

Equilibrium Solubility of CO₂ in 2-Amino-2-Methyl-1-Propanol Solvent promoted by Piperazine and Monoethanolamine Blends

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Abstract

In this work, experimental data for equilibrium solubility of CO₂ in novel 2-amino-2-methyl-1-propanol (AMP) promoted by piperazine (PZ) and monoethanolamine (MEA) blends was analyzed and reported at 25 °C, 40 °C and 60 °C at CO₂ partial pressure range of 2 – 100 kPa. At 93.93 kPa CO₂ partial pressure and absorption temperature of 40 °C, the concentration of this novel blend was studied at 2 M AMP – 0.5 M PZ – 2.5 M MEA, 2 M AMP – 0.5 M PZ – 3 M MEA, and 2 M AMP – 1 M PZ – 2 M MEA. This highest solution concentration of 5.5 M did not precipitate when the rich solution was cooled to 20 °C. In addition, it showed superior CO₂ absorption working capacity, aWC (10 – 16.6 %) compared to the conventional 5 M MEA. The blend of 2 M AMP – 0.5 M PZ – 3 M MEA was further analyzed for CO₂ solubility and it was reported as function of CO₂ partial pressures at the temperature range investigated.

Keywords: Carbon dioxide Solubility, 2-amino-2-methyl-1-propanol, Piperazine, Monoethanolamine, Absorption Working Capacity

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1. INTRODUCTION

The capture of carbon dioxide (CO₂) has taken the center stage globally due to the increasing adverse effects of CO₂ emissions. These emissions are generated from anthropogenic activities during utilization of fossil fuels to power, transportation and residential purposes. The International Energy Agency (2013) stated that the global emissions in 2011, coal and crude oil accounted for the most CO₂ emissions when compared to natural gas, while the generation of electricity accounted for the most in terms of sector emissions. Coal which is relatively cheap and available globally will most likely be the preferred fuel for power plants in decades to come (Tontiwachwuthikul et al., 2011). Therefore, the highest sources of CO₂ from fossil fuels come from post-combustion, pre-combustion, oxyfuel and industrial processes. The absorption of CO₂ can be achieved by absorption, adsorption, membrane or cryogenic processes. CO₂ absorption using chemical absorption has attracted more attention because its maturity, cost-effectiveness and ability to handle large volumes of flue gas streams (Rao and Rubin, 2002). The major property of the chemical solvent will be fast reaction kinetics, high absorption capacity, high mass-transfer performance, low degradation and corrosiveness and most importantly low energy penalty for solvent regeneration. The most common chemical absorbents for the capture of CO₂ are the amines. Most of them are currently commercially available in the industry covering the primary alkanolamines; monoethanolamine (MEA) and diglycolamine (DGA), secondary alkanolamines; diethanolamine (DEA) and diisopropanolamine (DIPA) and tertiary alkanolamines; methyldiethanolamine (MDEA) and triethanolamine (TEA). Several other commercially available amines known are sterically hindered amine like 2-amino-2-methyl-1-propanol (AMP) and polyamines like piperazine (PZ). The most widely used amine in the industry is MEA which is because of its high rate of absorption/fast reaction kinetics, low chemical cost and ability to capture CO₂ at low pressure flue gases (Kohl and Nielsen, 1997; Artanto et al., 2014). Nevertheless, it is constrained with high energy penalty for solvent regeneration. According to Aaron and Tsouris (2005), heat required to regenerate MEA accounts for up to 70 – 80 % of the operational cost. More so, the amine-based CO₂ capture is targeted at 90 % capture efficiency (Rao and Rubin, 2006; Rao and Rubin 2002; Abu-Zahra et al., 2007). Thus, the main research focus have been to develop novel solvents, solvent blends that will be competitive in both the absorption capacity and rate of absorption, but will require less energy penalty compared to MEA. Several binary amine blends have been investigated by

researchers (Dugas and Rochelle, 2009; Nainar and Veawab, 2009; Yang et al, 2010; Samanta and Bandyopadhyay, 2014), and its success is gradually leading to ternary and quaternary amine blends (Haghtalab et al., 2014; Esmaeili and Roozbehani, 2014). The idea behind the application of binary amine blends is to utilize their individual potentials and as well minimize their limitations (precipitation, limited absorption capacity, low rate of reaction, high energy penalty etc.). Ternary blends have the potentials of utilizing the potentials of 3 amine solvents which will be highly beneficial for the capture of CO₂. This leads to the aim of this research project which is to combine the high absorption capacity of AMP (Sartori and Savage,1983), very high rate of reaction and high capacity of PZ (Bishnoi and Rochelle, 2000; Freeman et al., 2010) and the good rate of reaction of MEA (Sartori and Savage,1983). The 3rd solvent MEA also have a unique property whereby it does not precipitate when you use it at its pure state of 16.5 M. Pure MEA (16.5 M) was tested for CO₂ capture by Bruder and Svendsen (2012) without reporting any precipitation, and this was also confirmed in our experimental analysis. The CO₂ solubility in the novel ternary blend of AMP-PZ-MEA was experimentally studied and reported at temperatures between 25 - 60 °C at CO₂ partial pressure range of 2 – 100 kPa. At CO₂ partial pressure 93.93 kPa and temperature of 40 °C, the ternary blend concentrations of 2 M AMP – 0.5 M PZ – 2.5 M MEA , 2 M AMP – 0.5 M PZ – 3 M MEA, and 2 M AMP – 1 M PZ – 2 M MEA were investigated. Their CO₂ loading and possibility of precipitation were monitored. In terms of precipitation, none of the solutions formed a precipitate when their rich solutions were cooled to 20 °C for 480 hours, while they all showed superior equilibrium CO₂ loading (6.7 – 16.9) and absorption working capacity (10 – 16.6 %) than the conventional 5 M MEA. The blend of 2 M AMP – 0.5 M PZ – 3 M MEA was further analyzed for CO₂ solubility because of it possess the highest absorption working capacity and low PZ concentration which will not trigger precipitation. The CO₂ solubility results were reported as function of CO₂ partial pressures at the temperate range investigated.

2. EXPERIMENTAL

2.1 Chemicals and Apparatus

MEA (99 %) was acquired from Merck KGaA, Darmstadt, Germany while PZ (99 %) and AMP (99 %) were both acquired from ACROS ORGANICS, New Jersey, USA. All the

solvents were used without further purification. Hydrochloric acid (HCl) with 37% purity procured from RCI Labscan Limited, Thailand and methyl orange (0.10%) indicator were used to determine the exact concentration of all amines and their CO₂ loading used in this study. N₂ (99.99%) and CO₂ (99.99%) were both obtained from Praxair Inc., Bangkok, Thailand.

The experimental apparatus used for the analysis of CO₂ solubility is similar to those explained in the work of Tontiwachwuthikul et al., (2008). The set-up consists of an absorption reactor and saturation cell both immersed in a water bath (Memmert, GmbH + Co. KG Schwabach FRG, Germany, with a precision of 0.1 °C) which is equipped with a temperature controller. The cooling circulator (Peter Huber Kältemaschinenbau GmbH, Germany, model CC – K6 with temperature range between -25 °C to 200 °C and temperature stability of ± 0.02 °C) provided the cooling water for the condenser to recover all condensable species back to the absorption reactor. The flow rates of the mixed CO₂ and N₂ at a desired % CO₂ were controlled by the mass flow controllers (Electronic AALBORG GFC-17, with range of 0 – 200 mL/min and ±1.5 % accuracy). The desired % CO₂ in the mixed gas stream was verified by a portable infrared (IR) CO₂ gas analyzer (Quantek Instruments, Inc., Grafton, MA, USA, model 906 ranging from 0.0 % to 100% CO₂ with 0.1 % accuracy).

2.2 CO₂ Solubility Analysis

For each experimental run, 20 mL of the desired ternary amine solution was put into the absorption reactor (50 mL capacity), while 15 mL of distilled water (DI water) as put into the saturation cell. The saturation cell and absorption reactor containing the DI water and amine solution respectively were placed inside the water bath and allowed to reach thermal equilibrium at the required temperature. Prior to this, the concentration of the ternary amine solution was verified by acidification technique using 1 M of HCl solution to the end point of 0.10 wt% methyl orange indicator. After the CO₂ concentration in the mixed gas (by adjusting the flow rates of N₂ and CO₂ with their mass flow controllers) was confirmed by the IR-based CO₂ analyzer, the gas mixture was sent through the saturation cell (containing the DI water) and into the absorption reactor (containing the amine solution). All condensable species were recovered back to the absorption reactor with the help of a condenser located downstream of the absorption reactor. The condenser was continuously fed with cold water

(at 10 – 20 °C) in order to retain a minimal loss of the amine solution. The CO₂ loading in the amine solution samples was determined by acidification technique (Chittick apparatus) as explained by the Association of Official Analytical Chemists, AOAC (Horwitz, 1975). In summary, during the analysis of the CO₂ loading, excess 1 M HCl was introduced into the amine solution sample and the evolved absorbed CO₂ was collected and measured for the exact volume in a graduated gas measuring burette. The volume of the evolved CO₂ was used to determine the corresponding CO₂ loading expressed in terms of mol CO₂/ mol amine. The CO₂ loading analysis was repeated every 2 hours until equilibrium is attained. Equilibrium was attained when the CO₂ loading was constant or until two consecutive readings showed only slight difference of ± 0.009. The reported CO₂ loading was the average of the equilibrium data points. The absorption working capacity (aWC) of the ternary blend was also reported for each CO₂ solubility run. The aWC can be calculated by multiplying the equilibrium CO₂ loading of the amine solution (α_{CO_2}) by its molar concentration (Equation 1).

$$aWC \left(\frac{\text{mol } CO_2}{L \text{ amine solution}} \right) = \alpha_{CO_2}(\text{absorption}) \times \text{Amine Conc.} \quad 1$$

The reproducibility of experimental results was also confirmed because it's a vital parameter which indicates how accurate, reliable and repeatable the results are. The accuracy is also a factor of the minor uncertainties of both the water bath temperature (± 0.1 °C), concentration of the amine solution (± 0.05 M), and mole fraction of CO₂ in the simulated flue gas. The experimental data points were repeated and the estimated average uncertainty (absolute average deviations, %AAD) in the measured CO₂ loading was between 0.5 to 2 %.

2.3 Validation of Experimental Set-Up and Procedure

The experimental set-up and procedure as described in section 2.2 was validated prior to the solubility run of the ternary blend. The validation results were compared with literature data of standard solvents covering 5 M MEA, 30 wt% DEA and 3 M AMP (Shen and Li, 1992; Seo and Hong, 1996; Roberts and Mather, 1988). The validation results are shown graphically in Figure 1.

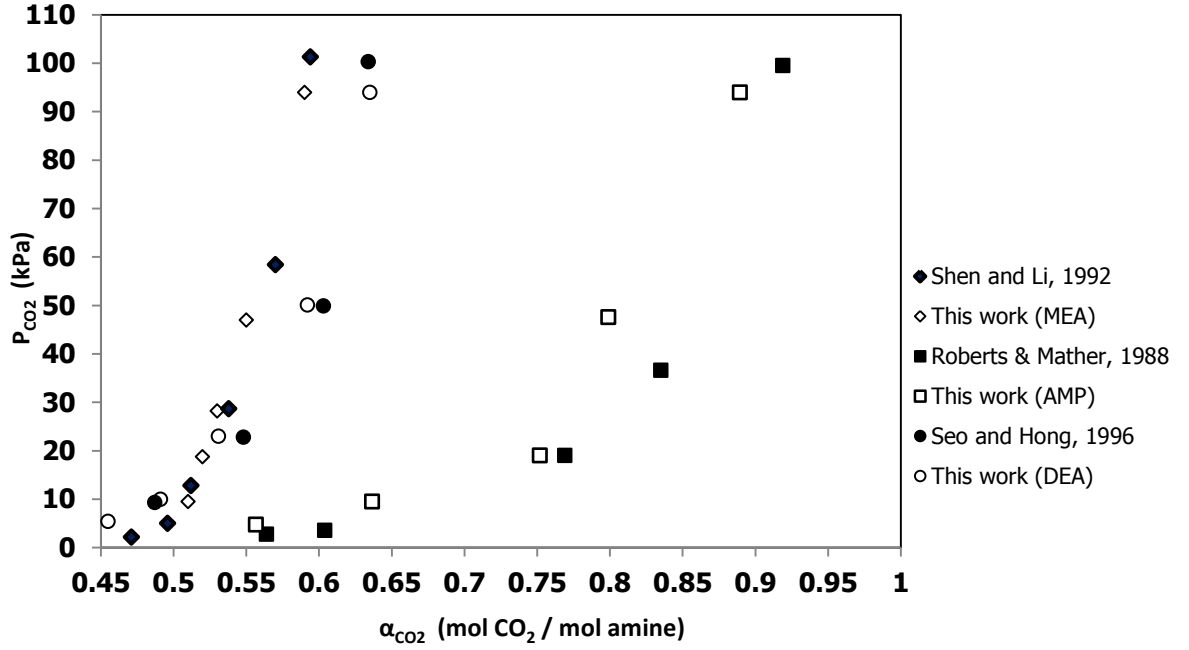


Figure 1 Validation results of 5 M MEA vs Shen & Li, 1992; 30 wt% DEA vs Seo & Hong, 1996; and 3 M AMP vs Roberts & Mather, 1988 all at 40 °C.

$$\%AAD = \frac{1}{n} \sum \left(\frac{X_{exp} - Y_{lit}}{X_{exp}} \right) \times 100\% \quad 2$$

The Equation 2 was used to estimate the absolute average deviations (%AAD), where 'n', X_{exp}, and Y_{lit} corresponds to the number of data points, the measured CO₂ loading from the experimental analysis, and from literature source, respectively. The validation results showed good agreement with the literature datas with 3 %AAD. This confirmed that the experimental apparatus and procedure can be accurately used to measure the equilibrium solubility of CO₂ in amine solvents studied in this research project.

3. RESULTS AND ANALYSIS

3.1 CO₂ Solubility in AMP-PZ-MEA

The Figure 2 depicts the CO₂ loading and absorption working capacity of the analyzed AMP-PZ-MEA ternary blends in comparison with 5 M MEA at 40 °C absorption temperature and CO₂ partial pressure of 93.93 kPa. The temperature and CO₂ partial pressure were both chosen for this comparison because it's the conventional absorption temperature and precipitation occurs at high concentration and high CO₂ partial pressure especially for amine solutions containing AMP and PZ. High CO₂ partial pressure also translates to high CO₂ loading which could trigger precipitation. From the results presented in Figure 2, it can be seen that the ternary blends possess higher CO₂ loading (6.7 % to 16.9 %) and aWC (10 – 16.6 %) compared to 5 M MEA. In addition, precipitation was also monitored prior to and after CO₂ loading for the different concentrations of the ternary blend. It was confirmed that no precipitation occurred even after the rich solution was cooled to 20 °C for 480 hours. This further confirms that this novel ternary blend is a potential chemical solution for the capture of CO₂.

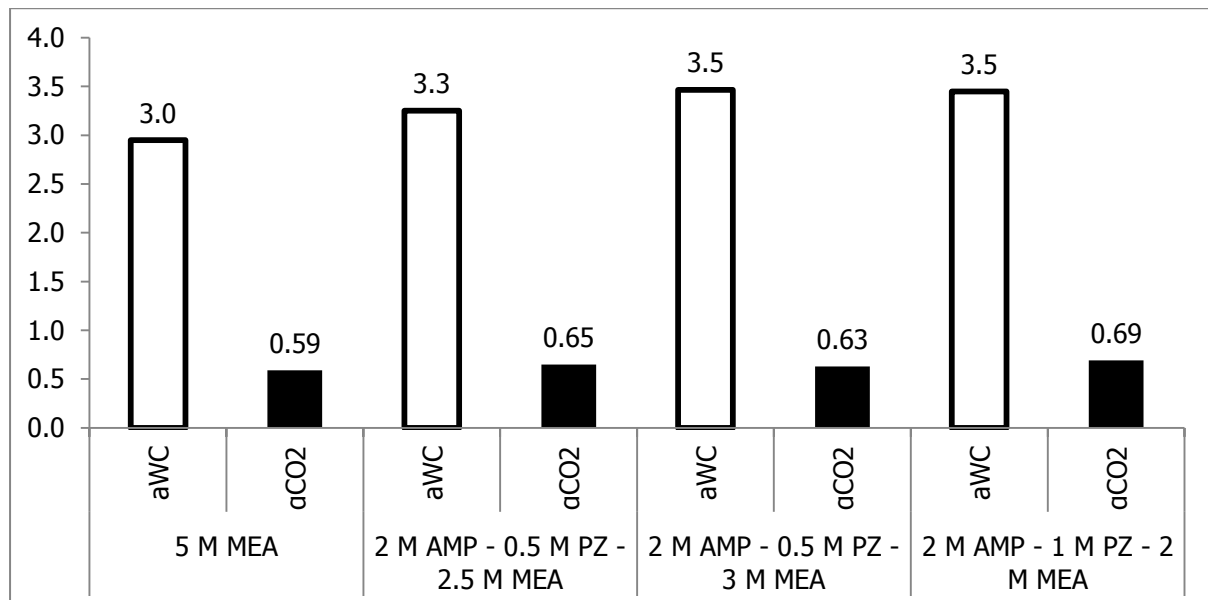


Figure 2 Comparison of 3 different concentrations of AMP-PZ-MEA ternary blend with 5 M MEA 40 °C and 93.93 kPa CO₂ partial pressure.

3.1.1 Influence of PZ Concentration

The promoter effect of PZ for activating high absorption capacity amines have been documented by several researchers (Yang et al, 2010; Bruder et al., 2011; Samanta and Bandyopadhyay, 2014). From the results in Figure 2 as the concentration of PZ is increased the equilibrium CO₂ loading also increased. This was evident in 2 M AMP – 0.5 M PZ – 2.5 M MEA and 2 M AMP – 1 M PZ – 2 M MEA, where the CO₂ loading increased by about 6.2 %. Looking at 2 M AMP – 0.5 M PZ – 2.5 M MEA and 2 M AMP – 0.5 M PZ – 3 M MEA, it was also observed that the promoting effect of PZ was more evident in the solution with lower amine solution concentration. In this case, the equilibrium CO₂ loading increased by 3.1 %. Considering that all the analyzed ternary blend of AMP-PZ-MEA showed higher CO₂ loading and absorption working capacity than the conventional 5 M MEA, the amine solution with low PZ concentration and highest absorption working capacity (2 M AMP – 0.5 M PZ – 3 M) was further analyzed.

3.1.2 Influence of MEA Concentration

The influence of MEA in the ternary blend was also studied and it can be seen that an increase in MEA concentration reduces the equilibrium CO₂ loading, but most importantly the absorption working capacity which is a more relevant parameter increases. From Figure 2, it can be deduced that at constant AMP – PZ concentration, as MEA concentration increased the CO₂ loading dropped by 3.1 % while the absorption working capacity increased by 6.1 %. This decrease in CO₂ loading due to increase in MEA concentration is believed to be due to the limited stoichiometric CO₂ loading of MEA. This development is different in terms of PZ because due to the high absorption capacity of PZ, an increase in its concentration increases the equilibrium CO₂ loading of the solution. The limited theoretical CO₂ loading of MEA (compared to AMP with low carbamate stability) was highlighted by Satori and Savage (1983) which he attributed to the stability of the carbamate formed. Nevertheless, the unique advantage of MEA is its non-precipitation when used in a pure state of 16.5 M. Therefore, in lieu of using PZ at high concentration as a promoter, MEA (a 3rd solvent) is used as a secondary promoter (non-precipitating and reactive).

These reasons prompted the choice of 2 M AMP – 0.5 M PZ – 3 M MEA for further CO₂ solubility analysis.

3.2 CO₂ Solubility in 2 M AMP – 0.5 M PZ – 3 M MEA

This ternary blend concentration was chosen for further CO₂ loading analysis citing its low PZ concentration and higher MEA concentration. This translates to the least possibility of forming precipitates and more importantly possess higher absorption working capacity than the other ternary blend concentrations and the conventional 5 M MEA (Figure 2). The further analysis ranged from 25 – 60 °C and CO₂ partial pressures between 2 – 100 kPa. Figure 3 shows the temperature and CO₂ partial pressure effects on equilibrium CO₂ loading.

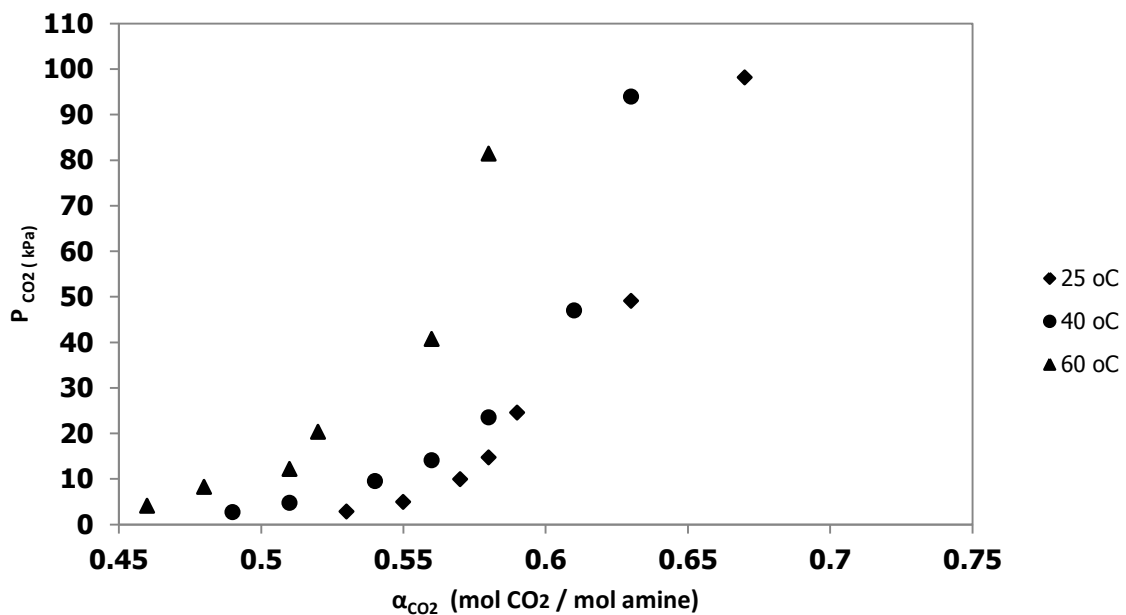


Figure 3 Equilibrium CO₂ solubility data for 2 M AMP – 0.5 M PZ – 3 M MEA.

It can be deduced from Figure 3 that as temperature increases the equilibrium CO₂ loading decreases while as CO₂ partial pressure increases the equilibrium CO₂ loading increases. It's also important to note that this ternary amine solution possess a considerable high CO₂ loading and corresponding absorption working capacity at 60 °C. This shows a slight advantage of using this solvent at high absorption temperature and still retains a considerable

absorption working capacity. Such advantage will help reduce the temperature difference between the absorption and stripping sections, thereby reducing energy penalty during solvent regeneration.

4. CONCLUSION

The ternary blend of AMP-PZ-MEA has proven to be a promising solvent for the capture of CO₂ from flue gas streams. Conclusions are highlighted below;

- At 40 °C and 93.93 kPa CO₂ partial pressure as shown in Figure 2, the analyzed concentrations of the AMP-PZ-MEA showed higher in both the equilibrium CO₂ loading (6.7 – 16.9) and absorption working capacity (10 – 16.6 %) when compared to the conventional 5 M MEA.
- The rich solutions of the analyzed ternary blend of AMP-PZ-MEA formed no precipitate when they were cooled to 20 °C for 480 hours.
- The viscous solvent, AMP which is also less reactive than PZ and MEA, though possess higher absorption capacity was kept constantly at 2 M. This low AMP concentration will minimize any possibility of precipitation and will as well increase the reaction kinetics of the ternary blend.
- The primary promoter (PZ) which has solubility limitations in water was varied between 0.5 – 1 M to avoid triggering precipitation.
- The concentration of the non-precipitating and non-viscous secondary promoter (MEA) was varied between 2 – 3 M to increase the absorption working capacity of the ternary blend.

An advantage of this ternary is that all the individual solvents are well investigated, known and commercially available in the industry. In addition, more analysis for several other concentrations of the AMP – PZ – MEA solution needs to be conducted for proper understanding.

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NOMENCLATURE

P_{CO_2} = partial pressure of CO_2 , kPa

aWC = absorption working capacity, (mol CO_2 /L amine solution)

M = moles/L or kmol/ m^3

Greek Letters

α = CO_2 loading, (mol CO_2 /mol amine)

REFERENCES

1. Aaron, D., Tsouris, C. 2005. Separation of CO_2 from Flue Gas: A Review. *Separation Science and Technology*. (40), 1-3, 321-348. DOI: 10.1081/SS-200042244
2. Abu-Zahra, M.R.M., Schneiders, L.H.J., Niederer, J.P.M., Feron, P.H.M., Versteeg, G.F. 2007. CO_2 from power plants Part I. A parametric study of the technical performance based on monoethanolamine. *International Journal of Greenhouse Gas Control*. 1, 37–46.
3. Artanto, Y., Jansen, J., Pearson, P., Puxty, G., Cottrell, A., Meuleman, E., Feron, P. 2014. Pilot-scale evaluation of AMP/PZ to capture CO_2 from flue gas of an Australian brown coal-fired power station. *International Journal of Greenhouse Gas Control*. 20, 189–195.

4. Bishnoi, S., Rochelle, G.T., 2000. Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility. *Chem. Eng. Sci.* 55, 5531–5543.
5. Bruder, P., Svendsen, H.F., 2012. Capacity and Kinetics of Solvents for Post-Combustion CO₂ Capture. *Energy Procedia*, 23, 45-54.
6. Bruder, P., Grimstvedt, A., Mejdell, T., Svendsen, H.F., 2011. CO₂ capture into aqueous solutions of piperazine activated 2-amino-2-methyl-1-propanol. *Chemical Engineering Science*. 66, 6193–6198.
7. Dugas, R., Rochelle, G.T., 2009. Absorption and Desorption rates of Carbon dioxide with Monoethanolamine and Piperazine. *Energy Procedia*, 1, 1163–1169.
8. Esmaeili, H., Roozbehani, B., 2014. Pilot-scale Experiments for Post-combustion CO₂ Capture from Gas Fired Power Plants with a Novel Solvent. *Intl. J. of Greenhouse Gas Control*. 30, 212–215.
9. Freeman, S.S., Dugas, R., Wagener, D.D., Nguyen, T., Rochelle, G.T., 2010. Carbon dioxide Capture with Concentrated Aqueous Piperazine. *Int. J. Greenhouse Gas Contr.* 4, 119–124.
10. Haghtalab A., Eghbali, H., Shojaeian, A., 2014. Experiment and Modeling Solubility of CO₂ in Aqueous Solutions of Diisopropanolamine + 2-amino-2-methyl-1-propanol + Piperazine at High Pressures. *J. Chem. Thermodynamics*. 71, 71–83.
11. Horwitz W. Association of official analytical chemists (AOAC) methods. 12th ed. Gaithersburg, MD, USA: George Bant; 1975.
12. International Energy Agency. 2013. CO₂ Emissions from Fuel Combustion. Available at: <http://www.iea.org/statistics/topics/CO2emissions/>
13. Kohl, A.L., Nielsen, R.B., 1997. *Gas Purification*, fifth ed. Gulf Publishing Company, Houston, USA.
14. Nainar, M., and Veawab, A. 2009. Corrosion in CO₂ Capture Process Using Blended Monoethanolamine and Piperazine. *Ind. Eng. Chem. Res.* (48), 9299–9306.
15. Rao, A.B., Rubin, E.S., 2006. Identifying cost-effective CO₂ control levels for amine based CO₂ capture systems. *Industrial & Engineering Chemistry Research* 45 (8), 2421–2429.
16. Rao, A.B., Rubin, E.S., 2002. A technical, economical, and environmental assessment of amine based CO₂ capture technology for power plant greenhouse gas control. *Environmental Science and Technology* 36 (20), 4467–4475.
17. Roberts, B.E., Mather, A.E., 1988. Solubility of CO₂ and H₂S in a Hindered Amine solution. *Chemical Engineering Communications*. 64, 105-111.

18. Samanta, A., Bandyopadhyay, S.S. 2009. Absorption of carbon dioxide into aqueous solutions of piperazine activated 2-amino-2-methyl-1-propanol. *Chemical Engineering Science*, 64, 1185 – 1194.
19. Sartori, G., Savage, D. W., 1983. Sterically Hindered Amines for CO₂ Removal from Gases. *Ind. Eng. Chem. Fundam.* 22, 239-249.
20. Seo, D-J., Hong W-H., 1996. Solubilities of Carbon Dioxide in Aqueous Mixtures of Diethanolamine and 2-Amino-2-methyl-1-Propanol. *J. Chem. Eng. Data.* 41, 258-260.
21. Shen, K.P., Li, M.H., 1992. Solubility of Carbon dioxide in Aqueous mixtures of Monoethanolamine with Methyldiethanolamine. *J. Chem. Eng. Data.* 1, 96-100.
22. Tontiwachwuthikul, P., Idem, R., Gelowitz, D. et al, 2011. Recent progress and new development of post-combustion carbon-capture technology using reactive solvents. *Carbon Management.* 2, 261-263.
23. Tontiwachwuthikul, P., Wee, A. G. H., Idem, R. O., Maneeintr, K., Fan, G.-J., Veawab, A., Henni, A., Aroonwilas, A., Chakma. A., 2008. Method for Capturing Carbon dioxide from Gas Streams. US Patent Application. US Patent Application, No. US /2008/0050296 A1.
24. Yang, Z., Soriano, A.N., Caparanga, A.R., and Li, M. 2010 .Equilibrium solubility of carbon dioxide in (2-amino-2-methyl-1-propanol + piperazine + water). *J. Chem. Thermodynamics*, (42), 659–665.