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Effect of Piperazine on CO_2 Loading in Aqueous Solutions of MDEA at Low Pressure

B. Si Ali[1] and M. K. Aroua[1,2]

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Solubilities of CO_2 in aqueous solutions of activated methyldiethanolamine (MDEA) has been investigated for temperatures and CO_2 partial pressures ranging from 40 to 80°C and 0.1 to 100 kPa, respectively. Piperazine (PZ) is used as activator, with a concentration ranging from 0.01 to 0.1 M, keeping the amine total concentration in the aqueous solution at 2 M. The experimental solubility results were represented by the mole ratio of CO_2 per activated amine present in the liquid mixture. The addition of piperazine, as activator for MDEA, increased the solubility of CO_2 in the region of low CO_2 partial pressure compared to pure MDEA. The CO_2 loading increased with decreasing temperature, increasing CO_2 partial pressure, and increasing PZ concentration.

KEY WORDS: activated amines; carbon dioxide; MDEA; piperazine; solubility.

1. INTRODUCTION

Aqueous alkanolamine solutions are widely used for the removal of acid gases such as CO_2 and H_2S from natural and refinery gas streams. Methyldiethanolamine (MDEA) is one of the industrially important alkanolamines used for this purpose. The use of MDEA solutions was first described by Frazier and Kohl [1]. Being a tertiary alkanolamine, MDEA is characterized by a slow reaction rate with CO_2 compared with primary

[1]Department of Chemical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia.
[2]To whom correspondence should be addressed. E-mail: mk_aroua@um.edu.my

and secondary amines. In order to enhance the absorption rate of CO_2 and at the same time maintain the advantages of using MDEA, Chakravarty [2] suggested the use of aqueous alkanolamine blends consisting of a mixture of MDEA and a primary or a secondary alkanolamine. Following this suggestion, numerous investigations were devoted for the measurement of CO_2 solubility in MDEA-based solvents. A comprehensive set of data on CO_2 equilibrium solubility in MDEA–DEA and MDEA–MEA systems under various operating conditions can be found in the open literature [3–7].

Another important development in alkanolamine technology is the use of activated amine solutions which consist of a conventional amine doped with small amounts of an accelerator (activator) that enhances the overall CO_2 absorption rate. Piperazine (PZ) is one activator that has been the focus of many researchers. Hongyi and Rochelle [8] studied the solubility and absorption rate of CO_2 into the MEA–PZ–H_2O system for a temperature range of 40 to 60°C and a piperazine concentration ranging from 0 to 1.2 M. Most previous studies on piperazine as activator focused on the kinetics of the absorption of CO_2. Data on the equilibrium solubility of CO_2 in alkanolamine–piperazine mixtures are still scarce. Xu et al. [9] studied the effect of piperazine on CO_2 loading in MDEA solutions, and reported that piperazine is beneficial to CO_2 loading in these solutions. Only nine experimental data points are given at a very narrow temperature range. Liu et al. [10] provided more data on CO_2 equilibrium solubility in aqueous mixtures of MDEA and piperazine for temperatures and CO_2 partial pressures ranging from 30 to 90°C and 13.16 to 935.3 kPa, respectively. The concentration of piperazine was varied from 0.17 to 1.55 M. Recently, Kamps et al. [11] presented data and a model describing the phase equilibrium for the absorption of CO_2 into aqueous piperazine and its mixtures with MDEA. Their experimental solubility data were collected at high CO_2 partial pressures (>70 kPa) and relatively high PZ concentrations (>2.0 M). They concluded that the existing experimental database on phase equilibrium in the CO_2–MDEA–PZ–H_2O system is very limited and that additional information is required in order to develop a rigorous thermodynamic model with a predictive character.

In this current study additional data on the equilibrium solubility of CO_2 in the MDEA–PZ–H_2O system are presented. The data are collected at temperatures and CO_2 partial pressures ranging from 40 to 80°C and 0.1 to 100 kPa, respectively. Such low CO_2 pressures are generally encountered at the top of the industrial absorption towers and in systems involving flue gases such as in power plants. Throughout this study the total concentration of amine is kept constant at 2.0 M and the PZ concentration is varied from 0.01 to 0.1 M.

2. EXPERIMENTAL

Two types of amines have been selected in this work, MDEA (obtained from Riedel-de-Haen with 98.5% purity) and PZ (obtained from Merck with 99.9% purity). Absorption experiments of CO_2 into alkanolamine solution were conducted using a stirred cell reactor where the amine solution was exposed to a flowing gas consisting of a mixture of CO_2 and N_2 of known composition. Details of the experimental apparatus and procedure are provided by Haji-Slaiman and Aroua [12]. The experiment was terminated once equilibrium was achieved, as indicated by a constant pH value of the loaded solution. The liquid was analyzed for CO_2 loading using the procedure described by Haji-Sulaiman et al. [13]. In this study, the CO_2 partial pressure in the flowing gas stream was varied from 0.05 to 100 kPa at temperatures and PZ concentrations ranging from 40 to 80°C and 0.01 to 0.1 M, respectively.

3. RESULTS AND DISCUSSION

To ensure the reliability of the experimental data, it is important that the concentration of amine in the solution is maintained constant throughout each run. Analysis on the total amine concentration, performed before and at the end of each run, showed that in most cases the variation between the readings was less than 3%. However, slightly higher variations of about 5% were obtained for experiments at low CO_2 partial pressure and high temperature, which normally required more than 20 h to reach equilibrium, where the evaporation of water is likely to occur. Nonetheless, glycerin was added to the water bath and a condenser was adjusted at the gas vent to overcome this problem. The measured variations also included errors in the analysis, which have been estimated to be around 2%. Thus, without introducing any significant errors, it can be concluded that the total amine concentration in the solution remained constant throughout each experimental run.

In order to assess the reliability of the data generated in this work, a comparison of CO_2 loadings in pure MDEA generated using our experimental setup and procedures with values available in the literature is made. Such comparison is illustrated in Fig. 1, which clearly shows good agreement among the various sources of data, especially at CO_2 partial pressures higher than 1.0 kPa.

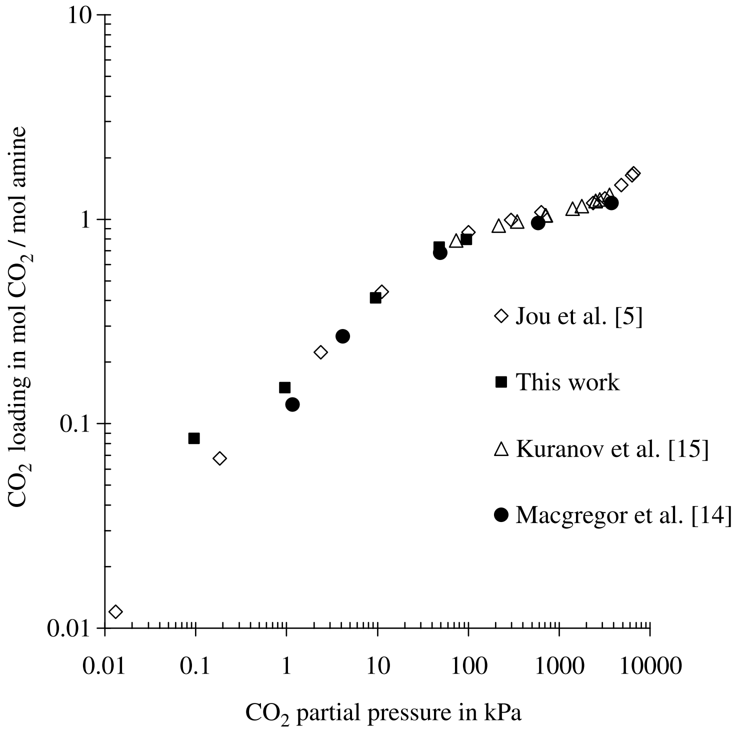

Fig. 1. Comparison between published data and this work at 40°C and 2.0 M MDEA solution.

The results of CO_2 solubility in MDEA–PZ–H_2O solutions are given in Tables I and II where the CO_2 solubility is expressed in terms of loading (mol of CO_2 absorbed)/(mol of amine). The values shown in these tables are the averages of three determinations.

These results show that in activated MDEA solutions, the CO_2 loading increases with CO_2 partial pressure and decreases with the absorption temperature. This trend is similar to the one observed in conventional alkanolamine solutions. The effect of piperazine concentration on the ultimate CO_2 loading was found to be dependent on both the CO_2 partial pressure and solution temperature. As shown in Fig. 2, at high temperature and high CO_2 partial pressure, the addition of piperazine did not show any significant effect. The same figure shows a slight decrease in loading at low temperature. Figure 3 depicts the effect of piperazine concentration on CO_2 loading at low partial pressure. It is clear in this figure that a significant increase in loading is observed at the three investigated temperatures.

Table I. Solubility of Carbon Dioxide in Aqueous Solutions of 2 M MDEA and (1.98 M MDEA + 0.01 M PZ) at Various CO_2 Partial Pressures and Solution Temperatures

Amine Concentration ($mol \cdot L^{-1}$)	T (°C)	P_{CO_2} (kPa)	Loading (mol CO_2/mol amine)
2 M MDEA	80	55.48	0.34
		27.57	0.24
		5.56	0.12
		0.55	0.07
		0.08	0.05
	60	82.91	0.63
		41.37	0.45
		8.31	0.24
		0.83	0.10
		0.06	0.05
	40	95.61	0.80
		47.72	0.73
		9.53	0.41
		0.96	0.15
		0.10	0.08
1.98 M MDEA + 0.01 M PZ	80	55.31	0.35
		27.57	0.25
		5.55	0.13
		0.56	0.09
		0.06	0.06
	60	83.07	0.63
		41.20	0.49
		8.26	0.25
		0.83	0.10
		0.08	0.07
	40	95.28	0.86
		47.55	0.74
		9.54	0.40
		0.95	0.14
		0.10	0.08

4. CONCLUSION

The equilibrium solubilities of CO_2 in aqueous solutions of MDEA/PZ were investigated at 40, 60, and 80°C and CO_2 partial pressure ranging from 0.05 to 100 kPa. The addition of small concentration of piperazine to activate MDEA increases the CO_2 loading in the low CO_2 partial pressure.

Table II. Solubility of Carbon Dioxide in Aqueous Solutions of (1.90 M MDEA + 0.05 M PZ) and (1.80 M MDEA + 0.1 M PZ) at Various CO_2 Partial Pressures and Solution Temperatures

Amine Concentration ($mol \cdot L^{-1}$)	T (°C)	P_{CO_2} (kPa)	Loading (mol CO_2/mol amine)
1.90 M MDEA + 0.05 M PZ	80	55.64	0.35
		27.49	0.23
		5.55	0.13
		0.55	0.05
		0.06	0.04
	60	83.24	0.63
		41.28	0.48
		8.29	0.25
		0.83	0.07
		0.08	0.06
	40	95.78	0.82
		47.55	0.75
		9.58	0.44
		0.95	0.17
		0.10	0.09
1.80 M MDEA + 0.1 M PZ	80	55.48	0.36
		27.74	0.27
		5.58	0.15
		0.55	0.07
		0.06	0.06
	60	83.07	0.60
		41.45	0.49
		8.31	0.23
		0.83	0.11
		0.08	0.06
	40	95.78	0.82
		47.64	0.71
		9.59	0.46
		0.95	0.18
		0.10	0.10

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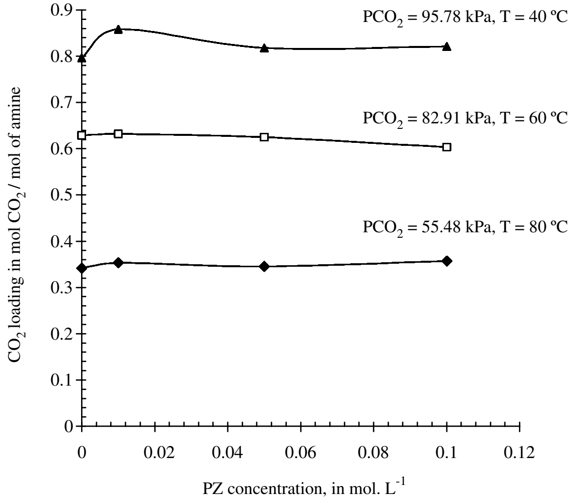

Fig. 2. Effect of PZ concentration and solution temperature on CO_2 loading for MDEA/PZ at high CO_2 partial pressure.

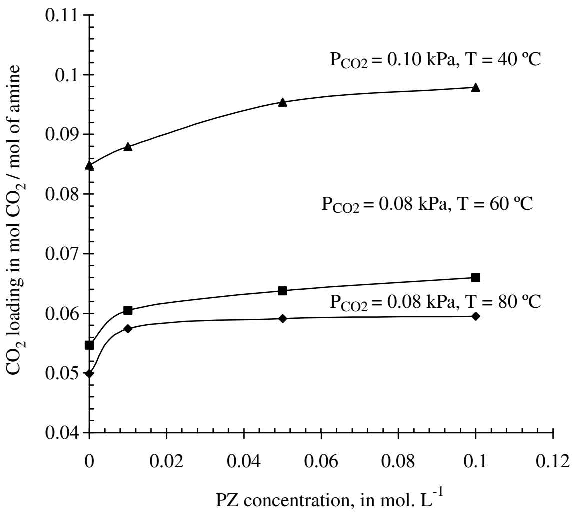

Fig. 3. Effect of PZ concentration and solution temperature on the CO_2 loading for MDEA/PZ at low CO_2 partial pressure.

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