

Equilibrium solubility of CO₂ in aqueous binary mixture of 2-(diethylamine)ethanol and 1, 6-hexamethyldiamine

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Abstract—CO₂ solubility data are important for the efficient design and operation of the acid gas CO₂ capture process using aqueous amine mixture. 2-(Diethylamino)ethanol (DEEA) solvent can be manufactured from renewable sources like agricultural products/residue, and 1,6-hexamethyldiamine (HMDA) solvents have higher absorption capacity as well as reaction rate with CO₂ than conventional amine-based solvents. The equilibrium solubility of CO₂ into aqueous binary mixture of DEEA and HMDA was investigated in the temperature range of 303.13-333.13 K and inlet CO₂ partial pressure in the range of 10.133-20.265 kPa. Total concentration of aqueous amine mixtures in the range of 1.0-3.0 kmol/m³ and mole fraction of HMDA in total amine mixture in the range of 0.05-0.20 were taken in this work. CO₂ absorption experiment was performed using semi-batch operated laboratory scale bubble column to measure equilibrium solubility of CO₂ in amine mixture, and CO₂ absorbed amount in saturated carbonated amine mixture was analyzed by precipitation-titration method using BaCl₂. Maximum equilibrium CO₂ solubility in aqueous amine mixture was observed at 0.2 of HMDA mole fraction in total amine mixture with 1.0 kmol/m³ total amine concentration. New solubility data of CO₂ in DEEA+HMDA aqueous mixtures in the current study was compared with solubility data available in previous studies conducted by various researchers. The study shows that the new absorbent as a mixture of DEEA+HMDA is feasible for CO₂ removal from coal-fired power plant stack gas streams.

Keywords: Equilibrium Solubility, Carbon Dioxide, 2-(Diethylamine)ethanol, 1,6-Hexamethyldiamine

INTRODUCTION

Global warming and climate change are serious environmental issues due to continuous release of major greenhouse gas CO₂ into the atmosphere. CO₂ is present in the waste gas stream which is released from various process industries like coal-fired thermal power plants, iron and steel plants, cement industries, natural gas treatment plants, chemical and petro-chemical manufacturing units. Among these sources, fossil fuel based coal-fired power plants are responsible for a major contribution in anthropogenic emissions of CO₂ worldwide [1,2]. So, capture of CO₂ from power plant waste gas streams has become a major challenge for environmentalists. The removal of CO₂ from power plant flue gas using aqueous amine solutions based on chemical absorption is a preferred CO₂ separation technology due to its cost effectiveness, maturity and handling huge amount of gas streams to a very low CO₂ concentration [3]. In this technology, various types of conventional alkanolamines such as primary amine monoethanolamine (MEA), secondary amine diethanolamine (DEA) and di-isopropanolamine (DIPA) and tertiary amine N-methyl diethanolamine (MDEA) and triethanolamine (TEA), and sterically-hindered amine 2-amino-2-methyl-1-propanol (AMP), have been used for capturing CO₂ from gas stream in gas treating plants as well as fossil fuel based thermal power

plants [4]. Cyclic polyamines like piperazine (PZ) and piperazine derivatives 1-(2-aminoethyl)piperazine (AEP), non-cyclic polyamine 1,6-hexamethyldiamine (HMDA), 2-(2-aminoethylamino)ethanol (AEEA) and 1,3-Diamino-2-propanol (DAP), have also been also tested for CO₂ removal from various gas streams at different operating conditions under lab-scale operation [5-8].

But, novel tertiary amine solvent, particularly DEEA shows better absorption performance than conventional tertiary amine solvent MDEA, and it can also be manufactured from renewable sources like agricultural products/residue as well as it shows efficient absorbance performance in CO₂ capture process [9,10]. Also, polyamine solvents have a good potential for CO₂ capture, because two or more amino groups are present in their chemical structure and, also, absorption capacity and higher reaction rate with CO₂ than conventional amine-based solvents [11]. Particularly, a polyamine solvent HMDA has a good potential for capturing CO₂ because it has high CO₂ absorption capacity and absorption rate [12, 13]. Further, addition of polyamine solvent as an activator with tertiary amine has been proven to exhibit good potential for CO₂ capture.

In past few years, for improving the CO₂ capture performance, a mixture of tertiary amine, particularly DEEA and polyamine, has been new research of interest due to advantages of each individual amine solvent. Many researchers investigated the evaluation of CO₂ capture performance parameters in terms of absorption capacity, cyclic capacity, absorption rate, absorption heat, absorption mass transfer co-efficient and reaction rate constant of CO₂ in various aqueous

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ous binary amine mixture of DEEA and polyamine such as DEEA+N-Methyl-1,3-diaminopropane (MAPA) [14], DEEA+Piperazine (PZ) [15-17,19,20] DEEA+1, 4-Butanediamine (BDA) [18], DEEA+1,6-hexamethyldiamine (HMDA) [19], DEEA+2-(2-aminoethyl-amino)ethanol (AEEA) [19,20], DEEA+Diethylenetetramine (DETA) [21,22]. A little information is available on equilibrium solubility of CO_2 in DEEA+HMDA aqueous mixture, but it requires wide ranges of solubility data at various operating conditions for the efficient design and operation of acid gas CO_2 capture process. Also, solubility of CO_2 in amine mixture is a prime steps design parameter to determine the absorption capacity and has a significant role in screening of any novel solvents. So, the present work is based on the improvement on CO_2 absorption performance in an aqueous binary mixture of DEEA and HMDA.

In this present research, equilibrium CO_2 solubility in aqueous mixture of DEEA and HMDA was measured using laboratory scale gas-liquid contactor bubble column in the temperature range of 303.13-333.13 K and CO_2 partial pressure range of 10.133-20.265 kPa. Total concentration of aqueous mixture was taken in the range of 1.0-3.0 kmol/m³ and HMDA mole fraction in total amine mixture was taken in the range of 0.05-0.20.

EXPERIMENTAL SECTION

1. Materials

The reagent grade chemicals DEEA and HMDA with mass purity greater than 99% were purchased from Sisco Research Laboratory, Mumbai and Tokyo Chemical Industry Co. Ltd., Japan, respectively. Aqueous binary mixtures of DEEA and HMDA were prepared without any purification using double distilled water in various

concentrations as per experimental need. Simulated CO_2 gas stream consisting of required concentration in the range of (10-20% by volume) was prepared by mixing two types of gas streams having one cylinder containing 20% CO_2 with balanced N_2 and other cylinders containing pure N_2 with the help of gas mixing chamber. The gas flow meter (0 to 3 LPM) was used to measure volume of gas out from gas cylinder with an accuracy of $\pm 1.0\%$. An infrared flue gas analyzer (model: Gas Board-3800P; Wuhan Cubic Optoelectronics Co. Ltd., Wuhan, China; with CO_2 measuring range of 0-100% by volume) was used to measure CO_2 in gas phase with an accuracy of $\pm 0.1\%$. A constant-temperature water bath (model: CE404, Narang Scientific Works Pvt. Ltd., New Delhi) was used for required operating temperature of aqueous mixture of amines (273 K to 473 K) within minute variation of ± 0.1 K. Other analytical reagent (AR) grade chemicals NaOH, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and HCl were used without any purification for analysis of liquid phase CO_2 .

2. Experimental Set-up and Procedure

A schematic diagram of experimental set-up for measuring equilibrium CO_2 solubility in aqueous mixture of DEEA and HMDA is shown in Fig. 1. This experimental set-up, described in our previous work [23], was used for experimentation with some few modifications. The gas-liquid (DEEA-HMDA- CO_2) system can be divided into three parts: simulating gas stream, an absorber, and for gas sampling analyzer. The experimental study on CO_2 solubility in aqueous amine mixture was conducted in laboratory scale borosilicate glass bubble column as an absorber in semi-batch mode. A known amount of aqueous amine mixture loaded in absorber was placed in a temperature-controlled water bath and maintained to require working temperature. Then, thermometers with subdivisions of 0.1 K were used to measure both the temperature of

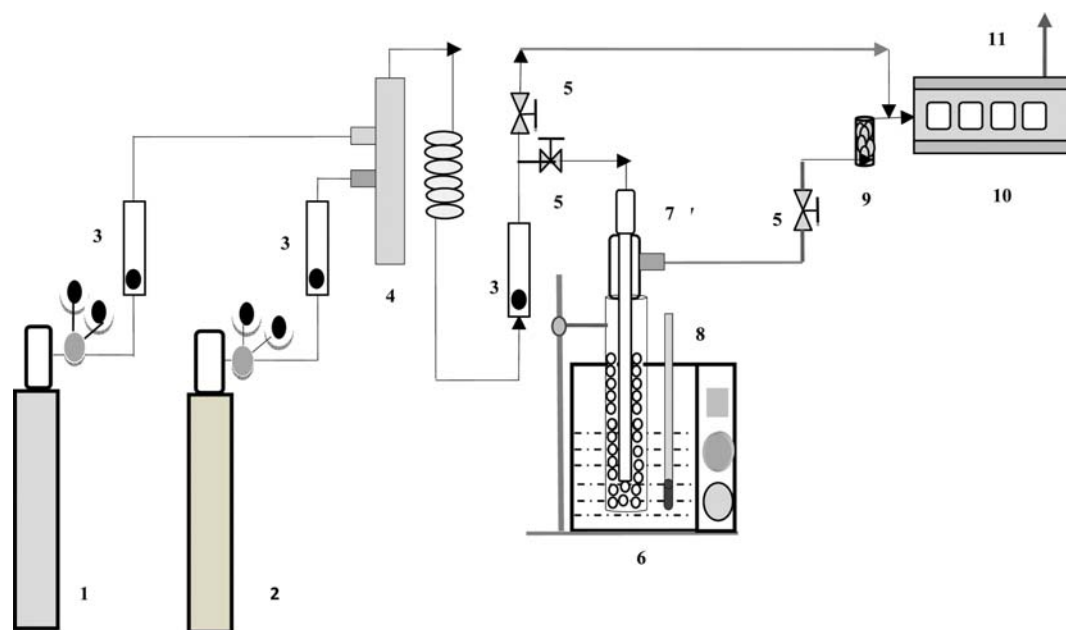


Fig. 1. Schematic diagram for CO_2 solubility measurement.

1. CO_2 gas cylinder
2. N_2 gas cylinder
3. Gas flow meter

4. Gas mixing chamber
5. Stainless steel valves
6. Water bath

7. Bubble column
8. Thermometer
9. Moisture absorber column

10. Multi-flue gas analyzer
11. Exhaust

water bath and liquid placed inside absorber. After that, N₂ gas was passed slowly through the absorber for approximately 10 min for removing trace gases already present in the column. Then, a fixed composition of CO₂ gas stream through gas flow meter with minimum flow rate was entered into the absorber and maintained continuous flow of CO₂ gas stream with non-interruption of amine mixture to create bubbles during absorption process moving from bottom to the upper surface of liquid. After a regular interval of time (5 min), the CO₂ outlet gas stream concentration was analyzed by infrared multi-flue gas analyzer, and this procedure was continued until the concentration of CO₂ gas stream in inlet and outlet was approximately the same to reach gas-liquid equilibrium phase. Then, saturated CO₂ solutions were analyzed by titration method using BaCl₂ and HCl as described in detail elsewhere [24]. At a given temperature and pressure, three aliquots of CO₂ loaded amine were taken to check the reproducibility, and the data were found to be reproducible to within 1%. The temperature was controlled within ± 0.1 K from 303.13 to 333.13 K, and the partial pressure was monitored for each run with an uncertainty of 0.01 kPa from 10.133 to 20.265 kPa.

RESULTS AND DISCUSSION

The equilibrium solubility of CO₂ in an aqueous binary mixtures of DEEA and HMDA was measured at wide ranges of operating parameters such as total amine concentration (C_T) ranging from 1.0 to 3.0 kmol/m³, HMDA mole fraction (X) in amine mixture

Table 1. Experimental CO₂ solubility in aqueous binary mixture of DEEA and HMDA at different operating conditions

S. N.	Operating conditions				β_{CO_2} (mol CO ₂ /mol amine)
	X	C_T (kmol/m ³)	T (K)	P_{CO_2} (kPa)	
1	0.05	1	313.13	20.265	0.644
2	0.05	2	313.13	20.265	0.585
3	0.05	3	313.13	20.265	0.547
4	0.1	1	313.13	20.265	0.704
5	0.1	2	313.13	20.265	0.648
6	0.1	3	313.13	20.265	0.602
7	0.15	1	313.13	20.265	0.791
8	0.15	2	313.13	20.265	0.738
9	0.15	3	313.13	20.265	0.692
10	0.2	1	313.13	20.265	0.926
11	0.2	2	313.13	20.265	0.874
12	0.2	3	313.13	20.265	0.841
13	0.2	2	313.13	10.133	0.761
14	0.2	2	313.13	12.666	0.782
15	0.2	2	313.13	15.199	0.801
16	0.2	2	313.13	17.732	0.831
17	0.2	2	313.13	20.265	0.874
18	0.2	2	313.13	20.265	0.932
19	0.2	2	313.13	20.265	0.874
20	0.2	2	313.13	20.265	0.812
21	0.2	2	313.13	20.265	0.771

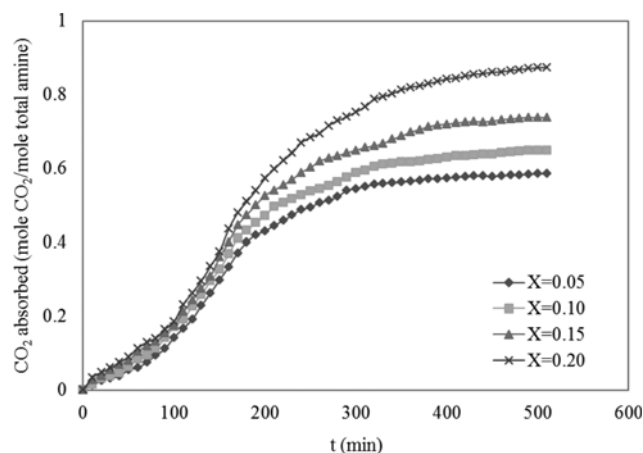


Fig. 2. CO₂ absorbed against time t with different mole fraction of HMDA in total amine mixture X at temperature T 313.13 K, partial pressure of CO₂ 20.265 kPa and total amine concentration C_T 2 kmol/m³.

from 0.05 to 0.20, amine mixture temperature (T) from 303.13 to 333.13 K and inlet CO₂ partial pressure (P_{CO_2}) in the range of 10.132 to 20.265 kPa. The experimental data obtained at various operating conditions for equilibrium CO₂ solubility in aqueous mixtures are shown in Table 1, where the equilibrium CO₂ solubility is expressed in terms of CO₂ loading as the number of moles of CO₂ absorbed per mole of total amine.

Fig. 2 shows the variation in the CO₂ amount in liquid phase as a function of time for different mole fraction of HMDA in a fixed concentration of total amine mixture for temperature of 20.265 kPa and inlet partial pressure of 313.13 K. The effect of HMDA mole fraction on CO₂ solubility was investigated by changing the composition of amine mixture with the help of varying concentration of HMDA as well as DEEA for a fixed total amine concentration of 2 kmol/m³. For a fixed HMDA mole fraction with a particular concentration of amine mixture, the CO₂ absorbed increased with time and then remained constant, which reveals that no more

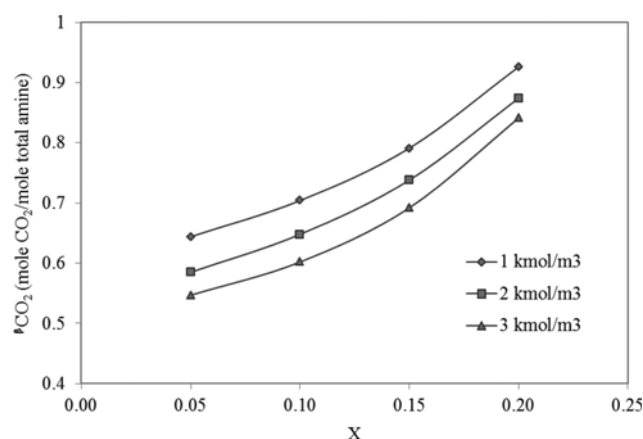


Fig. 3. CO₂ solubility β_{CO_2} against mole fraction of HMDA in total amine mixture X with different total amine concentrations C_T at temperature T 313.13 K and partial pressure of CO₂ 20.265 kPa.

amount of CO_2 was absorbed in this amine mixture and solution became completely saturated to achieve gas-liquid equilibrium.

Fig. 3 shows the variation of CO_2 solubility with HMDA mole fraction (from 0.05 to 0.20) for different total amine mixture concentration ranging from 1 to 3 kmol/m^3 . From Fig. 3, the solubility of CO_2 increases with increasing of HMDA mole fraction in total amine mixture, and maximum of equilibrium CO_2 solubility was observed at HMDA mole fraction of 0.2. The CO_2 solubility in amine mixture is enhanced by addition of more amount of HMDA in total amine mixture corresponding to increased CO_2 absorption, because HMDA possesses two primary amino groups available for reaction with CO_2 . Fig. 4 shows the effect of concentration of aqueous mixture of DEEA and HMDA on CO_2 solubility at a temperature of 313.15 K, CO_2 partial pressure of 20.265 kPa, and HMDA mole fraction of 0.2. From Fig. 4 there is a decrease in CO_2 solubility with increase in amine mixture concentration, because at higher concentration a smaller extent of reversion of

carbamate to bicarbonate can occur.

The inlet partial pressure of CO_2 plays a significant role in CO_2 gas absorption. The influence of CO_2 partial pressure on CO_2 solubility was studied at fixed concentration of amine mixture of 2.0 kmol/m^3 with an HMDA mole fraction of 0.20, temperature 313.13 K and CO_2 partial pressures varied from 10.133 to 20.265 kPa. As shown in Fig. 5, it is clearly seen that the CO_2 partial pressure incorporates a little result on CO_2 solubility between the variation of 10.199–12.63 kPa and 17.732–20.265 kPa. The CO_2 solubility increases from (0.76 to 0.87) mol of CO_2 per mole of total amine mixture as the CO_2 partial pressure increases from (10.133 to 20.265) kPa. Fig. 6 shows that the equilibrium CO_2 solubility increases with increasing inlet partial pressure of CO_2 in gas stream as a result of gas-phase mass transfer increases due to driving force rise, from the bulk gas phase to the gas-liquid interface.

Fig. 7 shows the effect of temperature on equilibrium CO_2 solubility in DEEA+HMDA amine mixture over the temperature range (303.15 to 333.15) K. In this regard, CO_2 partial pressure in gas

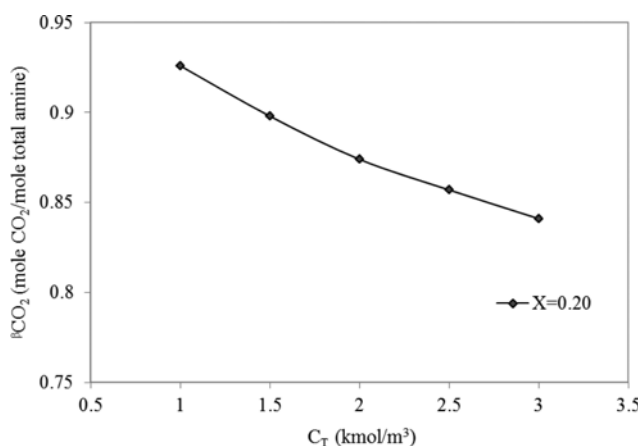


Fig. 4. CO_2 solubility βCO_2 against total amine concentrations C_T at temperature T 313.13 K, mole fraction of HMDA in total amine mixture X 0.20 and partial pressure of CO_2 20.265 kPa.

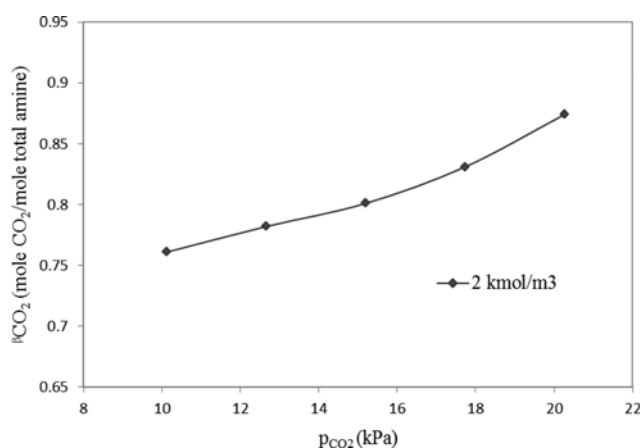


Fig. 6. CO_2 solubility βCO_2 against partial pressure of CO_2 at total amine concentration C_T 2 kmol/m^3 , temperature T 313.13 K and mole fraction of HMDA in total amine mixture X 0.2.

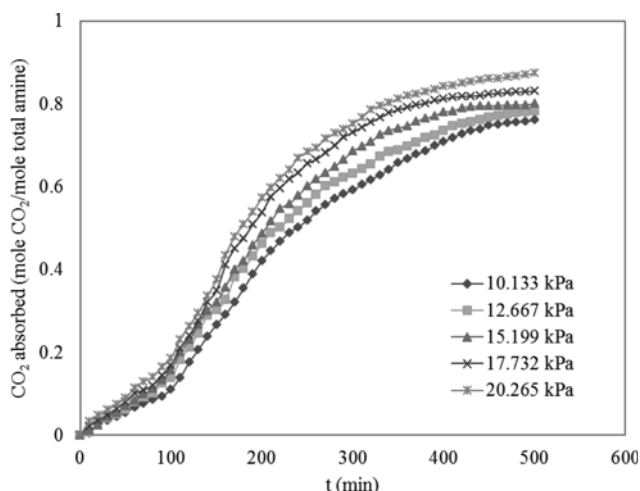


Fig. 5. CO_2 absorbed against time t with different partial pressure of CO_2 at temperature T 313.13 K, mole fraction of HMDA in total amine and total amine concentration C_T 2 kmol/m^3 .

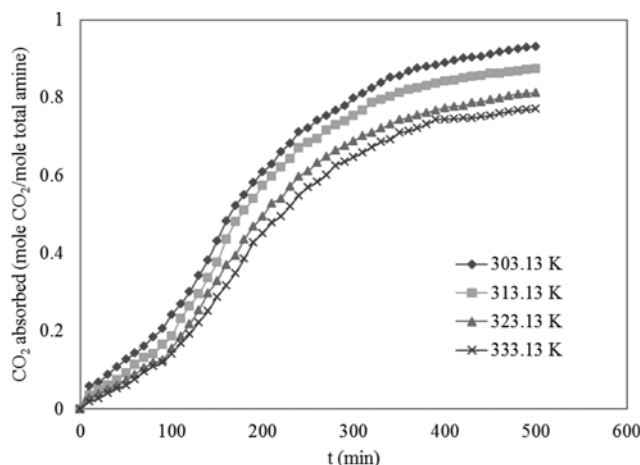


Fig. 7. CO_2 absorbed against time t with different temperature T at partial pressure of CO_2 20.265 kPa, total amine concentration C_T 2 kmol/m^3 and mole fraction of HMDA in total amine mixture X 0.20.

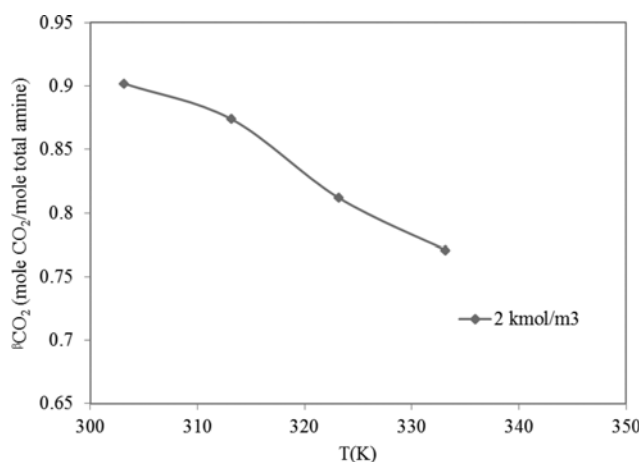


Fig. 8. CO₂ solubility β_{CO_2} against temperature T at total amine concentration C_T 2 kmol/m³, partial pressure of CO₂ 20.265 kPa and mole fraction of HMDA in total amine mixture X 0.20.

stream, total amine concentration, and HMDA mole fraction within the amine mixture were kept as 20.265 kPa, 2.0 kmol/m³, and 0.2, respectively. From Figs. 7 and 8, the solubility of CO₂ decreases with increasing temperature, and it is in agreement with information reported by Kundu and Bandyopadhyay [25] and Mondal [23]. The reactions between CO₂ and amines in absorption process are reversible, and as the temperature is increased then gas-liquid equilibrium is shifted to the reverse direction. Also, at higher temperatures, desorption of CO₂ takes place, and finally solubility of CO₂ decreases with increasing temperature.

Maximum CO₂ solubility obtained by different researchers during absorption of CO₂ in various amine mixtures is given in Table 2. It has been observed that the present amine aqueous mixture DEEA+HMDA has a higher solubility value than the previous studied amine mixture.

CONCLUSIONS

Absorbed amount of CO₂ in amine mixtures as a function of time has been presented, and it is observed a similar tradition of

plots with studied operating parameters such as HMDA mole fraction in total amine, total amine mixture concentration, CO₂ partial pressure, and temperature. At initial stage of experiment, absorption of CO₂ occurred appreciably within 0 to 150 min, and then very slowly to achieve complete dissolution of CO₂ in aqueous amine mixture to form saturated carbonated amine solution. Further, more and more dissolution of CO₂ in the mixture occurred due to the presence of two N groups (-NH₂ groups) in HMDA, finally enhanced CO₂ absorption capacity corresponds to higher CO₂ solubility. The equilibrium CO₂ solubility in amine mixture was found to be maximum 0.932 mol CO₂/mol amine with HMDA mole fraction in total amine of 0.2 at 1.0 kmol/m³ total amine mixture concentration, CO₂ partial pressure of 20.265 kPa and 303.13 K. The total time elapsed to achieve equilibrium varied from 400 to 600 min, depending on concentration of amine mixture and operating parameters. The equilibrium CO₂ solubility in DEEA+HMDA mixture increased with increasing partial pressure of CO₂ but showed decreasing value as temperature was increased. Also, the CO₂ solubility in present amine mixture was more than the other previous studied amine mixture of same kind available in the literature. So, the present absorbent aqueous amine mixture of DEEA and HMDA is promising for the removal of CO₂ from coal-fired power plant stack gas stream.

NOMENCLATURE

AEEA	: 2-(2-aminoethylamino)ethanol
AEP	: 1-(2-aminoethyl)piperazine
AMP	: sterically-hindered amine 2-amino-2-methyl-1-propanol
BDA	: 1, 4-Butanediamine
DAP	: 1, 3-Diamino-2-propanol
DEA	: diethanolamine
DEEA	: 2-(Diethylamine)ethanol
DETA	: diethylenetetramine
DIPA	: di-isopropanolamine
HMDA	: 1, 6-hexamethyldiamine
MAPA	: N-methyl-1, 3-diaminopropane
MDEA	: N-methyl diethanolamine
MEA	: monoethanolamine
PZ	: piperazine

Table 2. Comparison of the solubility of CO₂ in various aqueous mixtures of amines

Amine mixture	Operating conditions			β_{CO_2} (mol CO ₂ /mol amine)	References
	C_T (kmol/m ³)	T(K)	p_{CO_2} (kPa)		
DEEA+HMDA	2	303	20.27	0.932	This work
DEEA+HMDA	2	313	20.27	0.874	This work
DEEA+HMDA	2.5	313	20.27	0.857	This work
DEEA+HMDA	2.6	303	4.9	0.844	Sutar et al. [19]
DEEA+PZ	2.5	303	5.80	0.690	Sutar et al. [19]
DEA+AEEA	2	303	20.27	0.740	Bajpai and Mondal [24]
MDEA+DEA	2	313	20.00	0.696	Kundu and Bandyopadhyay [25]
DEEA+MEA	2.58	313	20.00	0.531	Luo et al. [26]
MDEA+PZ	2	313	15.20	0.750	Ali and Aroua [27]
DEEA+MAPA	5+2	313	17.40	0.374	Arshad et al. [28]

TEA : triethanolamine
 β_{CO_2} : CO₂ loading or Solubility [mol CO₂/mol amine]
 C_T : total amine concentration [kmol/m³]
 p_{CO_2} : partial pressure of CO₂ [kPa]
 T : temperature [K]
 X : mole fraction of HMDA in total amine mixture

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REFERENCES

1. D. Adams and J. Davison, IEA, *Greenhouse Gas R&D Programme* (2007).
2. M. Zaman and J. H. Lee, *Korean J. Chem. Eng.*, **30**, 1497 (2013).
3. A. B. Rao and E. S. Rubin, *Environ. Sci. Technol.*, **36**, 4467 (2002).
4. A. L. Kohl and R. B. Nielsen, *Gas Purification*, 5th Ed., Gulf Publishing, Houston (1997).
5. S. Bishnoi and G. T. Rochelle, *Chem. Eng. Sci.*, **55**, 5531 (2000).
6. J. H. Choi, Y. E. Kim, S. C. Nam, S. H. Yun, Y. I. Yoon and J.-H. Lee, *Korean J. Chem. Eng.*, **33**, 3222 (2016).
7. B. K. Mondal, S. S. Bandyopadhyay and A. N. Samanta, *Int. J. Green H. Gas Con.*, **56**, 116 (2017).
8. A. Wilk, L. Więclaw-Solny, A. Tatarczuk, A. Krótki, T. Spietz and T. Chwoła, *Korean J. Chem. Eng.*, **34**, 2275 (2017).
9. F. A. Chowdhury, H. Yamada, T. Higashii, K. Goto and M. Onoda, *Ind. Eng. Chem. Res.*, **52**, 8323 (2013).
10. P. D. Vaidya and E. Y. Kenig, *Chem. Eng. Sci.*, **62**, 7344 (2007).
11. P. Muchan, J. Narku-Tetteh, C. Saiwan, R. Idem and T. Supap, *Sep. Purif. Technol.*, **184**, 128 (2017).
12. Y. E. Kim, S. H. Yun, J. H. Choi, S. C. Nam, S. Y. Park, S. K. Jeong and Y. I. Yoon, *Energy Fuels*, **29**, 2582 (2015).
13. B. K. Mondal, S. S. Bandyopadhyay and A. N. Samanta, *Fluid Phase Equilib.*, **402**, 102 (2015).
14. U. Liebenthal, D. D. D. Pinto, J. G. M.-S. Monteiro, H. F. Svendsen and A. Kather, *Energy Procedia*, **37**, 1844 (2013).
15. P. D. Vaidya and E. Y. Kenig, *Ind. Eng. Chem. Res.*, **47**, 34 (2008).
16. P. B. Konduru, P. D. Vaidya and E. Y. Kenig, *Environ. Sci. Technol.*, **44**, 2138 (2010).
17. D. Fu, L. Wang, C. Mi and P. J. Zhang, *Chem. Thermodyn.*, **101**, 123 (2016).
18. Z. Xu, S. Wang and C. Chen, *Ind. Eng. Chem. Res.*, **52**, 9790 (2013).
19. P. N. Sutar, P. D. Vaidya and E. Y. Kenig, *Chem. Eng. Sci.*, **100**, 234 (2013).
20. H. Gao, B. Xu, H. Liu and Z. Liang, *Energy Fuels*, **30**, 7481 (2016).
21. L. Wang, S. An, S. Yu, S. Zhang, Y. Zhang, M. Li and Q. Li, *Int. J. Green H. Gas Con.*, **64**, 276 (2017).
22. J. Lee, Y. K. Hong and J. K. You, *Korean J. Chem. Eng.*, **34**, 1840 (2017).
23. M. K. Mondal, *J. Chem. Eng. Data*, **54**, 2381 (2009).
24. A. Bajpai and M. K. Mondal, *J. Chem. Eng. Data*, **58**, 1490 (2013).
25. M. Kundu and S. S. Bandyopadhyay, *Fluid Phase Equilib.*, **248**, 158 (2006).
26. X. Luo, S. Liu, H. Gao, H. Liao, P. Tontiwachwuthikul and Z. Liang, *Sep. Purif. Technol.*, **169**, 279 (2016).
27. B. S. Ali and M. K. Aroua, *Int. J. Thermophys.*, **25**, 1863 (2004).
28. M. W. Arshad, H. F. Svendsen, P. L. Fosbøl, N. V. Solms and K. Thomsen, *J. Chem. Eng. Data*, **59**, 764 (2014).