JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Solubility of CO_2 in an Aqueous Blend of Diethanolamine and Trisodium Phosphate

Hemant K. Balsora and Monoj K. Mondal*

Department of Chemical Engineering and Technology, Institute of Technology, Banaras Hindu University, Varanasi 221005, Uttar Pradesh, India

ABSTRACT: This work presents experimental results on the solubility of CO_2 in a new blend of diethanolamine (DEA) and trisodium phosphate (TSP) at temperatures ranging from (303.14 to 333.14) K and partial pressures from (10.133 to 20.265) kPa. Total concentrations of aqueous DEA + TSP blends were taken as (1.0, 1.5, and 2.0) $mol \cdot dm^{-3}$. In a particular blend, the mole fraction of TSP was in the range 0.02 to 0.20. The results show that CO_2 solubility in a blend with a particular total concentration increases with increasing mole fraction of TSP at fixed temperature and partial pressure of CO_2. The solubility of CO_2 in the blend decreases with increasing temperature but increases with increasing CO_2 partial pressure. The maximum CO_2 solubility in DEA + TSP blends was found to be 0.869 (mol of CO_2)$\cdot$(mol of absorbent)$^{-1}$ at 313.14 K, a total concentration of 2.0 $mol \cdot dm^{-3}$, and a TSP mole fraction of 0.2. The experimental results of the present study are compared with those for other blends available in the literature.

INTRODUCTION

Fossil fuels are the main source of energy and also, unfortunately, of pollutants, greenhouse gases (GHGs), and other trace atmospheric varieties. Coal is the primary fuel in thermal power plants; gasoline and diesel are the primary fuels for automobiles. There is also limited use of natural gas in these energy activities. Combustion of fossil fuels releases a massive amount of CO_2 into the atmosphere. It has been reported that as a result of human activities, roughly (26 to 30) % of the total CO_2 comes from fossil fuel combustion used for electricity generation.[1−3] Scientists have found a direct relationship between CO_2 emissions and global warming and climate change (CO_2 accounts for more than approximately 55 % of the total observed global warming).[4] Amine-based chemical absorption is a well-established and mature technology among several technologies available to reduce CO_2 emission from industrial gas streams. Commonly used amines are monoethanolamine (MEA), diethanolamine (DEA), *N*-methyldiethanolamine (MDEA), and di-2-propanolamine (DIPA).[5,6] Other absorbents, such as diglycolamine (DGA), 2-(2-aminoethylamino)ethanol (AEE), 2-amino-2- methyl-1-propanol (AMP), *N*-(2-aminoethyl)-1,3-propanediamine ($AEPDNH_2$), triethanolamine (TEA), triethylenetetramine (TETA), piperazine (PZ), glucosamine (GA), sodium hydroxide (NaOH), ammonia (NH_3), potassium carbonate (K_2CO_3), potassium hydroxide (KOH), sodium carbonate (Na_2CO_3), and so on w?>were also tested for CO_2 removal. Most of the amines mentioned have been used in large-scale units for CO_2 removal successfully for decades.

Blends of alkanolamines have also recently been suggested to capitalize on the advantages of each amine (e.g., a primary or secondary alkanolamine and a tertiary alkanolamine or a sterically hindered alkanolamine). Activation of alkanolamine solvents for CO_2 removal to take advantage of a relatively high rate of reaction of CO_2 with the activating agent can be combined with the advantages of the high loading capacity of tertiary alkanolamines or hindered alkanolamines and the relatively low cost of regeneration of the activated solvent.[7]

Many researchers have reported the absorption characteristics of CO_2 in blended amines. The low vapor pressure of DEA makes it suitable for low-pressure operations, as vaporization losses are quite negligible. Further, DEA solutions are less corrosive than MEA solutions. In view of this, DEA-based blends appear to be potential solvents for gas treatment processes.[8] The solubilities of CO_2 in various DEA blends have been reported in the literature.[8−14]

Trisodium phosphate (TSP) is an inorganic solvent that is highly alkaline and nonvolatile in nature and undergoes negligible thermal degradation. It has properties suitable for use as an absorbent for acid gas treatment. There is no work listed to date in the literature concerning the solubility of CO_2 in aqueous blends of DEA and TSP. In this work, the absorption of CO_2 by aqueous blends of DEA and TSP has been experimentally studied to generate new solubility data at total blend concentrations in the range (1.0 to 2.0) $mol \cdot dm^{-3}$, temperatures from (303.14 to 333.14) K, and CO_2 partial pressures from (10.133 to 20.265) kPa.

EXPERIMENTAL SECTION

Materials. All of the chemicals used were AR-grade. DEA with minimum purity 98 % (Sisco Research Laboratories Pvt. Ltd., Mumbai, India) was used to prepare amine blends. TSP with minimum purity 98 % (RFCL Ltd., New Delhi, India) was used without further purification. All solutions were prepared using deionized water. Two gas streams, one from a cylinder containing

Special Issue: Kenneth N. Marsh Festschrift

Received: July 4, 2011
Accepted: October 12, 2011
Published: November 01, 2011

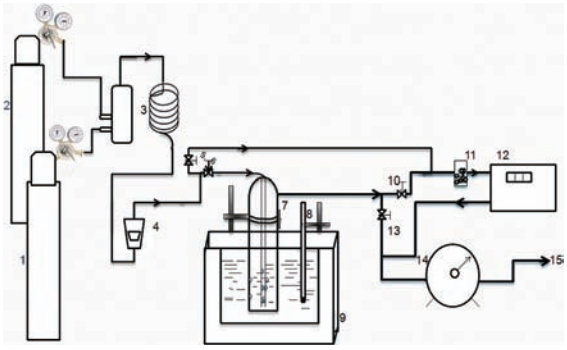

Figure 1. Schematic diagram of the experimental setup: 1, CO_2 gas cylinder; 2, N_2 gas cylinder; 3, mixing device; 4, gas-flow rotameter; 5, 6, 10 and 13, SS valves; 7, bubble column; 8, thermometer 9, water bath; 11, silica gel bed; 12, gas analyzer; 14, wet-gas flow meter; 15, exhaust.

20 % CO_2 in N_2 and another from a cylinder containing 99.99 % pure N_2, were mixed together in a gas-mixing and pressure-release chamber to get the desired composition of CO_2 in the inlet gas stream. The volume of gas passed was measured using a wet-gas flow meter. A microprocessor-based CO_2 analyzer [UNIPHS 225 p.m., (0 to 100) % CO_2 by volume] with an accuracy of ± 0.2 % was used for CO_2 analysis in the gas phase. A constant-temperature water bath (CE404, Narang Scientific Works Pvt. Ltd., New Delhi, India) with a range of (0 to 200) °C and an accuracy of ± 0.1 °C was used to monitor the operating temperature.

Apparatus and Procedure. The experimental setup described in our earlier communication[12] with little modification was used for the measurement of CO_2 solubility in aqueous blends of DEA and TSP in the present work. A schematic diagram of the experimental apparatus is shown in Figure 1. The bubble column containing an aqueous solution of DEA + TSP blend was placed into the constant-temperature water bath. Thermometers with subdivisions of 0.1 K were used to regulate both the bath and the liquid temperature inside the column. The bubble column of about 500 cm^3 capacity was filled with an aqueous solution of blend prior to the start of the experiment. After a constant temperature was maintained inside the bath, the main gas stream was slowly turned on, and the gas was allowed to bubble into the liquid at the minimum possible flow rate to ensure that the bubbles did not collapse during the flow in the liquid. After a regular time interval of 10 min, the CO_2 composition in both the inlet and outlet gas streams was measured using the microprocessor-based CO_2 analyzer. This procedure was continued until the CO_2 composition in the outlet gas stream became same as the inlet gas composition, indicating that equilibrium had been attained. The CO_2 solubility in the liquid phase was estimated by acidifying a known volume of the loaded liquid sample with 0.6 mol % HCl solution. At a given temperature and pressure, at least two liquid equilibrium samples 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 of the desired value, and the equilibrium total pressure was measured with an accuracy of ± 0.5 kPa in the range studied.

RESULTS AND DISCUSSION

The CO_2 solubility was determined for aqueous DEA + TSP blends having total concentrations of blend (C_T) in the range (1.0 to 2.0) $mol \cdot dm^{-3}$ and TSP mole fractions from 0.02 to 0.20 over the temperature range (303.14 to 353.14) K at partial pressures of CO_2 from (10.133 to 20.265) kPa. The experimental data on the solubility of CO_2 in aqueous DEA + TSP blends are given in Table 1. The effect of the mole fraction of TSP on CO_2 solubility was investigated by varying the TSP mole fraction in the DEA + TSP blend from 0.02 to 0.20 with changing proportions of DEA and TSP for a fixed total blend concentration of 2.0 $mol \cdot dm^{-3}$ (Figure 2). At a particular mole fraction of TSP in the blend, the amount of CO_2 absorbed increases with time to a maximum value and then remains constant at this value, indicating that no further absorption takes place (i.e., equilibrium is achieved). It is clearly seen from Figure 2 that the CO_2 solubility increases with increasing mole fraction of TSP in the blend. At the onset of the experiment, the amounts of CO_2 absorbed in blends having TSP mole fractions of 0.02, 0.05, and 0.10 are higher than that for a TSP mole fraction of 0.20 up to certain time, whereas at later times the CO_2 loading is highest in the blend with a TSP mole fraction of 0.20, followed by the blends with TSP mole fractions of 0.10, 0.05, and 0.02. At the early stage,

Table 1. Experimental Data on the Solubility of CO_2 in Aqueous DEA + TSP Blends

	T		C_T	p_{CO_2}	m_{CO_2}
run	K	X	$mol \cdot dm^{-3}$	kPa	$(mol\ of\ CO_2) \cdot (mol\ of\ absorbent)^{-1}$
1	313.14	0.02	1.0	15.199	0.6200
2	313.14	0.05	1.0	15.199	0.6548
3	313.14	0.10	1.0	15.199	0.6980
4	313.14	0.20	1.0	15.199	0.7344
5	313.14	0.02	1.5	15.199	0.6380
6	313.14	0.05	1.5	15.199	0.6770
7	313.14	0.10	1.5	15.199	0.7100
8	313.14	0.20	1.5	15.199	0.7861
9	313.14	0.02	2.0	15.199	0.6780
10	313.14	0.05	2.0	15.199	0.7165
11	313.14	0.10	2.0	15.199	0.7395
12	313.14	0.20	2.0	15.199	0.8419
13	313.14	0.02	2.0	10.133	0.6910
14	313.14	0.05	2.0	10.133	0.7050
15	313.14	0.10	2.0	10.133	0.7180
16	313.14	0.20	2.0	10.133	0.8290
17	313.14	0.02	2.0	12.666	0.7030
18	313.14	0.05	2.0	12.666	0.7110
19	313.14	0.10	2.0	12.666	0.7280
20	313.14	0.20	2.0	12.666	0.8310
21	313.14	0.02	2.0	17.732	0.7290
22	313.14	0.05	2.0	17.732	0.7320
23	313.14	0.10	2.0	17.732	0.7530
24	313.14	0.20	2.0	17.732	0.8510
25	313.14	0.02	2.0	20.265	0.7450
26	313.14	0.05	2.0	20.265	0.7490
27	313.14	0.10	2.0	20.265	0.7690
28	313.14	0.20	2.0	20.265	0.8690
29	303.14	0.20	2.0	15.199	0.8690
30	323.14	0.20	2.0	15.199	0.7946
31	333.14	0.20	2.0	15.199	0.7424

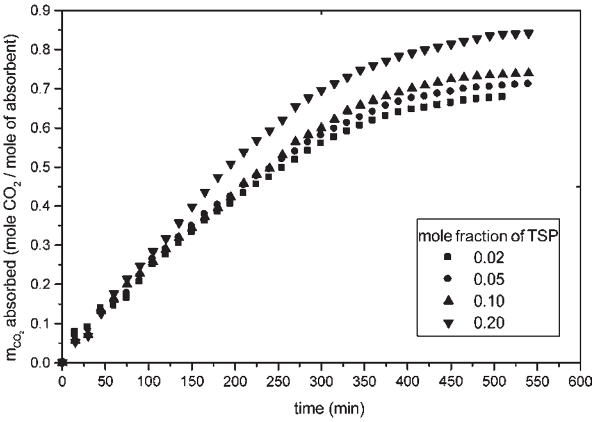

Figure 2. Time variation of the amount of absorbed CO_2 (m_{CO_2}) in 2.0 $mol \cdot dm^{-3}$ DEA + TSP blends with various mole fractions of TSP at $T = 313.14$ K and $p_{CO_2} = 115.199$ kPa.

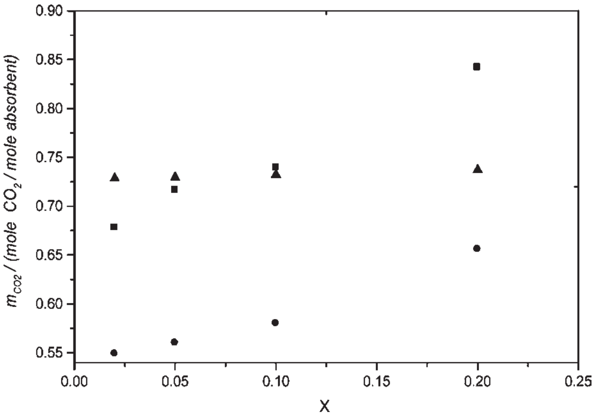

Figure 3. CO_2 solubility m_{CO_2} in blends of DEA with various additives (PZ, AMP, TSP) as a function of X, the mole fraction of the additive, at $T = 313.14$ K and $p_{CO_2} = 15.199$ kPa: ●, DEA + PZ (Mondal[12]); ▲, DEA + AMP (Seo and Hong[13]); ■, DEA + TSP (this work).

CO_2 absorption due to the reaction between CO_2 and the dissolved alkalinity mostly offered by DEA seems to occur very fast. As time proceeds, the active amount of DEA in the solution decreases. As a result, more and more dissolution of TSP occurs as a result of the decrease in the pH of the solution. Therefore, in the latter stage, absorption is dominated by TSP, which leads to higher equilibrium solubility of CO_2 in the blend for larger TSP mole fractions. In Figure 3, the experimental results for the present DEA + TSP blends are also compared with those for other DEA-based blends available in the literature. From Figure 3, it is clear that the present system has greater solubility of CO_2 than the DEA + PZ and DEA + AMP blends.

Figure 4 shows the effect of the total blend concentration on the CO_2 solubility at a temperature of 313.14 K, a CO_2 partial pressure of 15.199 kPa, and a TSP mole fraction of 0.2. The CO_2 solubility in blends usually decreases with C_T because of the smaller extent of reversion of carbamate to bicarbonate at higher concentrations. This behavior was observed by Lee et al.[15] and Mondal,[12] as shown in Figure 4. In contrast, in the present DEA + TSP blends, the CO_2 solubility increases as C_T increases. This may be due to the fact that TSP has a higher equilibrium CO_2 solubility and that continuous reversion of carbamate to bicarbonate at higher concentrations can occur because of the presence of TSP.

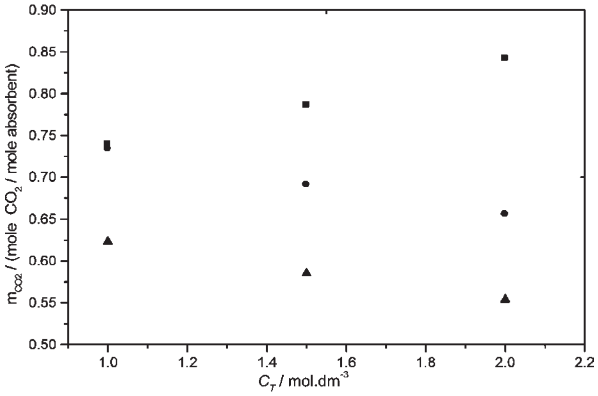

Figure 4. CO_2 solubility m_{CO_2} at different total absorbent concentrations C_T at $T = 313.14$ K: ■, DEA + TSP (this work); ●, DEA + PZ (Mondal[12]); ▲, DEA (Lee et al.[15]).

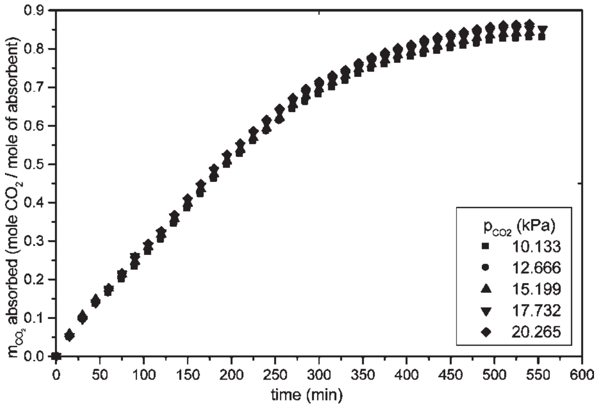

Figure 5. Time variation of the amount of absorbed CO_2 at various inlet partial pressures of CO_2 in a 2.0 $mol \cdot dm^{-3}$ DEA + TSP blend with a TSP mole fraction of 0.2 at 313.14 K.

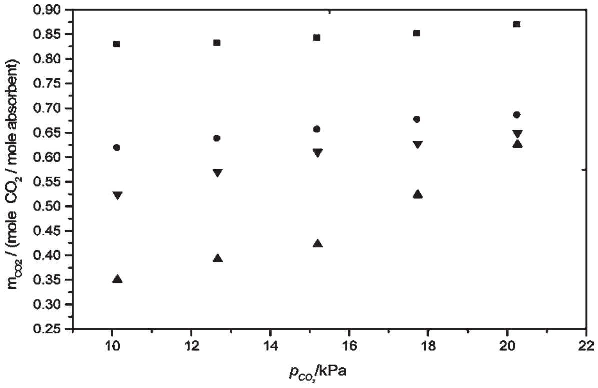

Figure 6. CO_2 solubility m_{CO_2} in various DEA blends as a function of the inlet partial pressure p_{CO_2} at $T = 313.14$ K: ■, DEA + TSP (this work); ●, DEA + PZ (Mondal[12]); ▼, DEA + AMP (Seo and Hong[13]); ▲, DEA + MDEA (Kundu and Bandyopadhyay[8]).

The inlet CO_2 partial pressure also plays an important role in CO_2 absorption. Its effect on the CO_2 solubility was studied in a 2.0 $mol \cdot dm^{-3}$ DEA + TSP blend with a TSP mole fraction of

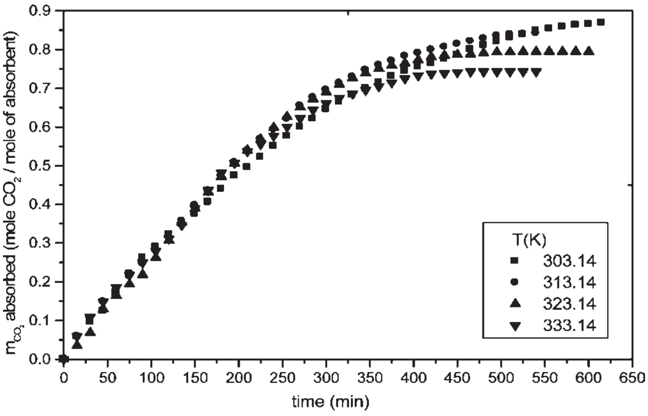

Figure 7. Time variation of the amount of adsorbed CO_2 with temperature in a 2.0 mol·dm^{-3} DEA + TSP blend having a TSP mole fraction of 0.2 at 15.199 kPa.

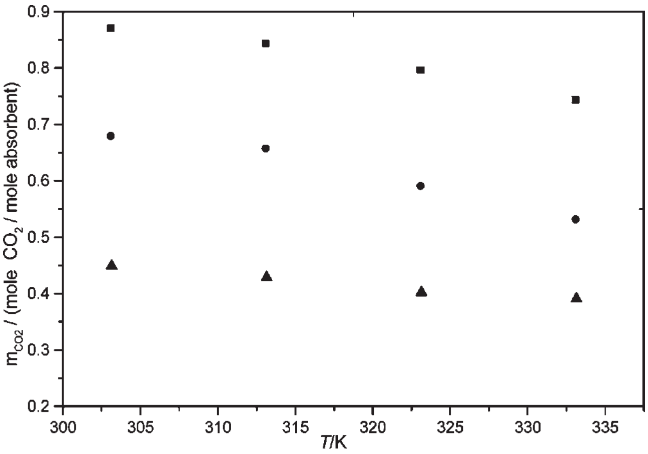

Figure 8. CO_2 solubility m_{CO_2} in various DEA-based blends as a function of temperature T: ■, DEA + TSP (this work); ●, DEA + PZ (Mondal[12]); ▲, DEA + MDEA (Kundu and Bandyopadhyay[8]).

0.20 at 313.14 K for CO_2 partial pressures in the inlet gas stream ranging from (10.199 to 20.265) kPa. Figure 5 shows that the CO_2 partial pressure has a very small effect on the CO_2 solubility for the range studied. The CO_2 solubility increases from (0.83 to 0.87) (mol of CO_2)·(mol of absorbent)$^{-1}$ as the CO_2 partial pressure increases from (10.133 to 20.265) kPa. The experimental results were also compared with the published data (Figure 6). Figure 6 shows that the CO_2 solubility increases with increasing CO_2 partial pressure in the inlet gas stream because it increases the interfacial mass transfer by dominating the gas-phase mass transfer as a result of the increase in the driving force from the bulk of the gas phase to the gas–liquid interface. The experimental data obtained in DEA + TSP blends show a higher absorption capacity relative to the results available in the literature.[8,12,13]

The effect of temperature on the CO_2 solubility in DEA + TSP blends over the temperature range (303.14 to 333.14) K is shown in Figure 7. The inlet CO_2 partial pressure, total blend concentration, and TSP mole fraction in the blend were 15.199 kPa, 2.0 mol·dm^{-3}, and 0.2, respectively. From Figures 7 and 8, the solubility of CO_2 decreases with increasing temperature, in agreement with the data reported by Kundu and Bandyopadhyay[8] and Mondal.[12] There may be two reasons for this: (1) most of the reactions involved in CO_2 absorption in amines are reversible, and as the temperature is increased, equilibrium shifts in the backward direction; (2) at higher temperatures, desorption of CO_2 also takes place, which is quite natural because the solubility of gases generally decreases with increasing temperature. Maximum CO_2 loadings reported by various researchers for different blends are given in Table 2. It has been observed that the present DEA + TSP blends have a higher loading value than the other blends reported in the literature.

Table 2. Maximum CO_2 Solubilities in Various Blends

entry	amine blend	m_{CO_2} / (mol of CO_2)·(mol of absorbent)$^{-1}$	reference
1	DEA + TSP	0.869	this work
2	MDEA + PZ	0.75	Ali and Aroua[16]
3	DEA+ MDEA	0.706	Benamor and Aroua[17]
4	DEA + MDEA	0.690	Kundu and Bandyopadhyay[8]
5	DEA + PZ	0.662	Mondal[12]
6	DEA + AMP	0.614	Seo and Hong[13]
7	DEA + MDEA	0.585	Murrieta-Guevara et al.[11]
8	MDEA + PZ	0.561	Jenab et al.[18]
9	MDEA + PZ	0.500	Liu et al.[19]
10	DEA + MDEA	0.492	Austgen et al.[9]
11	TIPA + PZ	0.271	Daneshvar et al.[20]

■ CONCLUSIONS

Plots of the time variation of the amount of absorbed CO_2 have the same trend (i.e., the amount of absorbed CO_2 initially increases more rapidly and then with increasing time increases more slowly, finally attaining a constant value showing equilibrium) irrespective of the CO_2 partial pressure, TSP mole fraction, and total blend concentration. The total blend concentration showed a positive effect on the CO_2 solubility, which is the opposite of the behavior for other blends available in literature. The time required to reach equilibrium was varied from (285 to 615) min. At the early stage, CO_2 absorption in the DEA + TSP blends seemed to be dominated by DEA. As time proceeds, more and more dissolution of TSP occurs because of the decrease in the pH of the solution. Therefore, in the latter stage, the absorption is dominated by TSP. The addition of a small amount of TSP to an aqueous DEA solution significantly enhances the CO_2 absorption, and a higher proportion of TSP in the blend leads to a higher CO_2 loading. The CO_2 solubility increases with increasing inlet CO_2 partial pressure but decreases as temperature increases. The solubility of CO_2 in the present DEA + TSP blends is larger than those in other published works, so the present blends may become suitable and feasible absorbents for removal of postcombustion CO_2 from power plants.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mkmondal13@yahoo.com.

Funding Sources

The authors thank Banaras Hindu University for providing necessary help and financial support to carry out the present work.

REFERENCES

(1) Lyngfelt, A.; Leckner, B.; Mattisson, T. A Fluidized-Bed Combustion Process with Inherent CO_2 Separation: Application of Chemical-Looping Combustion. *Chem. Eng. Sci.* **2001**, *56*, 3101–3113.

(2) Kourosh, E. Z.; Shafeen, A.; Salvador, C. CO_2 Capture and Development of an Advanced Pilot-Scale Cryogenic Separation and Compression Unit. *Energy Proc.* **2008**, *1*, 247–252.

(3) Lu, J. G.; Cheng, M.; Ji, Y.; Hui, Z. Membrane-based CO_2 Absorption into Blended Amine Solutions. *J. Fuel Chem. Technol.* **2009**, *37*, 740–746.

(4) Intergovernmental Panel on Climate Change. Summary for Policymakers. In *Climate Change 2007: The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; World Meteorological Organization/United Nations Environment Program: Geneva, 2007.

(5) Kohl, A. L.; Nielsen, R. B. *Gas Purification*, 5th ed.; Gulf Publishing: Houston, TX, 1997.

(6) Mamun, S.; Dindore, V. Y.; Svendsen, H. F. Kinetics of the Reaction of Carbon Dioxide with Aqueous Solutions of 2-((2-Aminoethyl)amino)ethanol. *Ind. Eng. Chem. Res.* **2007**, *46*, 385–394.

(7) Samanta, A.; Bandyopadhyay, S. S. Kinetics and Modeling of Carbon Dioxide Absorption into Aqueous Solutions of Piperazine. *Chem. Eng. Sci.* **2007**, *62*, 7312–7319.

(8) Kundu, M.; Bandyopadhyay, S. S. Solubility of CO_2 in Water + Diethanolamine + *N*-methyldiethanolamine. *Fluid Phase Equilib.* **2006a**, *248*, 158–167.

(9) Austgen, D. M.; Rochelle, G. T.; Chen, C. Model of Vapor—Liquid Equilibria for Aqueous Acid Gas—Alkanolamine Systems. 2. Representation of H_2S and CO_2 Solubility in Aqueous MDEA and CO_2 Solubility in Aqueous Mixtures of MDEA with MEA or DEA. *Ind. Eng. Chem. Res.* **1991**, *30*, 543–555.

(10) Dawodu, O. F.; Meisen, A. Solubility of Carbon Dioxide in Aqueous Mixtures of Alkanolamines. *J. Chem. Eng. Data* **1994**, *39*, 548–552.

(11) Murrieta-Guevara, F.; Rebolledo-Libreros, M. E.; Romero-Martinez, A.; Trejo, A. Solubility of CO_2 in Aqueous Mixtures of Diethanolamine with Methyldiethanolamine and 2-Amino-2-methyl-1-propanol. *Fluid Phase Equilib.* **1998**, *150—151*, 721–729.

(12) Mondal, M. K. Solubility of Carbon Dioxide in an Aqueous Blend of Diethanolamine and Piperazine. *J. Chem. Eng. Data* **2009**, *54*, 2381–2385.

(13) Seo, D.; Hong, W. Solubilities of Carbon Dioxide in Aqueous Mixtures of Diethanolamine and 2-Amino-2-methyl-1-propanol. *J. Chem. Eng. Data* **1996**, *41*, 258–260.

(14) Mandal, B. P.; Biswas, A. K.; Bandyopadhyay, S. S. Absorption of Carbon Dioxide into Aqueous Blends of 2-Amino-2-methyl-1-propanol and Diethanolamine. *Chem. Eng. Sci.* **2003**, *58*, 4137–4144.

(15) Lee, J. I.; Otto, F. D.; Mather, A. E. Solubility of Carbon Dioxide in Aqueous Diethanolamine Solutions at High Pressures. *J. Chem. Eng. Data* **1972**, *17*, 465–468.

(16) Ali, B. S.; Aroua, M. K. Effect of Piperazine on CO_2 Loading in Aqueous Solutions of MDEA at Low Pressure. *Int. J. Thermophys.* **2004**, *25*, 1863–1870.

(17) Benamor, A.; Aroua, M. K. Modeling of CO_2 Solubility and Carbamate Concentration in DEA, MDEA, and Their Mixtures Using the Deshmukh—Mather Model. *Fluid Phase Equilib.* **2005**, *231*, 150–162.

(18) Jenab, M. H.; Abdi, M. A.; Najibi, S. H.; Vahidi, M.; Matin, N. S. Solubility of Carbon Dioxide in Aqueous Mixtures of *N*-Methyldiethanolamine + Piperazine + Sulfolane. *J. Chem. Eng. Data* **2005**, *50*, 583–586.

(19) Liu, H.; Zhang, C.; Xu, G. A Study on Equilibrium Solubility for Carbon Dioxide in Methyldiethanolamine—Piperazine—Water Solution. *Ind. Eng. Chem. Res.* **1999**, *38*, 4032–4036.

(20) Daneshvar, N.; Moattar, M. T. Z.; Abdi, M. A.; Aber, S. Carbon Dioxide Equilibrium Absorption in the Multicomponent Systems of CO_2 + TIPA + MEA + H_2O, CO_2 + TIPA + PZ + H_2O, and CO_2 + TIPA + H_2O at Low CO_2 Partial Pressures: Experimental Solubility Data, Corrosion Study, and Modeling with Artificial Neural Network. *Sep. Purif. Technol.* **2004**, *37*, 135–147.