

Investigation on CO₂ Solubility in Aqueous Amine Solution of MDEA/PZ with SiO₂ Nanoparticles Additive as Novel Solvent

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Abstract

Conventional industrial processes for CO₂ capturing include gas absorption by solvent. The most common solvent consisting of an aqueous solution of methyl di-ethanol amine (MDEA) activated with Piperazine (PZ). This research however examines CO₂ solubility in absorption and desorption process using the above mentioned solvent that reinforced by nanoparticles additives at concentrations of 12, 25, 50, and 100 ppm, respectively. In this novel solvent Carbon dioxide solubility was studied at 40 and 120°C. These tests conducted at 0.1 to 26 atm partial pressure of CO₂ and Vapor-Liquid Equilibrium (VLE) data were obtained from laboratory setup. The results indicate an increase in CO₂ loading and changing on solubility equilibrium curve to more concentration of CO₂ in liquid phase for solvent containing nanoparticles. The solvent CO₂ loading was enhanced up to 37.5% by introducing 25 ppm of our novel nanoparticles.

Keywords: CO₂ capture; CO₂ solubility; MDEA; CO₂ VLE data; Nanoparticles

Introduction

Carbon dioxide in our atmosphere is among the most important factors responsible for global warming. The CO₂ removal from stacks and recycling it for other applications is essential to the environment. Therefore, researches in view of finding efficient and economical CO₂ gas absorbent is currently underway and is more attractive for many researchers now [1,2].

The chemical absorption with alkanol amine solutions has been used extensively in CO₂ capturing and gas sweetening industries. Solvents such as methyl ethanolamine (MEA) (amine type I), di-ethanolamine (DEA) (amine type II) and methyl di-ethanol amine (MDEA) (amine type III) are among conventional agents in CO₂ capturing processes. The first and second types of amines have high reaction rates with CO₂; however, amines type III display a slower reaction with CO₂. Whereas, amine type I and II requires more energy for regeneration than amine type III. Therefore, adding small amount of amine type I or II to amine type III transmutes the amine mixture to achieve a higher reaction rate with lower regeneration energy [3]. Activated methyl DEA (MDEA) is one of the most common amine mixtures for CO₂ capturing. MDEA blends with Piperazine (PZ) to be activated. Countless studies have been conducted on PZ effect on CO₂ absorption by alkanol amines. The results reveal that PZ possesses a higher reaction rate with CO₂ than MDEA. Consequently, a mixture of MDEA with PZ has higher capacity for CO₂ absorption than pure MDEA. In fact, some advantages of activated MDEA compare to MDEA are more absorption capacity and higher CO₂ reaction rate as well as lower energy consumption for solvent regeneration [3,4].

The chemical absorption with solvent, when compared to physical absorption, is usually more efficient due to the chemical bond carried out near the interfacial surface, where the resistance to mass transfer is high. The mass transfer resistance zone on the interfacial surface of the two phases is the main factor that reduces the diffusion rate. There are different methods to improve mass transfer rate; one of such methods is the addition of nanoparticles additives to the solvent [5]. Researchers utilized nanoparticles like magnetic iron oxide (Fe₃O₄), nano alumina (Al₂O₃), and nano silica (SiO₂) for this purpose. Park and Choi investigated effects of 12 nm silica nanoparticles on carbon

dioxide absorption rate in DEA aqueous solution. They reported that absorption rate will decrease with increasing nano particle concentration [6]. Also, they worked with silica nanoparticles in 2008 and reported that volumetric mass transfer coefficient decreases by increasing nanoparticles concentration [7].

Komati and Suresh added several volumetric percentages from magnetic iron oxide to MDEA and monitored its influences on mass transfer rate. Based on these results for 39.0% v/v of iron oxide nanoparticles, the mass transfer coefficient increased by 8.92% [8]. Kim et al. investigated carbon dioxide absorption by water nano solvent with particle sizes of 30, 70, and 130 nm of silica nano particles in bubble column. The results revealed that increasing concentration of silica nano particles raises the extent of absorptions by 76% during the first minute and the overall amount of absorption up to 24% [9].

Hwang and Park investigated the effect of silica nano particles additives with particle size of 7, 11, and 160 nm on the absorption of carbon dioxide with mono ethanol amine. They observed that absorption increased with nano particle size [10]. Li et al. dispersed titanium oxide (TiO₂) with 0.05, 0.2, 0.4 and 0.8 weight percent in an aqueous solution of 50% w/w of MDEA and analyzed the impact of these nano particles on carbon dioxide absorption. The results showed that by increasing the concentration of titanium nano particles, carbon dioxide absorption rate subsequently increases by 11.5% [11,12].

All published researches were about absorption rate and generally focused on mass transfer phenomena and experimental researches were conducted for measuring and comparing rate of mass transfer until now. From thermodynamic point of view absorption and desorption

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processes are vapor liquid equilibrium phenomena and process happen on two CO₂ solubility curves at process conditions. This research however investigated on the effect of nano particles on solubility of CO₂ in solvent (MDEA-PZ) from equilibrium point of view in absorption and desorption condition, and consequently investigate on CO₂ loading and net cycling of CO₂ by solvent. The experiments occur in an agitated reactor in several concentrations of nano particles and helped to find an optimum of nanoparticles concentration in solvent with maximum net cycling of CO₂.

Materials and Methods

Preparation of chemicals and solutions

Pure MDEA was prepared from Amine and Plasticizers Limited Company with more than 99% purity and PZ from Merck with more than 99% purity. Also distilled water was used to prepare amine solution. Carbon dioxide and nitrogen cylinders with a purity of 99.99% were used for the absorption experiments. Nano particles were prepared from Merck Company with mean size of particles between 10 and 15 nm and sphere shape with a purity of 99.99%.

Amine solution prepared with 28% wt. MDEA, 2.5% wt. PZ and 69.5% wt. water along with nano particles was added to the amine solution in several concentrations for each sample. Mixing was done using an early mechanical homogenizer (IKA-RW20™) along with 400 Watts ultrasonic probe for 30 min. Reasonable homogeneity distribution as well as stability of nano particles in solution was achieved in this way.

Apparatus

The experimental setup has been designed and constructed with feeding, reaction, and data gathering section. Schematic of the apparatus is shown in Figure 1. Feeding section has been utilized with N₂ and CO₂ gas cylinders, pressure regulators, and two MFC (indicating mass flow rate and control) from Brooks Company with accuracy of ± 7 ml/min. The reactor section is equipped with jacket and agitator. The reactor volume is 1 L with 90 mm ID and 160 mm height. The agitator has two impellers for gas and liquid phases. The reactor hasn't baffles and therefore when the liquid phase was rotated by mixer the liquid surface form like a paraboloid and contacting between gas and liquid phases take place at parabolic surface. Gas was inputted from the top side of the reactor. The reactor temperature would be controlled by a circulator with external temperature controller. Additionally, the apparatus is equipped with data gathering system that would record

reactor temperature in both gas and liquid phases, reactor pressure and volume of CO₂ and N₂ gases that goes into the reactor. All data uploaded into the computer at a measuring time of every 0.2 s. The trend of the reactor's temperature and pressure versus time displayed on the monitor. The pressure and temperature sensors have accuracies of ± 0.0175 bar and $\pm 0.25^\circ\text{C}$, respectively.

Test procedure for VLE experiments

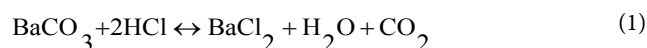
The reactor was vacuumed first; thereafter, 500 g of the amine solution fed to the reactor. Just then the reactor mixer switched on along with the circulator for attainment and control of the reactor's temperature at 40 and 120°C, respectively. Nitrogen was then supplied to pressurize the reactor up to 10 atm or any desired amount. As the reactor's temperature becomes stable, the reactor's mixer was turned off then 1000 normal ml of CO₂ gas fed into the reactor. Consequently, CO₂ gas line was shut and the mixer turns on again. Immediately, the pressure begins to decrease due to starting CO₂ absorption and reaction with amine. As soon as the reaction and absorption was complete, pressure stayed constant at its steady-state value or vapor – liquid equilibrium value. An hour after the reactor's pressure remaining constant, the mixer was stopped and the sample from liquid and gas phases was taken. Again, feeding of CO₂ gas into the reactor was continued and was repeated the stating procedure for another equilibrium point until amine solution becomes saturated from CO₂ and pressure begins to increase rapidly.

Test procedure for full loading experiments

To compare the CO₂ loading between several solvents, each solvent has to be saturated by CO₂. Thus, to find CO₂ full loading for each solvent, the reactor was fed with pure CO₂ until the vessel pressure reached to 35 atm and remain 60 minutes constant. Then CO₂ feeding would be stopped at 35 atm of reactor pressure. In this situation, the solvent is fully loaded with CO₂. After 60 min when pressure does not decrease. The sample would be taken from the liquid phase for CO₂ concentration measuring. Sampling from liquid phase was performed in a container filled with caustic solution and equipped with deep line to prevent CO₂ from discharging during sampling. As liquid sample entered to sample container, CO₂ reacts with NaOH and was converted to CO₃²⁻ which cannot leave the liquid phase.

CO₂ concentration measuring procedure in liquid and gas phase

The measurement of CO₂ concentration in liquid phase occurs with titration method. Liquid sample was transferred to a new container with BaCl₂ solution and after an ample time, all CO₃²⁻ reacted with BaCl₂ and precipitated as BaCO₃. Sediment was separated, collected, and washed several times to remove excess caustic. Thereafter, sediment was dissolved in HCl solution of 0.5 M as shown in the reaction below.



Volume of consumed HCl solution was recorded and new solution was kept to be titrated with caustic solution 0.5 M in the presence of phenol palatine. The mole content of CO₂ in the sample could be calculated using consumed volume of acid and base. Accuracy of the burette was ± 0.050 ml and the balance was ± 0.1 g. Gas sample was analyzed with gas chromatography technique using System Master GC Dani that was calibrated for this project.

Each experiment was being done two times when all conditions

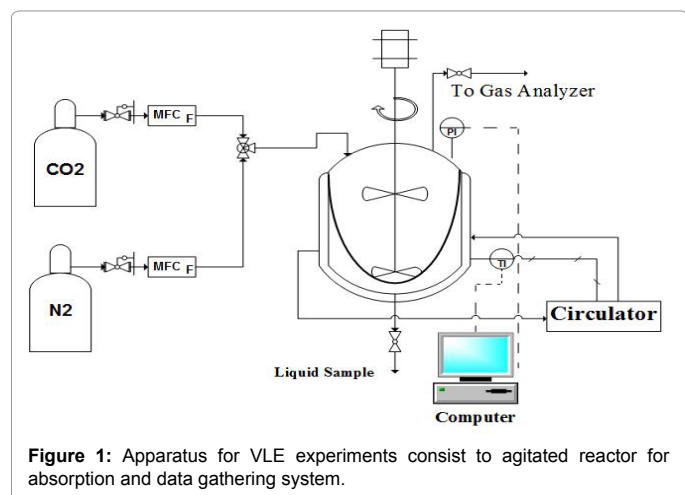


Figure 1: Apparatus for VLE experiments consist to agitated reactor for absorption and data gathering system.

were stable and equipment were at normal performance. The mean value of two experiment results was used as result.

Results and Discussion

Solubility of CO₂ in amine solution in different concentrations of nano particles at 40°C determined by previously stated experimental method. Six amine solutions were chosen for solubility test. Nano particles concentration in these solutions are 0, 12.5, 25, 50 and 100 ppm. The first solution is Base Solvent and the others is Nano solvent no.1 to 4. The results for CO₂ full loading experiment in Figure 2 indicate that the nano solvent no. 2 has the maximum CO₂ solubility. Also it states clearly that the nanoparticles have positive influence on equilibrium concentration of CO₂ at liquid phase and its effect increased with nanoparticles concentration at beginning, however, its effect disappear toward the more nanoparticles concentration. At the 25 ppm (w/w) of nanoparticles, solution evince the maximum solubility for CO₂ and with increasing nanoparticles concentration CO₂ solubility would be decreasing to the base solvent of CO₂ solubility value approximately.

VLE data is required for investigating on the effects of the nanoparticles on its behavior of the amine solution and also for comparing the base solvent to the nano solvent from CO₂ net cycling point of view. Thus, VLE experiments on base solvent and nano solvent No. 2, with maximum effect on CO₂ absorption, performed at 40 and 120°C, generally absorption process take place at 40°C and desorption occurs at 120°C, Also, for comparison between two nano solvents, experiments were conducted for nano solvent no. 3 and their results are shown in Figure 3.

The Figure 2 indicates that the nanoparticles have effect on equilibrium concentration of CO₂ in liquid phase and it improves absorption capacity of solvent up to 25 ppm nanoparticles concentration and thereafter, increasing nanoparticles concentration decreases amine absorption capacity. These results reveal that nanoparticles influences on absorption decay after about 25 ppm. However, for better judgments, all VLE data for three solvents are shown in Figure 3. As it is indicated in this graph, both nano solvent 3 and base solvent have the same VLE solubility curves for all CO₂ partial pressures approximately. While the nano solvent 2 has more moles of CO₂ in liquid phase.

Absorption process has two steps, physical and chemical absorption. The first step is diffusion of gas phase CO₂ into liquid phase physically and forming aqua CO₂, and in the second step it reacts chemically with the solution components. These two phenomena are in equilibrium with each other and schematically are shown in Figure 4 as horizontal and vertical equilibrium.

Nano particles have no effect on chemical reaction step; however, it influences the physical step and diffusion rate [9,10]. Because this research investigate the equilibrium effect of Nano particles. All experiments designed to take the data at equilibrium conditions, in other words, each data taken after enough time to stabilize temperature and pressure. Therefore the bottle necks are eliminated and mass/ reaction rates effect are omitted. Since all data are taken after long time that the process to induce steady state situation.

The solution of MDEA, PZ, and water has electrolyte nature and SiO₂ nano particles dispersed in the solution with very low concentration. It seems that nano particles changed overall interactions of molecules and ions in liquid manner to cause more equilibrium concentration of CO₂ in liquid phase. It may happened by enhancing the attraction of CO₂ molecules in liquid phase with nanoparticles, this phenomena creates by the presence of nanoparticles and its role in

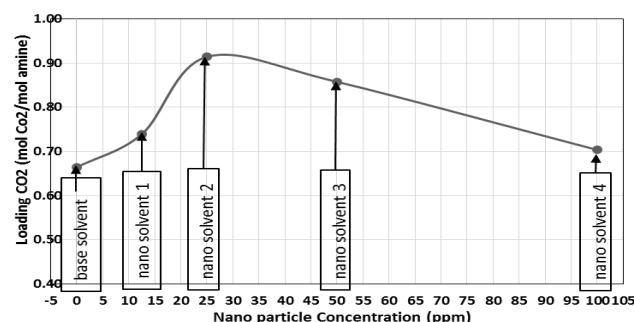


Figure 2: CO₂ loading in different nano solvent indicates 25 ppm concentration of nanoparticles have maximum loading.

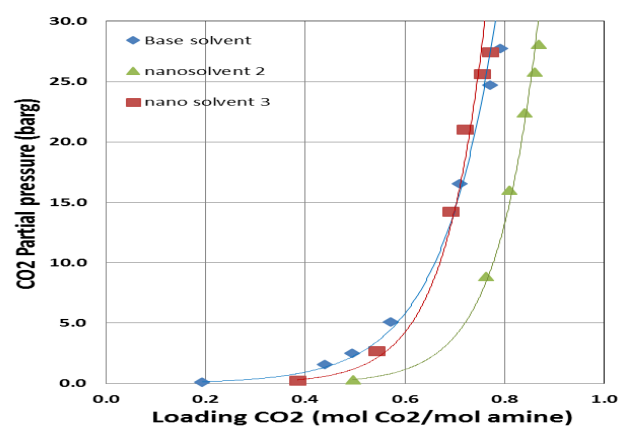


Figure 3: Solubility curves at absorption condition (40°C) for three solvents.

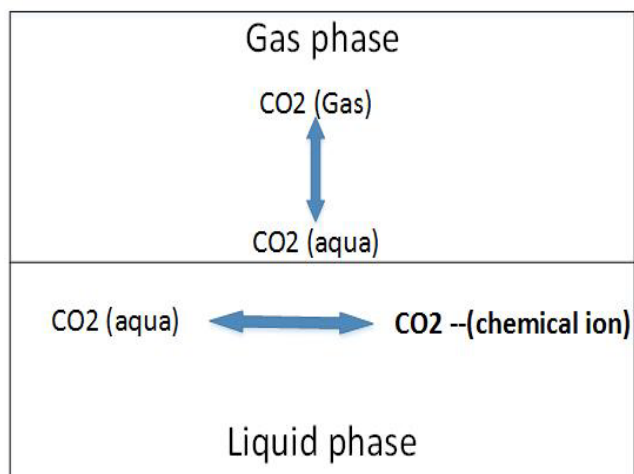


Figure 4: Two equilibrium in CO₂ absorption process.

changing the intermolecular forces of solution's molecules. Also it may happen due to change in chemical equilibrium balances. Conversely, the equilibrium experiments were done at 120°C (the desorption temperature) for more discovering of this phenomena. The results for base solvent and nano solvent no.2 are shown in Figure 5.

Figure 5 indicates that there is not any meaningful difference between equilibrium curves of nano solvent no.2 and base solvent at 120°C. Unlike what shown and concluded for the same two solvents

at 40°C. This is important for discovering role of nanoparticles in absorption solvents.

We have two facts. The first one is from Figure 2 indicates nano particles improve CO₂ solubility up to 25 ppm while increasing nano particles concentration more than 25 ppm CO₂ solubility decay. The second results conclude that no considerable influence of nanoparticles at high temperature of 120°C observed. The intermolecular forces naturally are weak at high temperature and kinetic energy of molecules is high and it dominate to the intermolecular forces therefore, if influences of nano particles were from effect on the intermolecular forces thereupon effect of nano particles must be reduced with temperature increasing. This matter confirmed with results that were shown in Figure 5.

The CO₂ gas removal process includes absorption and desorption units. Solvent absorbs CO₂ and exits from absorber column with maximum amount of CO₂ loading at 40°C and exits from the desorption column with minimum loading at 120°C. Difference between the minimum and the maximum is called CO₂ net cycling. Thus, the best solvent that studied and selected from VLE point of view in this research must be compared to base solvent with CO₂ net cycling amount in CO₂ removal process. The absorption process generally occurs at total pressure range of 5 to 30 atm or based on CO₂ content it varies at range 0.2 to 10 atm of partial pressure. As operation conditions in power plant, petrochemical and gas sweetening units. Desorption process occurs generally at 1 atm. The CO₂ loading values were estimated from VLE experimental results at 5 atm pressures for absorption and 1 atm pressure for desorption process. The CO₂ net cycling values of solvents were calculated and are shown in Table 1. We see 37.5 percent improvement in net cycling value compare to base solvent.

Conclusions

This research revealed that addition of 25 ppm nanoparticles into activated MDEA improved CO₂ absorption by 37.5% in respect to MDEA/PZ without nanoparticles. VLE was also found for base solvent

and nano solvent with 25 ppm nanoparticles at 40 and 120°C and have shown that nanoparticles have no effects on desorption process, and hence, have no influences on solvent regeneration energy. Thus, at a CO₂ capturing process based on nano solvent, there is almost 37.5% less solvent circulation and also less capital investment cost with respect to common activated MDEA/PZ processes. Therefore, the nanoparticles added process would become more feasible both efficiently and economically.

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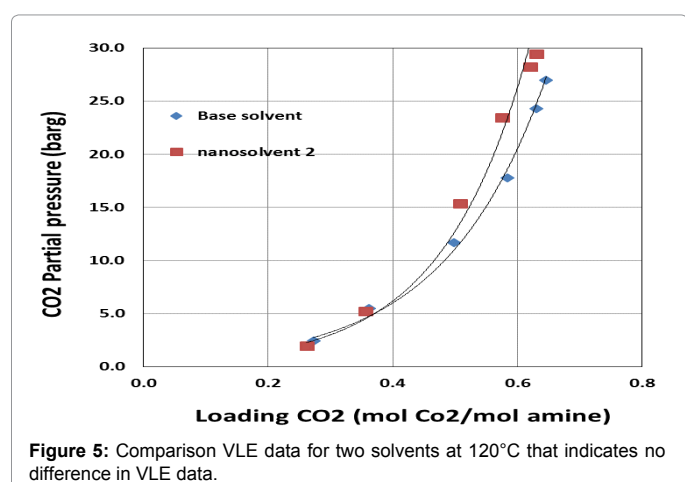


Figure 5: Comparison VLE data for two solvents at 120°C that indicates no difference in VLE data.

Solvent	Absorption loading (5 atm)	Desorption loading (1a)	Net Cycling improvement %
Base solvent	0.55	0.15	0
Nano solvent No. 2	0.7	0.15	37.50
Nano solvent No. 3	0.56	0.15	2.5

Table 1: Improvement in CO₂ net cycling.