

Effect of carbon nanotubes and activated carbon addition to the blends of monoethanolamine and triethanolamine on CO₂ absorption at low partial pressures

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ABSTRACT

Carbon dioxide is a major greenhouse gas that contributes to the global warming by more than %60. Absorption has been widely used to treat high concentrations of CO₂ in synthesis gas production, hydrogen manufacturing, and natural gas processing. The most well established method to capture CO₂ is its removal by absorption into amine solutions in the presence of activators. In this research, CO₂ absorption was measured in aqueous solutions of triethanolamine+monoethanolamine with different concentrations in the presence and absence of carbon nanotubes and activated carbon at temperatures ranging from 30 to 70 °C and low partial pressures in an absorption cell. Partial pressures were changed in the range of 10-70 kPa. The results revealed that the CO₂ absorption rate and capacity increases by adding small amounts of MEA to TEA. Moreover, CO₂ absorption rate and capacity increased with addition of carbon nanotubes and activated carbon to amine mixtures and the enhancement is higher for carbon nanotubes than activated carbon. Lowering the temperature increases CO₂ loading in solution.

KEYWORDS:

Carbon Dioxide, Absorption, Blended Amines, Carbon Nanotubes, Partial Pressures, Activated Carbon

1. INTRODUCTION

There are various technologies to separate CO₂ from flue gas of conventional fossil-fuel-fired power plants, e.g. chemical absorption, physical absorption, membrane separation and biological fixation. Chemical absorption is generally recognized as the most effective technology among all the technologies at present [1]. The most well-established method to capture CO₂ is its removal by absorption into amine solutions in conventional equipments. Amines are weak basic compounds that react with CO₂ to form weak chemical bonds. These chemical bonds are broken upon heating, leading to the regeneration of amine solution. Although chemical absorption

technology has important commercial significance, judicious selection of a competitive absorbent that is capable of high CO₂ loading, rapid absorption rate and low cost for regeneration remains as a challenge [2]. The absorption of acidic gases such as CO₂ in alkali solutions is a common and important industrial process especially in sweetening the natural gas, and has been used for many years. Examples of alkali solutions are alkanolamines, such as monoethanolamine (MEA), methyldiethanolamine (MDEA) and triethanolamine (TEA).

In 1968, Caplow [3] presented a hypothesized mechanism for carbamate (R₂NCOO⁻) formation,

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in the absorption of CO₂ by a secondary alkanolamine solution, involving the formation of an intermediate called zwitterion. This mechanism has two steps: formation of CO₂-amine zwitterion (reaction 1), followed by base-catalyzed deprotonation of zwitterion (reaction2) [4].



Where B_i designates any species in solution that can act as a base to abstract proton from the zwitterion (R₂NH⁺CO₂⁻) in the second reaction step. B_i can be diethanolamine, hydroxide ion, water and tertiary alkanolamines.

Reaction rates between CO₂ and primary, secondary and tertiary amines are different; it is slow in tertiary amines. The overall reaction for tertiary amines can be written as:

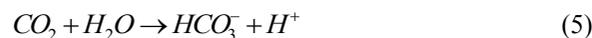


The following reactions can also occur in aqueous solutions of tertiary amines, which have role in total reaction rate [5, 6]:

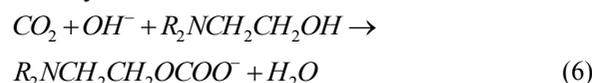
Bicarbonate formation:



Carbonic acid formation:



Alkyl carbonate formation:



Primary alkanolamines react with CO₂ to produce stable carbamate compounds, so they need more energy in regeneration step, while tertiary sterically hindered alkanolamines can not react with CO₂ directly and so, carbamate production is zero or minimum. So, they absorb CO₂ by acid–base reaction mechanism and as a result they have lower heat of reaction and will be regenerated with lower energy consumption to reverse the direction of reaction with CO₂ [7]. The absorption of acid gases in mixed amines has specific advantages over the use of single amines. The addition of small amounts of primary amines to conventional tertiary amine solutions can enhance the rate of CO₂ absorption to a large extent without appreciably affecting the stripping

characteristics. By varying the relative concentrations of primary and tertiary amines in solution, an optimum solvent can be designed for a specific absorption application [8]. Carbon nanotube (CNT) and activated carbon (AC) have large surface area and therefore may interact with CO₂ and solvent or act as a medium between them; this establishes a potential to enhance carbon dioxide absorption by alkanolamine solutions. So in this research, CO₂ absorption experiments were carried out at various amine blends in the presence and absence of CNT and AC at low CO₂ partial pressures in an absorption cell.

2. EXPERIMENTAL

2.1. Chemicals

The solutions were prepared using distilled water. MEA was from Merck with %99 purity. AC and TEA with %99 purity were from Merck, too. CNTs were with minimum purity of %95. CO₂ was from Ehterami Co. with minimum purity of %98 and argon was from Roham Gas Co. with certified purity of %99.999.

2.2. Apparatus and procedures

The solubility data were obtained using an atmospheric pressure apparatus (Fig. 1) similar to the one used by Xu et al [9]. The temperature in the reactor was fixed by a temperature controller (Jumo iTron 04, Germany) within ±0.1°C, adjusting the temperature in a thermostated water bath. A 270-cm³ glass cell containing 75 cm³ of alkanolamine solution and known amounts of AC or CNT, as suspension, was used. The proper flows of CO₂ and Argon were adjusted (Flow Controller, Supelco, VCD 1000, ±%0.3) and then mixed in a mixing tube to produce a proper CO₂ partial pressures in the range of 10-70 kPa. The total gas flow in all experiments was about 150 cm³/min. The resulting gas stream passed through a water saturator at room temperature then, the saturated gas stream was bubbled into the alkanolamine solution. The outlet gas passed through a room temperature condenser to return evaporated water into the cell. The CO₂ content in the liquid phase was determined by the addition of excess amounts of phosphoric acid into the solutions and then by measuring the evolved volume of CO₂ by a graduated burette (Fig. 2) [7].

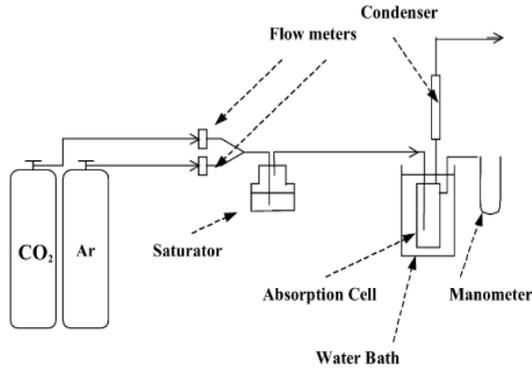


Fig.1: Simplified flow diagram of the atmospheric pressure system for the measurement of CO₂ equilibrium solubility.

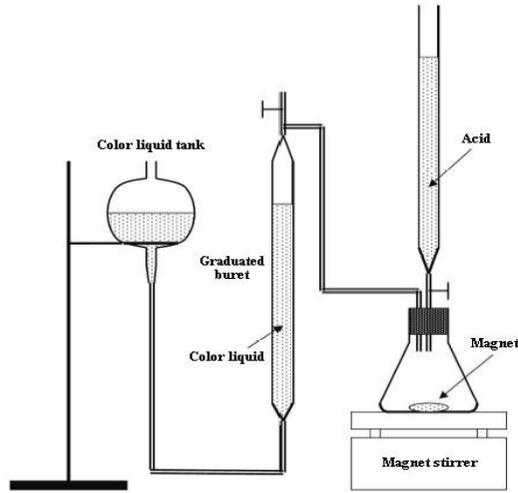


Fig.2: Simplified flow diagram of the atmospheric pressure system for measurement of CO₂ absorption

2.3. Typical calculations

We consider that CO₂ and Ar are mixed with each other with flow rates of F_{CO_2} (ml/min) and F_{Ar} (ml/min) respectively, and the mixture enters into amine solution with concentration of M (mol/L) at temperature of T (K). A known volume of solution (V_{sam} : ml) is selected as sample at equilibrium conditions and the volume of CO₂ gas released from the sample in room temperature (T_{Room} : K) is V_{1,CO_2} (ml). The ambient pressure (P : kPa) is obtained (± 0.1 kPa) from the meteorological office. CO₂ can be considered as an ideal gas and so, the calculation of released CO₂ volume in standard temperature and pressure (0°C and 1 atm) can be done as the followings:

$$\frac{P V_{1,CO_2}}{T_{Room}} = \frac{(101.325) V_{2,CO_2}}{273.15} \Rightarrow V_{2,CO_2} = \frac{P V_{1,CO_2} \cdot (273.15)}{T_{Room} \cdot (101.325)} \quad (7)$$

The moles of CO₂ released (m_1) is obtained by Eq. 8:

$$m_1 = V_{2,CO_2} / 22400 \quad (8)$$

The moles of CO₂ released from 1ml of solution (m_2) is calculated by $m_2 = m_1 / V_{sam}$. There are $M/1000$ moles of amine in 1ml of solution, so CO₂ loading in solution (α_{CO_2}) is found by:

$$\alpha_{CO_2} = m_2 / (M / 1000) \quad (9)$$

α_{CO_2} is moles of absorbed CO₂ per mole of amine in the solution. The equilibrium partial pressure of CO₂ above solution (P_{CO_2} : kPa) is obtained from Eq. 10:

$$P_{CO_2} + P_{Ar} + P_{ip} + P_{H_2O} = P \quad (10)$$

P_{Ar} , P_{H_2O} and P_{ip} are the partial pressures (kPa) of Argon, H₂O and impurities above solution, respectively. P_{H_2O} can be obtained from:

$$P_{H_2O} = X_{H_2O} \cdot P_{H_2O}^* \quad (11)$$

X_{H_2O} is mole fraction of H₂O in absorbent solution and $P_{H_2O}^*$ (kPa) is saturated H₂O vapor pressure in equilibrium temperature. Now we have:

$$F_{1,CO_2} = F_{CO_2} \cdot (W_{1,CO_2} / 100) \quad (12)$$

F_{1,CO_2} is the flow rate of pure CO₂ (ml/min) and W_{1,CO_2} is the volume percentage of CO₂ in its capsule. The pure CO₂ percent in total mixture of CO₂, Ar and impurities (W_{2,CO_2}) is calculated from:

$$W_{2,CO_2} = [F_{1,CO_2} / (F_{CO_2} + F_{Ar})] \times 100 \quad (13)$$

So we can calculate the partial pressure of CO₂ (P_{CO_2} : kPa) above amine solution in absorbance cell using Eq. 14:

$$P_{CO_2} = (P_{CO_2} + P_{Ar} + P_{ip}) \times (W_{2,CO_2} / 100) \quad (14)$$

3. RESULTS AND DISCUSSION

Fig. 3 compares our data with those reported previously by other researchers [7] for CO₂ absorption on a 15.3 %wt MEA aqueous solution at 40°C. It is obvious that our data are in good agreement with the literature and so, our system is calibrated.

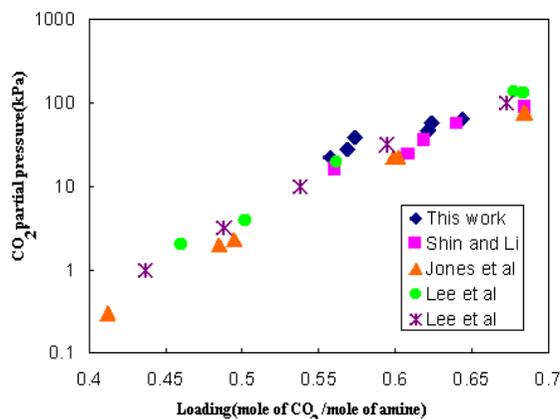


Fig.3: Comparison of CO₂ solubility in 15.3 %wt MEA aqueous solution at 40°C, between our data and those reported previously

3.1. The effect of MEA addition to TEA aqueous solution at 40°C

Increasing the MEA/TEA ratio, increases the CO₂ loading (Fig. 4) so that, 6% MEA + %18.75 TEA aqueous solution has the highest absorption capacity. This is because primary alkanolamines such as MEA react with CO₂ in alkaline solutions to produce stable carbamate as reaction (15). It is also possible the protonation of MEA according to reaction (16), but because of its low equilibrium constants (the mol fraction ratio of right hand reagents to left hand ones) compared to reaction (15) (Table 1), we can disregard it. Tertiary alkanolamines such as TEA, contrary to primary and secondary ones (secondary alkanolamines produce unstable carbamates), are unable to produce carbamates and so, only react with CO₂ via acid–base reaction mechanism (reaction 16) and have lower absorption capacity [7].

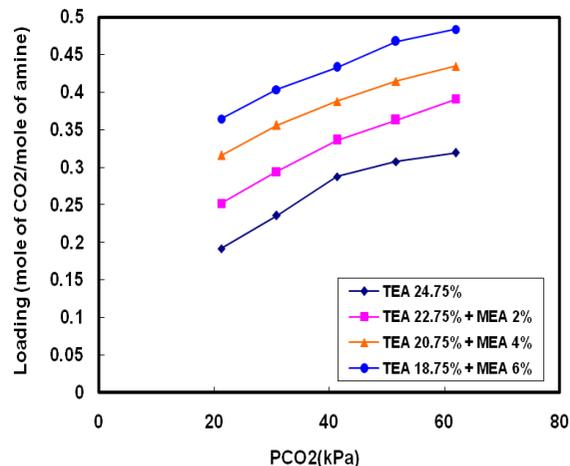
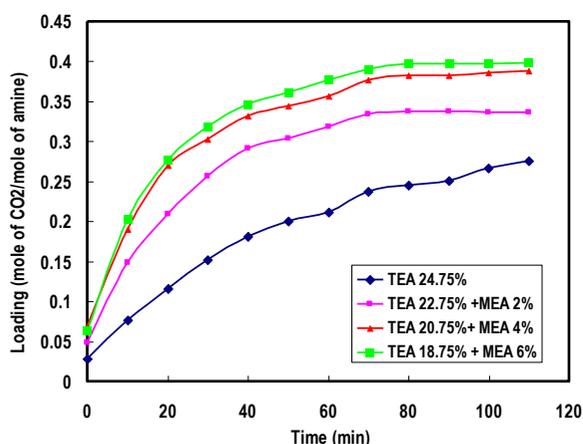


Fig. 4: CO₂ loading vs. time and its partial pressure at 40°C



Table 1.
Equilibrium constants of MEA in reactions (15) and (16) at various temperatures [7]

	303 K	318 K	333 K
Reaction 15	1.61×10^{13}	3.71×10^{12}	9.46×10^{11}
Reaction 16	5.27×10^3	1.83×10^3	6.55×10^2

The equilibrium constants are calculated using mole fractions and so, are dimensionless.

3.2. The effect of CNTs addition on the absorption behavior of different solutions of TEA+MEA at 40°C

Results showed that addition of 1 g/L CNTs to the solutions, increased the loading of CO₂ and absorption rate, and decreased the time necessary to reach equilibrium (Fig. 5). The increase in the absorption rate in the presence of CNTs may be explained by the shuttle mechanism [10], wherein it is proposed that the CNTs adsorb the dissolved gas in the gas-rich layer adjacent to the interface. CNTs then move to the bulk where desorption of the adsorbed gas takes place. This increases CO₂ uptake and enhances the rate of absorption.

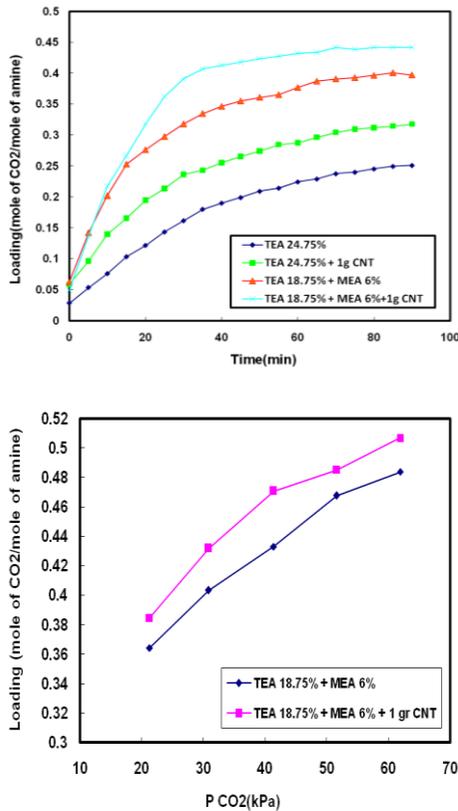


Fig. 5: The effect of CNTs on CO₂ absorption at 40°C

3.3. The effect of AC and CNTs on CO₂ absorption

In this study, AC and CNTs were used as additives in TEA %18.75 + MEA %6 solution at 40°C. The results showed that the addition of 1 g/l of CNTs into the solution increases CO₂ loading higher than the equal dosage of AC. This is perhaps related to small sizes and regular shapes of CNTs which provide more surface area to take part in interactions which are effective in the absorption of CO₂ (Fig. 6).

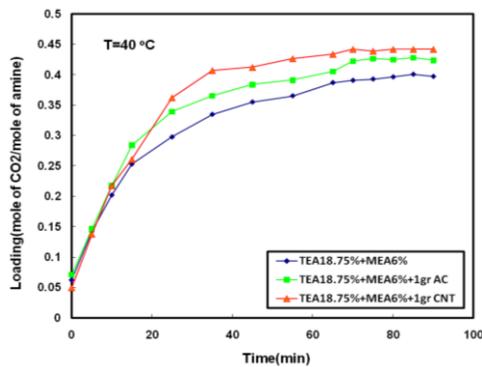


Fig. 6: The effect of AC and CNTs on CO₂ absorption in TEA %18.75 + MEA %6 solution at 40°C

3.4. The effect of CNT amount on CO₂ loading in different solutions of TEA+MEA

Experiments were done with the addition of 0.2, 0.5, 1 and 1.5 g/L CNT to different solutions of TEA+MEA. Results showed that increasing the amount of CNT is effective on CO₂ loading (Fig. 7).

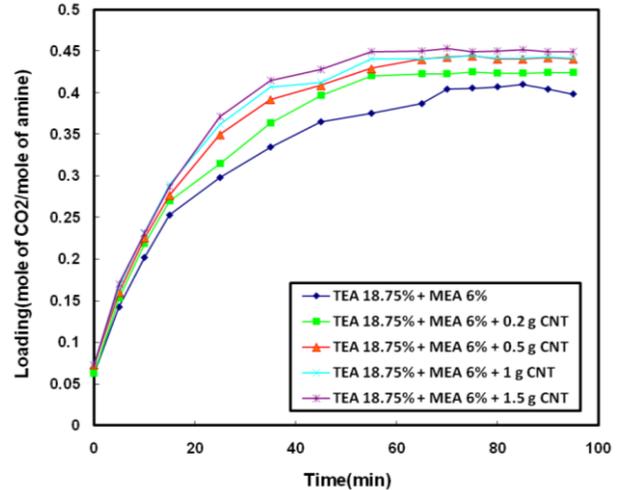


Fig. 7: The effect of carbon nanotubes amounts on CO₂ loading

3.5. The effect of AC amount on CO₂ loading in TEA+MEA solution

Experiments were done with the addition of 0.5, 1, 1.5 and 2 g/L AC to TEA+MEA solution. Results showed that increasing AC amount has no measurable influence on CO₂ loading (Fig. 8)

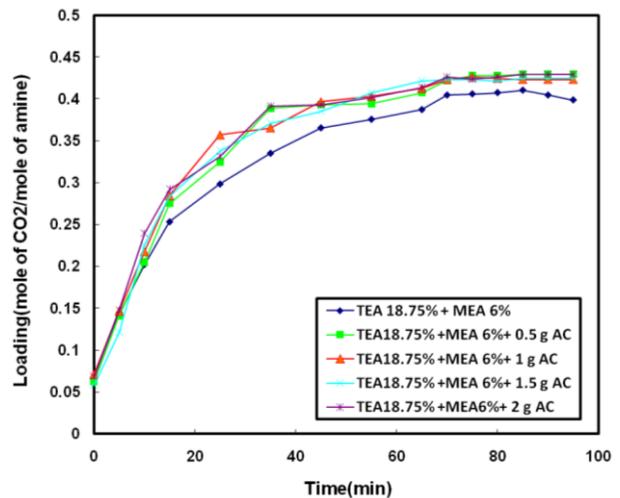


Fig. 8: The effect of AC amount on CO₂ loading

3.6. The effect of temperature on the behavior of CO₂ absorption into TEA+MEA mixture

Fig. 9 shows the loading of CO₂ in aqueous solutions of TEA %18.75 + MEA %6 at 30, 40, 50, 60 and 70 °C. It can be seen that increasing the temperature, decreases the CO₂ loading due to a decrease in physical solubility of gases. It should be noted that, CO₂ absorption in aqueous alkanolamine solutions has two steps. First, CO₂ molecules physically dissolve in water and then, they chemically react with alkanolamine species in the solution. Increasing the temperature, limits the first step and so, total absorption of CO₂ decreases

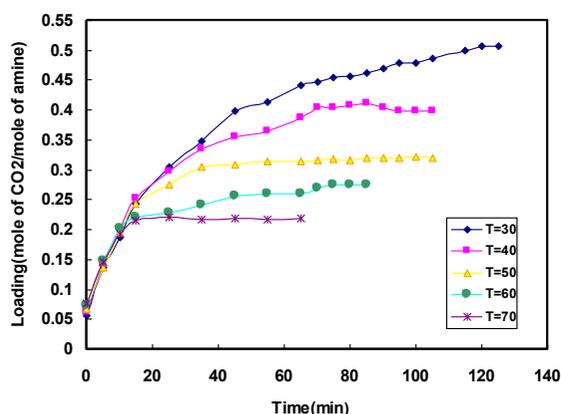


Fig.9: CO₂ loading vs. time at various temperatures in an aqueous solution of TEA % 18.75 + MEA%6.

4. CONCLUSION

In this work, aqueous solutions of TEA + MEA with different concentrations in the presence and absence of CNTs and AC at temperatures ranging from 30 to 70 °C and low partial pressures were used for CO₂ absorption from gas stream. The results showed that replacing some of TEA with MEA in the solution or addition of some CNTs or AC to the solution increases the CO₂ loading but CNTs have more influence on absorption process. CNTs addition increased CO₂ absorption rate and capacity but raising the absorption capacity was less noticeable. Lowering the temperature increased CO₂ loading in the solution.

5. ACKNOWLEDGEMENTS

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6. NOMENCLATURE

F_{CO_2}	Flow rates of CO ₂ [ml/min]
F_{l,CO_2}	Flow rate of pure CO ₂ [ml/min]
F_{Ar}	Flow rates of Ar [ml/min]
P	Ambient pressure [kPa]
P_{CO_2}	Equilibrium partial pressure of CO ₂ above solution [kPa]
P_{Ar}	Argon partial pressure above solution [kPa]
P_{H_2O}	H ₂ O partial pressures above solution [kPa]
P_{ip}	Partial pressure of gas impurities above solution [kPa]
$P_{H_2O}^*$	Saturated vapor pressure of H ₂ O in equilibrium temperature [kPa]
T	Temperature [K]
T_{Room}	Room temperature [K]
V_{sam}	Volume of sample solution [ml]
W_{1,CO_2}	Volume percentage of CO ₂ in its capsule
α_{CO_2}	Moles of absorbed CO ₂ per mole of amine in solution
X_{H_2O}	Mole fraction of H ₂ O in solution

Abbreviations

AC	Activated carbon
CNT	Carbon nanotube
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
TEA	Triethanolamine

7. REFERENCES

- [1] Y.F. Diao, X.Y. Zhang, B.S. He, C.H. Chen, X.C. Xu, "Experimental study on capturing CO₂ green house gas by ammonia scrubbing". *Energy Conversion and Management*, Vol. 45, pp. 2283–2296, 2004.
- [2] R. Wang, D.F. Li, D.T. Liang, "Modeling of CO₂ capture by three typical amine solutions in hollow fiber membrane contactors". *Chemical Engineering and Processing*, Vol. 43, pp. 849–856, 2004.
- [3] M. Caplow, "Kinetics of carbamate formation and breakdown". *J. Am. Chem. Soc.*, Vol. 90, pp. 6795–6803, 1968.
- [4] D.A. Glasscock, J.E. Critchfield, G.T. Rochelle, "CO₂ absorption/desorption in mixtures of methyldiethanolamine with monoethanolamine or diethanolamine". *Chem. Eng. Sci.*, Vol. 46, pp. 2829–2845, 1991.
- [5] S. Xo, Y. Wang, F.D. Otto, A.E. Mather, "Kinetics of the reaction of carbon dioxide with aqueous 2-piperidineethanol solution". *AIChE*, Vol. 39, pp. 1721–1725, 1993.
- [6] N. Daneshvar, D. Salari, H. Zamzami, M. Zarei, S. Aber, "Absorption of carbon dioxide into I) aqueous solutions of N,N-dimethylethanolamine II) aqueous blends of mono and diethanolamine with N,N-dimethylethanolamine". *Chem. Biochem. Eng. Q.*, Vol. 19, pp. 297–302, 2005.
- [7] N. Daneshvar, M.T. Zaafarani Moattar, M. Abedinzadegan Abdi, S. Aber, "Carbon dioxide equilibrium absorption in the

- multicomponent systems of CO₂+TIPA+MEA+H₂O, CO₂+TIPA+Pz+H₂O and CO₂+TIPA+H₂O at low CO₂ partial pressures: experimental solubility data, corrosion study and modeling with artificial neural network". *Separation and Purification Technology*, Vol. 37, pp. 135–147, 2004.
- [8] H.A. Rangwala, B.R. Morrell, A.E. Mather, F.D. Otto, "Absorption of CO₂ into aqueous tertiary amine/MEA solutions". *Can. J. Chem. Eng.*, Vol. 70, pp. 482–490, 1992.
- [9] G.W. Xu, C.F. Zhang, S.J. Qin, W.H. Gao, H.B. Liu, "Gas-liquid equilibrium in a CO₂-MDEA-H₂O system and the effect of piperazine on it". *Ind. Eng. Chem. Res.*, Vol. 37, pp. 1473–1477, 1998.
- [10] A.K. Saha, S.S. Bandyopadhyaya, "Absorption of carbon dioxide in alkanolamines in the presence of fine activated carbon particales". *Can. J. Chem. Eng.*, Vol. 70, pp. 193–196, 1992.