The low absorption capacity has been shown by DEEA+DMAPA blend, and DMAPA contains primary and tertiary amine, but at a low pressure of CO_2 tertiary amine has lower absorption capacity than primary amine as well as a secondary amine. The primary and secondary amines directly react with CO_2 to form carbamate ions and tertiary amine reacts with CO_2 to form bicarbonate. So, DMAPA component present in amine blend solution provides an extra tertiary amino group which decreases the absorption capacity of DEEA+DMAPA blend.

3.4.3 Absorption rate

The absorption performance of an absorbent in terms of absorption rate has a significant role in the CO_2 capture process. The fast absorption rate required the smaller size of the absorption column which corresponds to reduce the capital cost of the CO_2 capture process (Du al., 2016). The absorption profile in terms of absorption capacity versus time was shown in figure 3.6 to investigate the effect of different types of diamine activator in an aqueous solution of DEEA.

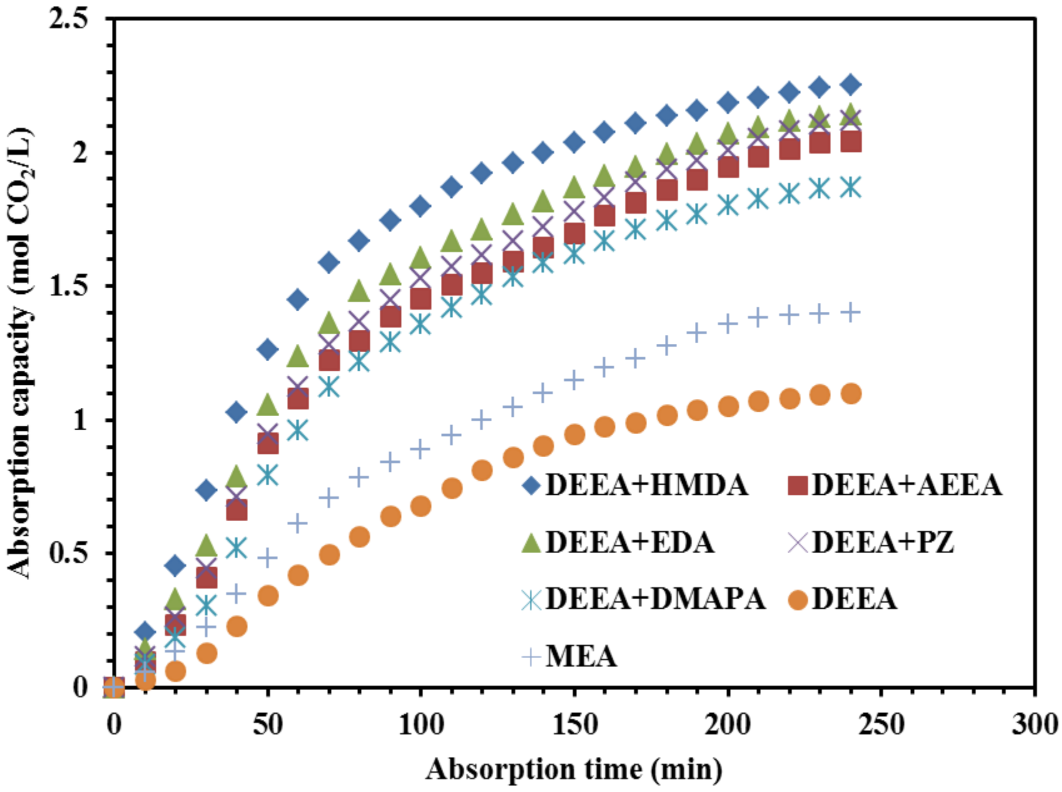

Figure 3.6 Absorption profile of CO_2 in various amine solutions at temperature 313.15 K and total concentration of 2.5 M

From figure 3.6, it can be seen that the entire amine solutions system showed a similar pattern in their profiles of absorption capacity with respect to time. It is also cleared that the absorption capacity of CO_2 significantly increased with increase in time within 60 min and then slowly achieved to a constant value. The enhanced absorption capacity of CO_2 attributed to the addition of diamine activators, which can be further used to prove the worth of the acquisition.

Finally, after blending diamine activators HMDA, EDA, PZ, AEEA, and DMAPA in DEEA solution, the absorption performance in terms of absorption capacity was increased by 100.09 %, 94.99 %, 92.94 %, 85.88 % and 70.39 % respectively, to single amine solution of DEEA as well as absorption capacity increased by 57.22, 52.58, 50.98, 45.41 and 33.33 respectively with respect to single solution of benchmark absorbent MEA. Further, the initial absorption rate of CO_2 was calculated with the help of the graph shown in figure 3.6, and a plot of the absorption rate of amine solutions was illustrated in figure 3.7 (Muchan et al., 2017). In figure 3.7, the order of initial absorption rate of amine solution follows as: DEEA + HMDA > DEEA + EDA > DEEA + PZ > DEEA + AEEA > DEEA+DMAPA > MEA > DEEA. All the DEEA blends have different types of diamine activators, which indicate that all the activators have two amine group provides more reaction sites, and they are successful in increasing the absorption rate. From the absorption data and for more clarification, a plot of absorption rate with an absorption capacity of entire amine solutions have presented in figure 3.8. From figure 3.8, it can be seen that the amine blend DEEA+HMDA, showed the best absorption performance in proposed amine blend and MEA. Also, the amine blend DEEA+PZ and DEEA+EDA showed similar absorption performance but better than DEEA+AEEA. Finally, the blend DEEA+DMAPA showed lower absorption performance but better than MEA and DEEA.

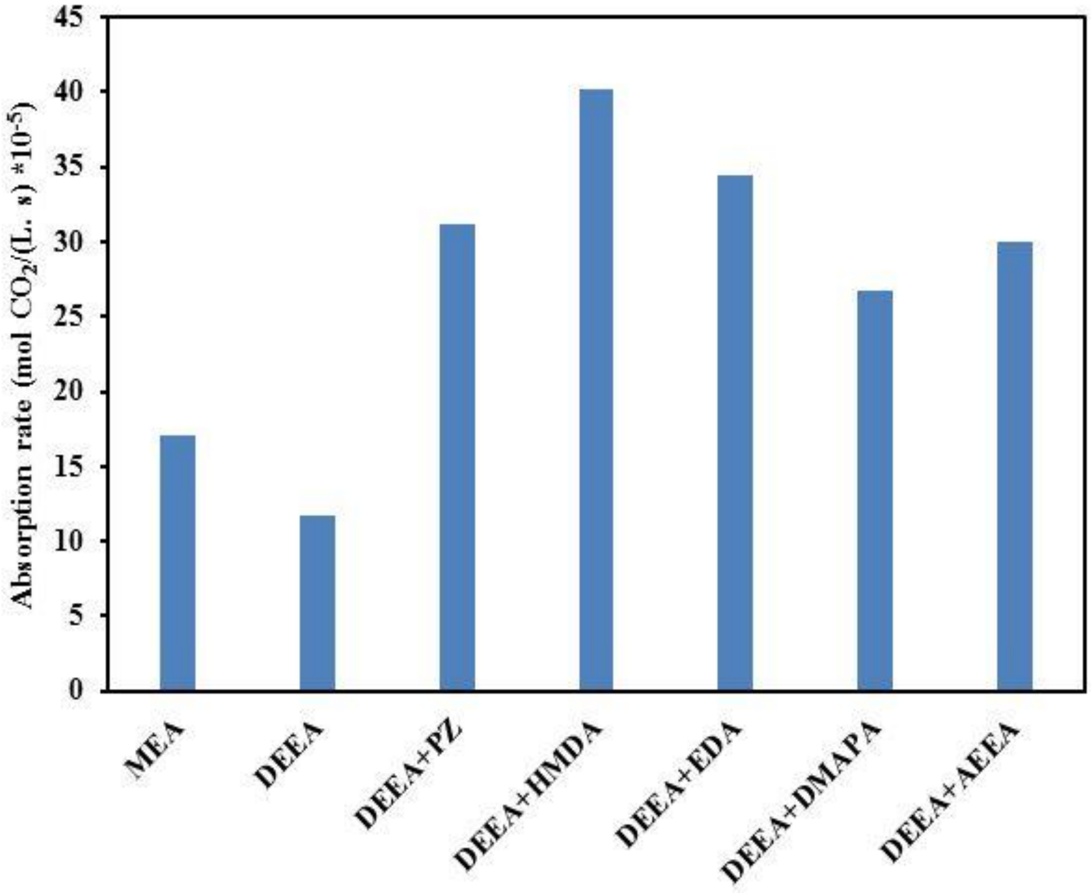

Figure 3.7 Absorption rate of CO_2 in various amine solutions of total concentration of 2.5 M

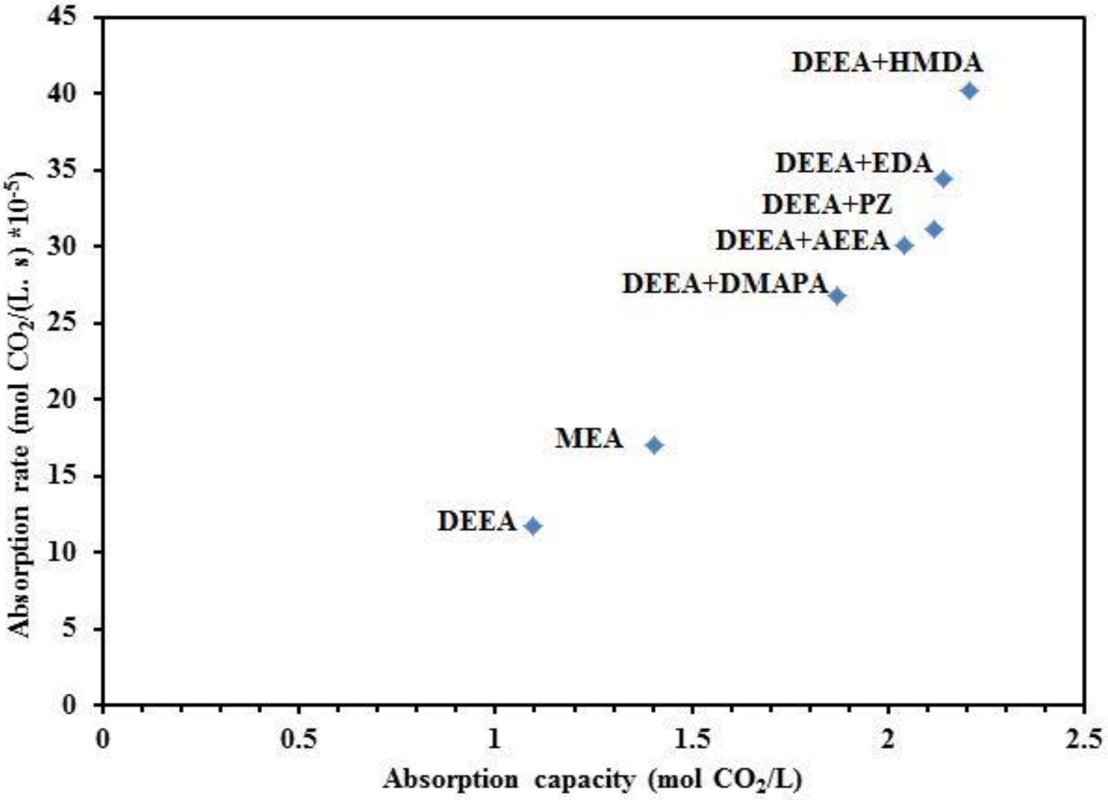

Figure 3.8 Plot of absorption rate versus absorption capacity in various amine solutions at temperature 363.15 K and the total concentration of 2.5 M

3.4.4 Desorption rate

As it is already known that reuse of absorbent is one of the most reliable ways to reduce the capital cost of CO_2 capturing industry, therefore desorption of CO_2 from amine solution is of utmost importance in a continuous process plant. Figure 3.9 shows the variation of CO_2 desorption capacity of the amine with stripping time, and it depicts a similar pattern like absorption. After the CO_2 released from carbonated amine solution, desorption capacity significantly decreased within 60 min and then became constant with time.

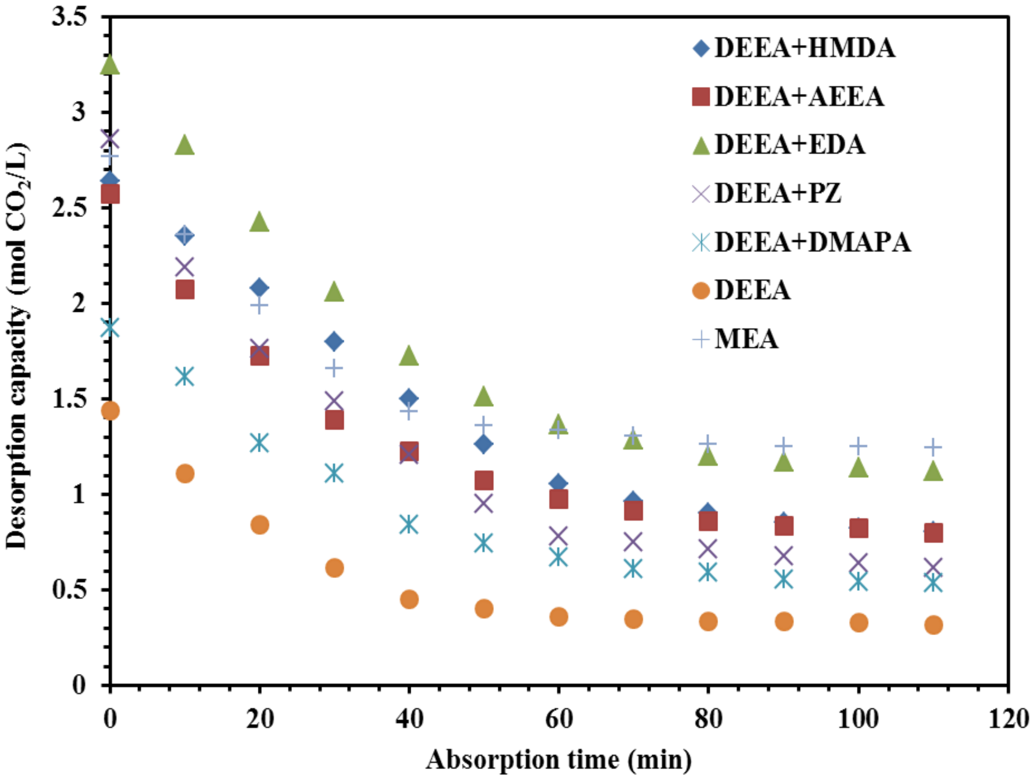

Figure 3.9 Desorption profile of CO_2 from various carbonated amine solutions at temperature 363.15 K and total concentration of 2.5 M

Further, the intial desorption rate of tested amine blend has been obtained by the slope of linear portion of plot between desorption capacity with time and represented in figure 3.10. It can be seen that, the initial desorption rate of all the tested amine blends follows the pattern as: DEEA + HMDA > DEEA + PZ > DEEA + EDA > DEEA + AEEA > DEEA+DMAPA > MEA > DEEA. So, the results showed that addition of diamine activators in DEEA solution significantly increased the desorption performance of tested entire amine blend. The absorbent DEEA+HMDA exhibited best desorption performance among the entire amine blend because HMDA has long carbon chain in chemical structure (Singh and Versteeg, 2008). DEEA showed the lowest initial desorption rate.

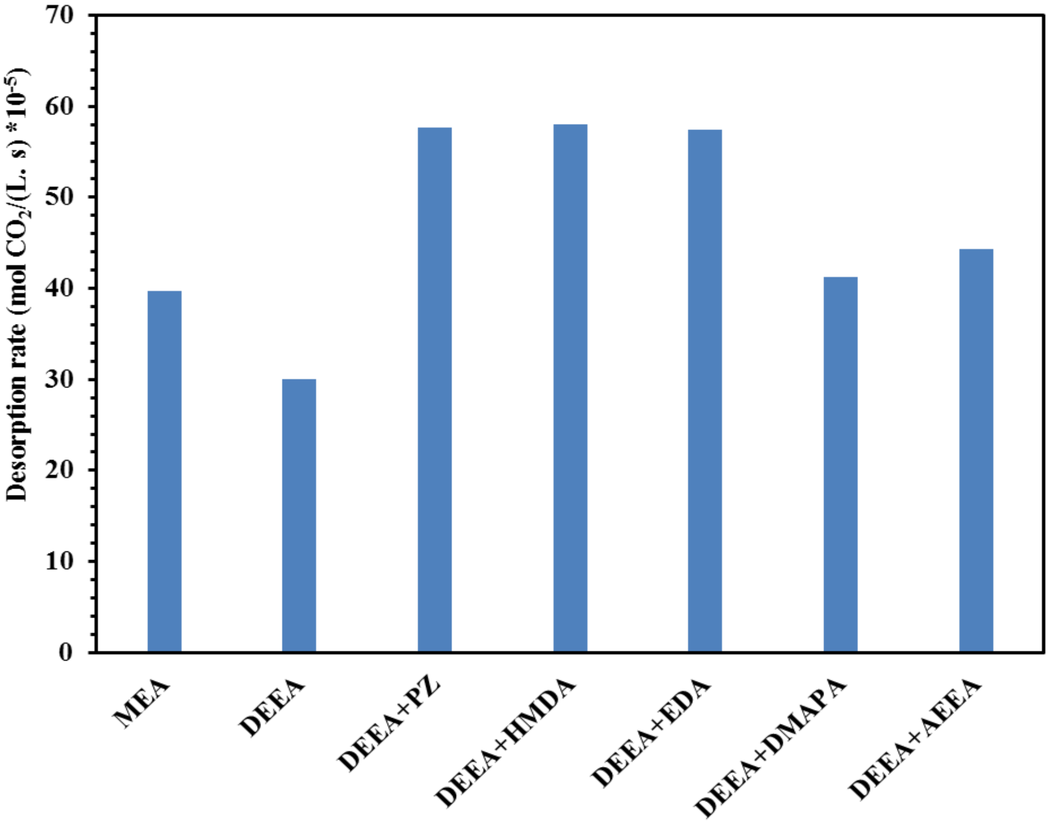

Figure 3.10 Desorption rate CO_2 in various amine solutions of total concentration of 2.5 M

From the desorption data and for more clarification, a plot of desorption rate verses desorption capacity has also shown in figure 3.11. As we know that, any absorbent is excellent for CO_2 capture when it has low desorption capacity and high desorption rate but from figure 3.11 it is cleared that the amine blend particularly DEEA+HMDA has high desorption rate because it is present in the upper right corner in the figure 3.11. So, absorbent represent the best desorption performance and it was further characterized by the evaluation of CO_2 cyclic capacity and regeneration efficiency.

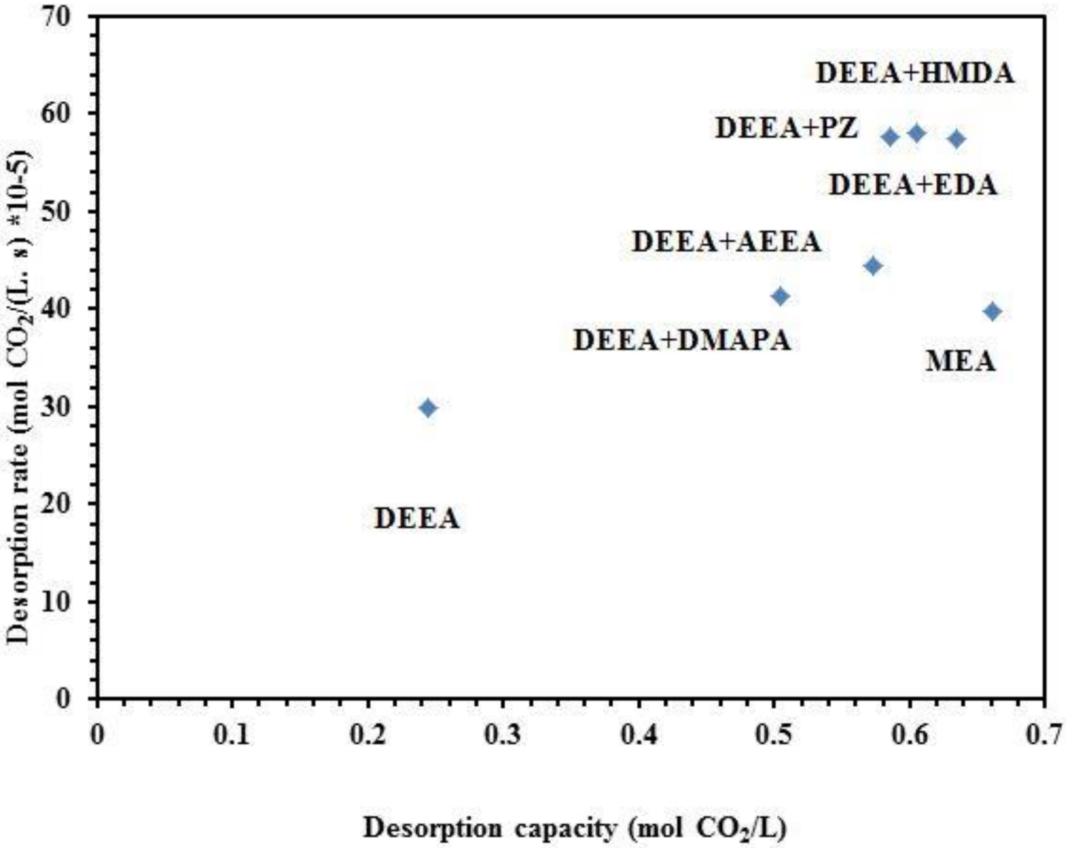

Figure 3.11 Plot of desorption rate versus desorption capacity from various amine solutions at temperature 363.15 K and the total concentration of 2.5 M

3.4.5 Cyclic capacity and Regeneration efficiency

In the regeneration process, the absorbent has continuously flowed from an absorption column to the desorption column in the CO_2 capture process. The absorbent having more cyclic capacity desired for less amount corresponds to low recirculation of absorbent through pumps and heat exchanger system, which can reduce the operating cost of the CO_2 capture process. Therefore, for the selection of absorbent for CO_2 capture application, an evaluation of the cyclic capacity of absorbent is required process parameter. The cyclic capacity was evaluated by the difference of CO_2 absorption capacity and desorption capacity at absorption-desorption conditions. The evaluated values of cyclic capacity of amine solutions are presented in figure 3.12.

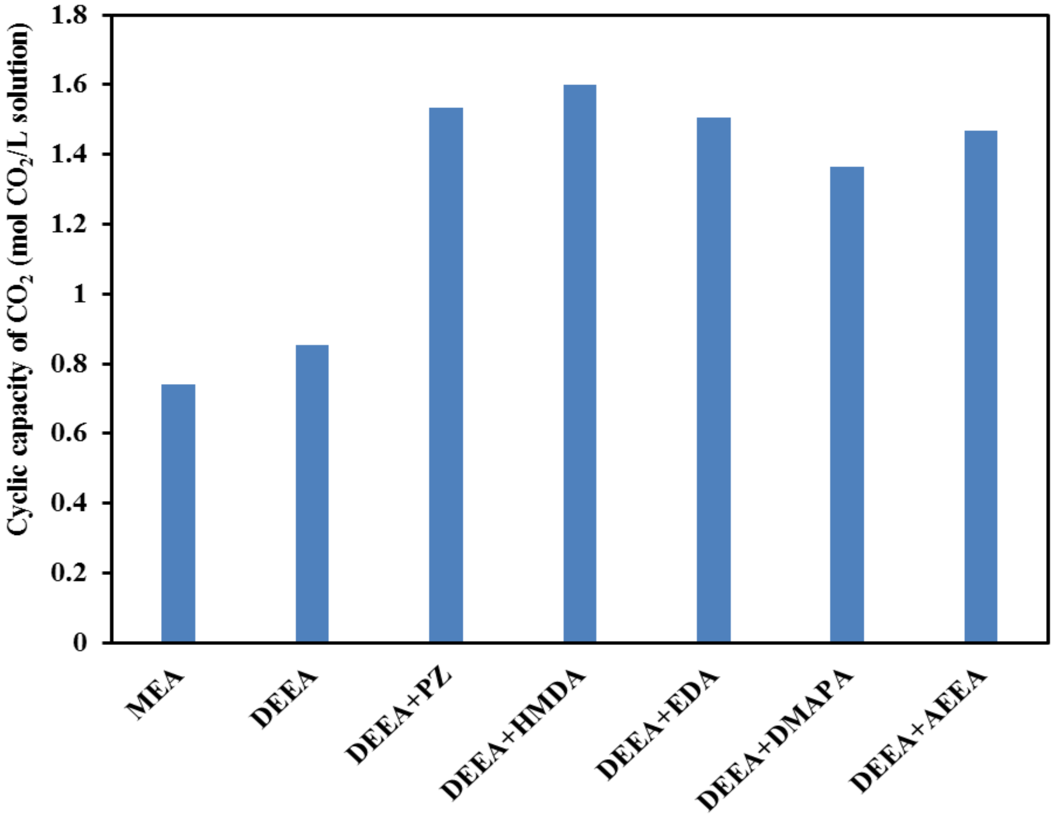

Figure 3.12 Cyclic capacity of CO_2 in various amine solutions

From figure 3.12, it can be seen that the order of CO_2 cyclic capacity is as DEEA+HMDA > DEEA+PZ > DEEA+EDA > DEEA+AEEA > DEEA+DMAPA > DEEA > MEA. It can be concluded that cyclic capacity of entire amine blend is more than single absorbent DEEA and benchmark absorbent MEA. Particularly, DEEA+HMDA blend showed the best regeneration performance in terms of cyclic capacity among the amine solutions because HMDA blended solution shows highest CO_2 absorption capacity and low desorption capacity of CO_2. The regeneration efficiency of CO_2 is represented as the percentage ratio of the cyclic capacity of CO_2 to the absorption capacity of CO_2. So in the evaluation of amine blend performance for continuous process, the regeneration efficiency of the studied amine blends for capturing CO_2 was investigated in five consecutive cycles using absorption-desorption experiment. The absorption and desorption experiments were performed within 60 min to see the effect of number of cycle, and results have been shown in figure 3.13. From figure 3.13, it was observed that the regeneration efficiency of all amine blends decreased slightly from one cycle to another cycle. It follows the same order as cyclic capacity of CO_2. Therefore, it can also be concluded that the studied amine blend can be considered for the continuous process used in the CO_2 capture applications.

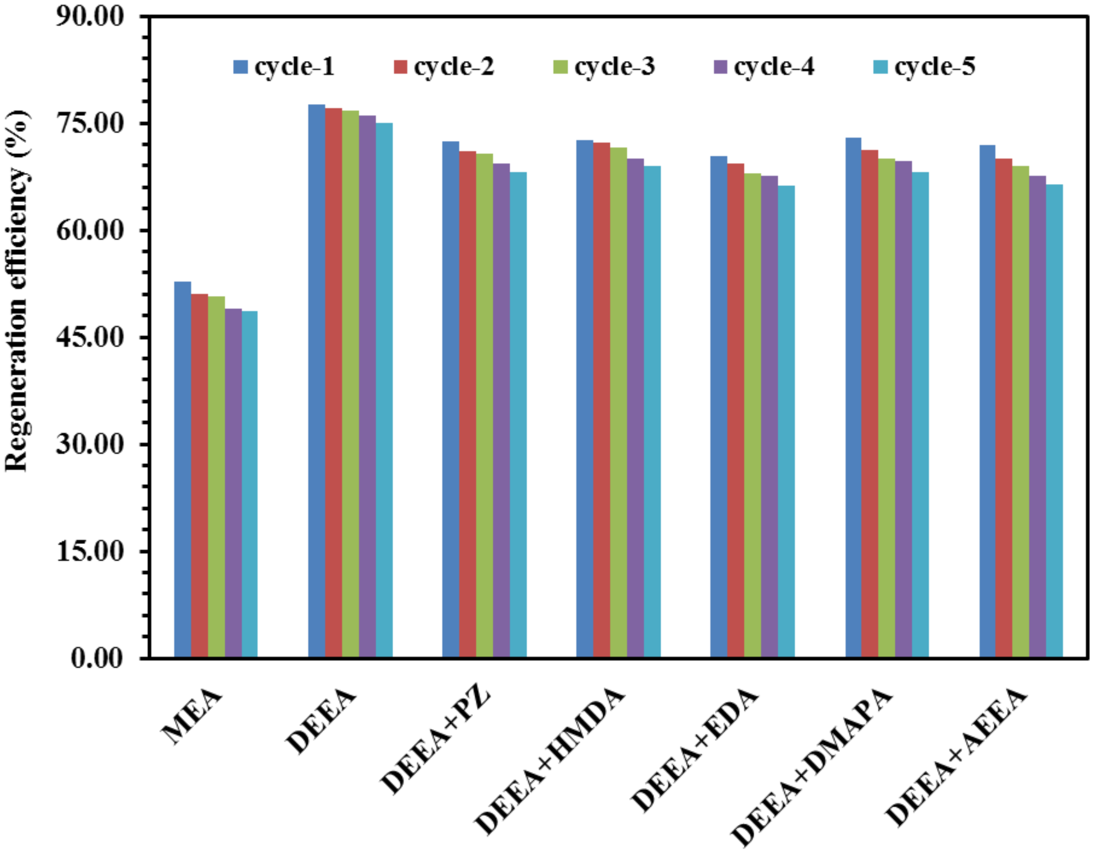

Figure 3.13 Regeneration efficiency of amine blends in different cycle

3.5 CONCLUSION

The different types of diamine activators PZ, EDA, AEEA, HMDA, and DMAPA were added into aqueous DEEA solution, making total amine blend solution of 2.5 M concentration. The relative comparison of amine blends for CO_2 capture was investigated by absorption-desorption experiments at an absorption temperature of 313.15 K and desorption temperature of 363.15 K with low partial pressure of CO_2 (20.26 kPa). The capture performance of amine blends was evaluated in terms of CO_2 loading, absorption rate, desorption rate, cyclic capacity, regeneration efficiency and number of regeneration cycle. The CO_2 loading drastically increased after the addition of diamine activator in single DEEA solutions and showed better capture performance than benchmark amine MEA and single amine DEEA. The absorption/desorption rate decreases with an increase in time, but both the rates are significantly improved after addition of diamine activator in DEEA solutions. The cyclic capacity of CO_2 follows the order as: DEEA+HMDA > DEEA+PZ > DEEA+EDA > DEEA+AEEA > DEEA+DMAPA > DEEA > MEA. Among all the tested amine blend and compared to MEA, the DEEA+HMDA solution shows good potential for absorption, desorption and regeneration indicating that this absorbent could be considered as an efficient solvent for CO_2 capture at low pressure of CO_2 applications.