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# Absorption of Carbon Dioxide into Aqueous Ammonia Solution using Blended Promoters (MEA, MEA+PZ, PZ+ArgK, MEA+ArgK)

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Absorption, Carbon Dioxide Capture. Promoted Ammonia solution, Organic Promoter, Amino Acid salts, blended promoter.

ABSTRACT

*Absorption of CO2 into promoted-NH3 solution utilize a packed column (1.25 m long, 0.05m inside diameter) was examined in the present work. The process performance of four different blended promoters monoethanolamine (MEA)+ piperazine (PZ), piperazine (PZ)+ potassium argininate (ArgK) and monoethanolamine +potassium argininate was compared with unpromoted-NH3 solution by evaluated the absorption rate (φ_(CO_2 )) and overall mass transfer coefficient (K_(G,CO_2.) a_v) over the operating ranges of the studied process variables (1-15Kpa initial partial pressure of CO2, 5-15 Liter/min gas flow rate, 0.25-0.85 Liter/min liquid flow rate). The results exhibit that the absorption behavior and efficiency can be enhanced by rising volumetric liquid flow rate and initial CO2 partial pressure. However, the gas flow rate should be kept at a suitable value on the controlling gas film. Furthermore, it has been observed that the (PZ+ArgK) promoter was the major species that can accelerate the absorption rate and reached almost 66.166% up to123.23% over that of the unpromoted-NH3 solution.*

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## 1. Introduction

Carbone dioxide is a non-toxic gas and one of the essential greenhouse gases (GHGs) which it has an important role contributing to serious global warming issues produced from large point-emission sources by various industrial processes. Ignoring the long-term impact of increased concentration of carbon dioxide causes a climate changes itself. Negative effects of the climate changes, such as drought and heat stress, are likely to override any direct benefits that high levels of carbon dioxide [1-3].Carbon dioxide capture is receiving great attentions in recent decades and the solvent-based chemical absorption is one of the most promising technologies due to its high reactivity, furthermore, it applied in industrial applicability for many years for efficient CO2 elimination technology [4-6].The most well-established one commercial solvents used in absorption are alkanolamines monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA) and N-methyldiethanolamine (MDEA)) and hot potassium carbonate process [7-10].

However, the amines processes have many disadvantages, such as low CO2 removal capacity, highly corrosive, degraded in the presence of O2 and other species such as SO2, NO2 present in the combustion exhaust gas and elevated energy consumption in the absorption process [5,6,11-12]. However, the essential challenge of the hot-K2CO3 solution is the slow reaction kinetics with CO2 as compared to the absorption by alkanolamines, mainly in post-combustion $CO_2$ - capture conditions: lower temperature and initial CO2 partial pressure [5]. However, alternative absorbents are required to overcome the drawbacks of alkanolamines and potassium carbonate. Among several alternatives, in natives, ammonia solution is attracting attention owing to their low cost, low levels of regeneration energy, little corrosion, not degradation like happened for the amines, and higher absorption capacity than the alkanolamines and potassium carbonate at the same operating temperature and pressure [13-14]. Experimental studies had been widely carried out for assessment the comparison performance between ammonia and monoethanolamine absorbents to minimize carbon dioxide had been extensively carried out systematically. They found that Aqueous ammonia (in comparison to aqueous amine) has much higher absorption and loading capacity, requiring lower energy for regeneration. Furthermore, Aqueous ammonia has better resistance to oxidative/thermal degradation relative to amine [15-21]. Nevertheless, firstly, the low absorption capacity of CO2, which would require larger absorption facilities, is restricted in its commercial application to absorb CO2, which increases the cost of capital. Secondly, furthermore high NH3 volatility resulted in low CO2 absorption conditions, further reducing the rate of CO2 reactions with the aqueous NH3 absorbent [22]. The Ammonia –based process can be make more efficient and economically suitable by accelerate capture reactions through the use of promoters to improve the CO2 mass transfer rates [22-25]. With the benefits of a high CO2 reaction rate, primary and secondary amines are considered as effective-rate promoters to increase the effectiveness of CO2 capture process based on ammonia [23-24,26-27]. Piperazine (PZ) is well known as an effective- rate promoter [ 28-29] and this applies to the ammonia process [24,30-33]. Particular attention was paid among the different candidate promoters, amino acids and amino acids salts, since they play a major role as a CO2 absorption agent. Therefore, amino acids are regarded to be eco-friendly compounds and therefore do not lead to environmental pollution. In addition, amino acids are highly resistant to oxidative degradation and an adequate CO2 absorption potential as an amino function group is present [22,34-35]. The aim of this work is to study the efficiency of CO2 capture in a packed column via promoted NH3 solutions. The effects of different CO2 capture operating parameters, namely, type of blended promoters, gas and liquid flow rate, and initial CO2 partial pressure. In addition, for the development and optimization of CO2 absorbers, the overall mass transfer coefficient is extremely important. Hence, it has been explained the fundamental relationships between this coefficient and the operating parameters.

## 2. Theoretical Aspects

### *I. Reaction mechanism of carbon dioxide into promoted ammonia solution*

Carbone dioxide absorption into promoted ammonia solutions involves a number of reversible reactions and protonation equilibria covering the species of carbonate, amine and carbamate [22-24,26,30,33]. The reaction between aqueous ammonia and carbon dioxide mainly occurred in the liquid phase of the gas-liquid interface, the reaction in liquid phase of the $CO_2$-ammonia system are given as follows [12,36-38]:

$$CO_2 + 2NH_3 \Leftrightarrow NH_2COONH_4 \qquad (1)$$

In fact, reaction (1) consists of the two steps:

$$CO_2 + NH_3 \Leftrightarrow NH_2COOH \qquad (2)$$

$$NH_3 + NH_2COOH \rightarrow NH_4^+ + NH_2COO^{-1} \qquad (3)$$

The reaction (2) is fast and irreversible while the reaction (3) is instantaneous; Therefore, the reaction between aqueous ammonia and carbon dioxide is mainly controlled by the reaction (2). In addition, the $NH_3/CO_2$ reaction takes place at the fast pseudo first-order reaction system [12,36]. Carbon dioxide capture "reaction" by primary and secondary alkanolamines solutions, including $NH_3$, can be described by a Zwitterion mechanism [38] which proposed by Caplow [40] and reintroduced by Danckwerts [41]. In this mechanism ammonia molecule firstly reacts with carbon dioxide to form a zwitterion that is later deprotonated in a second step [38].

$$CO_2 + 2NH_3 \Leftrightarrow NH_3^+COO^- \quad (4)$$

$$NH_3^+COO^- + B \Leftrightarrow NH_2COO^- + BH \quad (5)$$

The species B in the reaction (5) represents any base (molecule of ammonia, water or a hydroxide ion) that is available in the solution. However, MEA has several limitations as a solvent which led to the use as a promoter with the other solvent [42-45]. The Zwitterion mechanism pathway can be described MEA promotion of the $CO_2$ absorption. This mechanism suggested that primary (such as MEA) and also secondary (such as DEA) alkanolamines were first reacted with $CO_2$ to form zwitterions [40-41]and then the intermediate was instantaneously neutralized by the base (such hydroxyl ions ($OH^{-1}$), MEA itself, or $H_2O$) to form carbamate [46]: -

$$CO_2 + RNH_2 \Leftrightarrow RNH_2^+COO^- \quad (6)$$

$$RNH_2^+COO^- + RNH_2 \Leftrightarrow RNHCOO^- \quad (7)$$

Alternative promoters are still required even though the advantage of MEA promoter due to the problems of deterioration and corrosion. Recently Piperazine (PZ) are commonly used as a promoter because of its low vapor pressure, efficient promoting effect than other amine, low degradation [24,28-29,31-33]. Piperazine (PZ) as a cyclic diamine has two active nitrogen groups and react with CO2 through two main reactions that are rate limiting in a solvent containing PZ is the carbamate and di-carbamate formation as follows:

$$CO_2 + PZ \Leftrightarrow PZCOO^- \quad (8)$$

$$CO_2 + PZCOO^- \Leftrightarrow PZ(COO^-)_2 + H^+ \quad (9)$$

The $CO_2$ reaction (8) with free PZ is the dominant reacting route accompanied by the reaction (7) which is much lower than reaction (9). The amino acid salt solution (AAS) is another class of solvents used as promoters (22,34-35,47-50) for $CO_2$, and in aqueous solutions it is three different forms viz. acidic, zwitterion and basic which the acidic state does not take part in the reaction with $CO_2$ as the main solvent or promoter. Zwitterion mechanism [47] can be explained the reaction between AAS-promoter and $CO_2$ likewise MEA promoter as followes: -

Zwitterion carbamate formation: -

$$CO_2 + R_1NHCHR_2COO^- \Leftrightarrow \ ^-OOCN^+(R_1)NHCHR_2COO^- \quad (10)$$

Deprotonation:

$$^-OOCN^+(R_1)NHCHR_2COO^- + B \Leftrightarrow \ ^-OOCNR_1CHR_2COO^- + BH^+ \quad (11)$$

Based on the above overview, more research needs to be done to evaluate the reliability of different AAS as blended promoters with other types of promoters as alkanolamines or cyclic secondary diamine.

### *II. Overall mass transfer coefficient*

The absorption of $CO_2$, based on the two-film theory, can be determined by Eq. (12) into an promoted-$NH_3$ solution in a packed column [12,36]: -

$$r_{CO_2} = K_{G,CO_2}\left(P_{CO_2}^b - P_{CO_2}^*\right) \quad (12)$$

where $r_{CO_2}$ is the $CO_2$ absorption rate into aqueous promoted–$NH_3$(mol/($m^2$·s), $K_{G,CO_2}$ is the overall mass transfer coefficient (mol/s.$m^2$.kPa), $P_{CO_2}^b$ is the partial pressure of $CO_2$ in the balk gas (kPa), $P_{CO_2}^*$ is the equilibrium pressure of $CO_2$ corresponding to the promoted absorbent $P_{CO_2}^*$.Partial pressure of $CO_2$ in the balk ($P_{CO_2}^b$) is represented as the log mean average of the inlet and outlet partial pressures and is obtained according to the following Eq.(13)[12,36]:-

$$P_{CO_2}^b = \frac{\left[P_{CO_2,in} - P_{CO_2,out}\right]}{ln\left[\frac{P_{CO_2,in}}{P_{CO_2,out}}\right]} \quad (13)$$

Where $P_{CO_2,in}$ *and* $P_{CO_2,out}$ are inlet and exit $CO_2$ partial pressures (Kpa).

For the absorption of $CO_2$ into aqueous ammonia is fast and also using $CO_2$-free solution, the $P^*_{CO_2}$ can be neglected (i.e $P^b_{CO_2} \gg P^*_{CO_2}$ )[36], hence;

$$r_{CO_2} = K_{G,CO_2}\left(P^b_{CO_2}\right) \qquad (14)$$

According to the two film theory, the overall mass transfer coefficient $K_{G,CO_2}$ can theoretically calculated from individual gas and liquid coefficients as expressed in Eq.(15)[12,36,51]:-

$$\frac{1}{K_{G,CO_2}} = \frac{1}{k_{G,CO_2}} + \frac{H}{Ek_{L,CO_2}} \qquad (15)$$

$and$

$$\varphi_{CO_2} = K_{G,CO_2}.a_v\left(P^b_{CO_2}\right) \qquad (16)$$

Where $\varphi$ the overall absorption rate (mol/s).

In the packed columns, the effective gas-liquid interfacial area ($a_v$) is considered as an important parameters in mass transfer for $CO_2$ absorption in addition to the mass transfer coefficients ($K_{G,CO_2}$). Therefore, the overall mass transfer coefficients can be given as follows [36,51]: -

$$\frac{1}{K_{G,CO_2}.a_v} = \frac{1}{k_{G,CO_2}.a_v} + \frac{H}{Ek_{L,CO_2}.a_v} = \frac{P^b_{CO_2}}{\varphi_{CO_2}} \qquad (17)$$

For the chemical absorption of $CO_2$ in a packed column and fast reaction where the mole fraction of $CO_2$ in equilibrium with the bulk liquid is assumed zero and the differential mass balance is given by Eq. (18) [51]: -

$$-u_G\frac{dy}{dx} = K_{G,CO_2}.a_v.(RT).y_{CO_2} \qquad (18)$$

$integrating\ Eq(18)\ yields$:-

$$K_{G,CO_2}.a_v = \frac{u_G}{Z(RT)}\left[\frac{y_{CO_2.in}}{y_{CO_2.out}}\right] \qquad (19)$$

## 3. Experimental

*I. Materials and absorbent preparation*

Analytical grade $NH_3$ with weight concentration of 28% was purchased from Aladdin company(Iraq). The exact $NH_3$ concentration is determined via titration with standard hydrochloric acid solution (0.1M HCl) from fluke(Sigma-Aldrich). In the present work, a comparative study of four different types of blended prompters monoethanolamine (MEA, 99.8%, Sigma-Aldrich), piperazine (PZ, >99%, Sigma-Aldrich) and amino acids salt. The amino acid selected, which is relatively inexpensive, easily accessible and well performing in terms of CO2 absorption from the molecular structure point of view. The particular amino acid was used, arginine (99%, Sigma-Aldrich) to prepare the amino acid salt (potassium argininate, ArgK), by neutralizing selected amino acids in deionized, double-distilled water with an equimolar quantity of an alkaline hydroxide (KOH,99%, Sigma-Aldrich) solution. In this process 8 N KOH solution added slowly to the amino acid in order for the K+ ions to be attached at the correct location [52] as illustrated in Eq. (20):

$$\begin{array}{ll} HO_2C-R-NH_2 \xrightarrow{Aqueous\ phase} & {}^{-}O_2\ C-R-NH_3 \\ & Protonated\ amino\ group: loss\ of\ reactivity \\ & \swarrow \\ KO_2C-R-NH_2 & \\ Neutralization\ of\ amino\ group:\ necleophilic\ attack\ on\ CO_2 & \end{array} \qquad (20)$$

*II. Experimental set-up and procedure*

Figure.1 presents a schematic diagram of the experimental plant used during this study. The experiments were carried out in a stainless steel packed bed absorber consisting of a 1.25 m long, 0.05m inside diameter with 5 mm wall thickness. To avoid channeling effects in the packed column [53-54], the packing height of the absorber was made of 0.5m of ceramic Ranching rings (4mm i.d) which gives criteria absorber height/ particle diameter ($L_R$/dp) and absorber diameter/ particle diameter ($D_r$/dp) values of 100 and 12.5, respectively. This matched the critical value presented by [53-54] of 50 and 10, respectively. A stainless steel screen on the base of the column has held the packing and had a mesh hole wide enough to prevent flooding of the bed, but sufficiently narrow to inhibit the passage of particles. Three calibrated thermocouples (Type T) were situated within the bed at different axial positions to measure bed temperature throughout and the pressure throughout the bed were measured via pressure tap was set in the column head. The artificial flue gas feed ($N_2$ and $CO_2$) is introduced at the bottom of the packed absorber. Before the gaseous mixture was supplied to the packed column and passing through a calibrated rotameter to magnitude the gaseous feed rate. The promoted-$NH_3$ solution was pumped to the top of the packed absorber from the stainless steel feed tank by a metering dose pump (Dose pump, DDE6-10B-PVCLVLC-X311001FG, Italy), flow through the distributor which was set up at the head of the packed section. The liquid feed rate was controlled by the pump head setting, besides that the gaseous mixture($CO_2$+$N_2$) and absorbent liquor were in counter-current flow pattern, it is beneficial to make $CO_2$ and promoted-$NH_3$ solution contact and react thoroughly. The exiting solution is released via a pipe, linked to the three-way valve from the lower part of the column,meanwhile the liquid outlet stream was split into a sampling stream and a waste stream. The sampling stream was connected to a needle valve for withdrawal of samples to be analyzed. After reaching steady state, samples were collected within 10 min and subsequently analyzed. To avoid pressure building in gas and liquid delivery and discharge stream a pressure monitor and safety valve have been mounted, also to ensure the flow in one direction, one-way valve was installed in the entire lines (gas and liquid). All experiments were performed under atmospheric pressure ,$25^0$C temperature and using fresh solutions with initially zero $CO_2$ loading. All the details of operating conditions are given in Table 1.

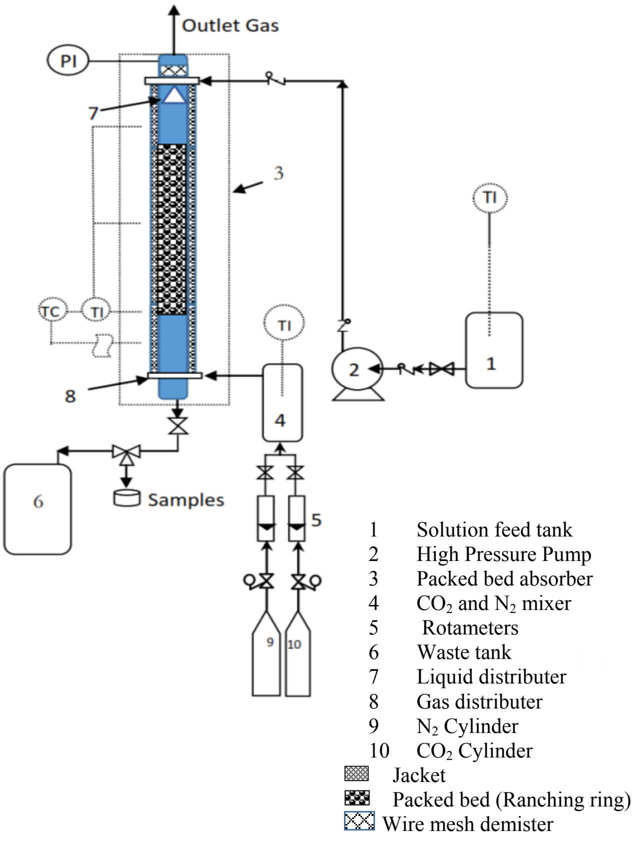


**Figure 1: Schematic diagram of the experimental apparatus.**

**Table 1: Experimental Operating Conditions.**

| Experimental parameter | Experimental |
|---|---|

| | **operating condition** |
|---|---|
| Column Pressure (Kpa) | 0.1 |
| Column Temperature ($^oC$) | 25± 1 |
| Aqueous $NH_3$ concentration | 8wt% |
| initial CO2 partial pressure (kPa) | 5-15 |
| liquid flow rate liter/min | 0.25-0.85 |
| gas flow rate liter/min | 5-15 |
| Promoter MEA+PZ | 0.3M-MEA |
| | 0.1,0.5,0.7M-PZ |
| Promoter PZ+ArgK | 0.3M-PZ |
| | 0.1,0.5,0.7M-ArgK |
| Promoter MEA+ArgK | 0.3M-MEA |
| | 0.1,0.5,0.7M-ArgK |

*III. Analysis of samples for $CO_2$ loading.*

The loading of carbon dioxide was estimated using the Chittick $CO_2$ analyzer device [55-57], where the Official Analytical Chemists Association (AOAC) described this. Figure 2 shows the schematic of the apparatus used in this work.

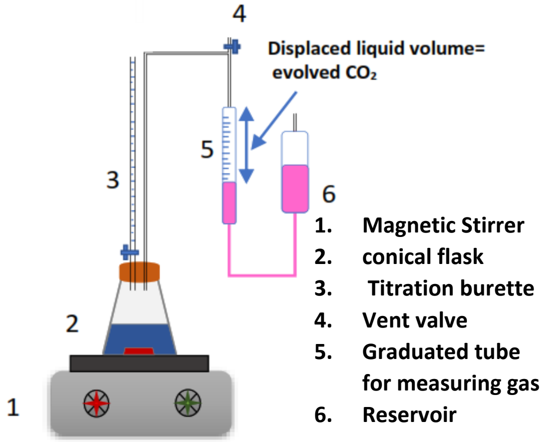


**Figure 2: Chittick $CO_2$ analyzer apparatus.**

The conical flask (titration flask) that is placed on a magnetic stirrer with methyl orange is applied to a specified volume of liquid samples (10-30 mL, depending on $CO_2$ content). The flask was fixed and firmly inserted into one side of the U-Tube manometer by a rubber stopper while the other side was vented to atmosphere. Hydrochloric acid (1.0 M) was gradually added from a burette to the liquid sample in the titration flask which was placed on a magnetic stirrer for homogenizing and help the solution release $CO_2$ as shown in Figure 2. Titration terminated when the indicator color was changed. After that, the colored fluid in the graduated gas measuring pipe was movement results from $CO_2$ releasing and the pressure produced by the $CO_2$ emitted from fluid is insignificant [56-57]. The quantity of $CO_2$ absorbed by the promoted-$NH_3$ solution ($CO_2$ loading) was obtained by [56]: -

$$\propto_{CO_2} = \frac{mol_{CO_2}}{mol_{solvent}} = \frac{\left(\frac{V_{CO_2}\times P}{RT}\right)}{C_1 \times V_1} \qquad (21)$$

Where

$V_{gas}$: Volume of displaced fluid in the graduated pipe(mL).
$V_{CO2}$ : Volume of $CO_2$ emitted, $V_{CO_2}$= $V_{gas} - V_{HCL}$ (mL).
$V_{HCL}$:Volume HCl added to the titration flask during(mL).
R: Gas constant (8.314 Liter.KPa)/(mol.K).
P: Atmospheric pressure (KPa).
T: Temperature (K)
$C_1$: Solution concentration (mol/L).
$V_1$: Volume of test sample (ml).

## 4. Experimental Results

*I. Effect of $CO_2$ partial pressure.*

Carbon dioxide partial pressure effect on the absorption rate $(\varphi_{CO_2})$ and overall mass transfer coefficient $(K_{G,CO_2}.a_v)$ for $CO_2$ absorption using promoted-$NH_3$ solution was presented in Figure 3. The $\varphi_{CO_2}$ *and* $K_{G,CO_2}.a_v$ increases gradually as the initial partial pressure of CO2 increases from 5 to 15 Kpa. Such behavior was also described by Zeng et al., [12,36], Ma et al., [58] , Jeon et al.,[59] and Khan et al.[60].

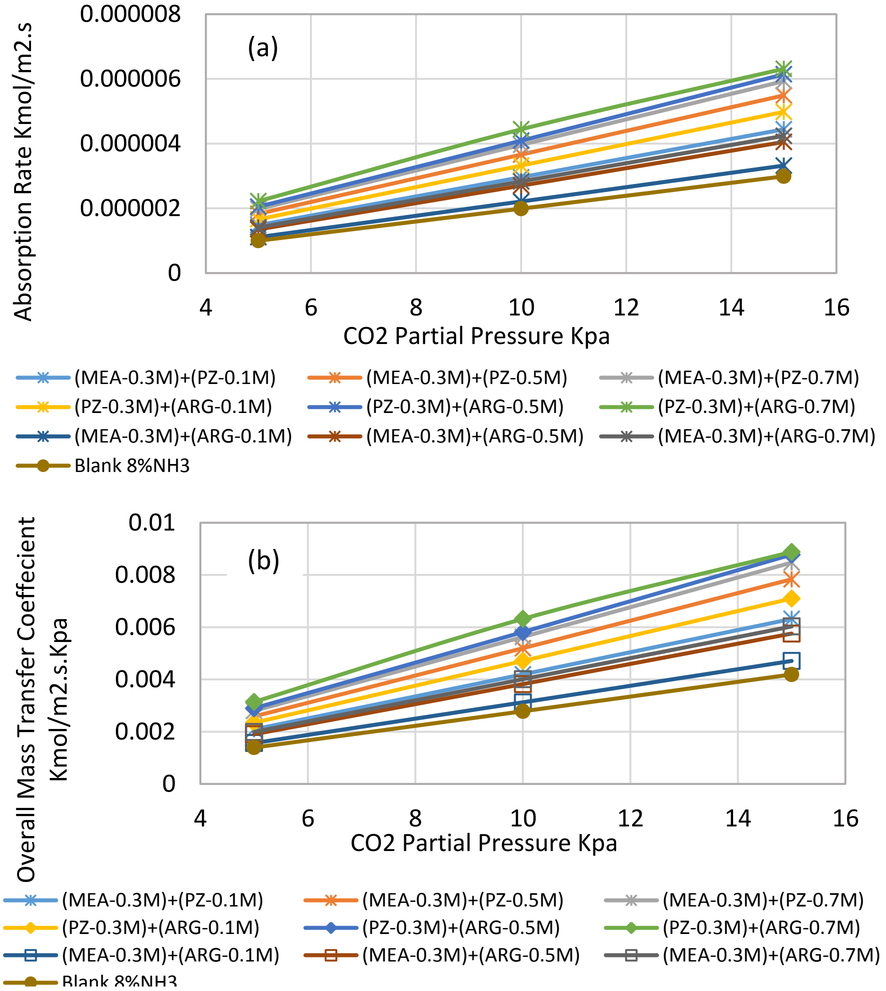
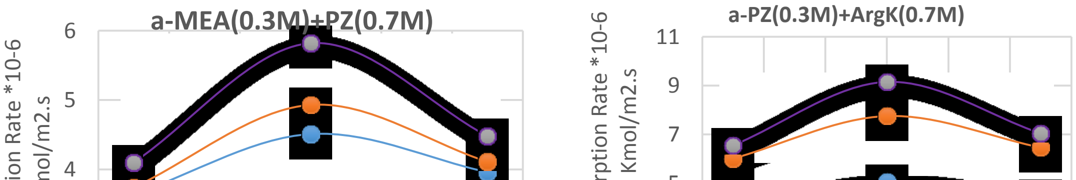


**Figure 3: a-Absorption rate of CO2, b- Overall mass transfer coefficient of CO2 vs CO2 partial pressure for promoted NH3 solution at gas flow rate (15liter/min) and liquid flow rate (0.25liter/min).**

According to the two-film theory, increasing $CO_2$ partial pressure (i.e., inlet $CO_2$ concentration) lead to decrease the mass transfer resistance of the gas phase and allows more amount of $CO_2$ to transfer from the bulk of gas to the gas-liquid interface, resulting in a higher performance of mass transfer. For the whole experimental runs, the average loading (α) rate of $CO_2$ after absorption has a lesser amount of than 0.24 which confirmed that the gas film resistance was not predominant.

### *II.Effect of Gas Flow Rate*

According to the experimental results achieved, increasing gas flow rate from 5 to 10 liter/min lead to initially witnessed a growth and increased absorption rate $(\varphi_{CO_2})$ and overall mass transfer coefficient $(K_{G,CO_2}.a_v)$ as shown in Figure 4 and but then steadily declined over the period studied when the gas flow rate exceeds 10 liter/min. . This is first might be due to the higher amount of $CO_2$ available under that condition for absorption, in consequence a higher value could be obtained for the $(K_{G,CO_2}.a_v)$ results for the mass transfer between the gas and liquid. However, a further increase in gas flow rate has a little effect on the overall mass transfer coefficient as shown in Figure 4. This is due to the contact time between the liquid and gas, which decreased as a higher gas flow rate was used.



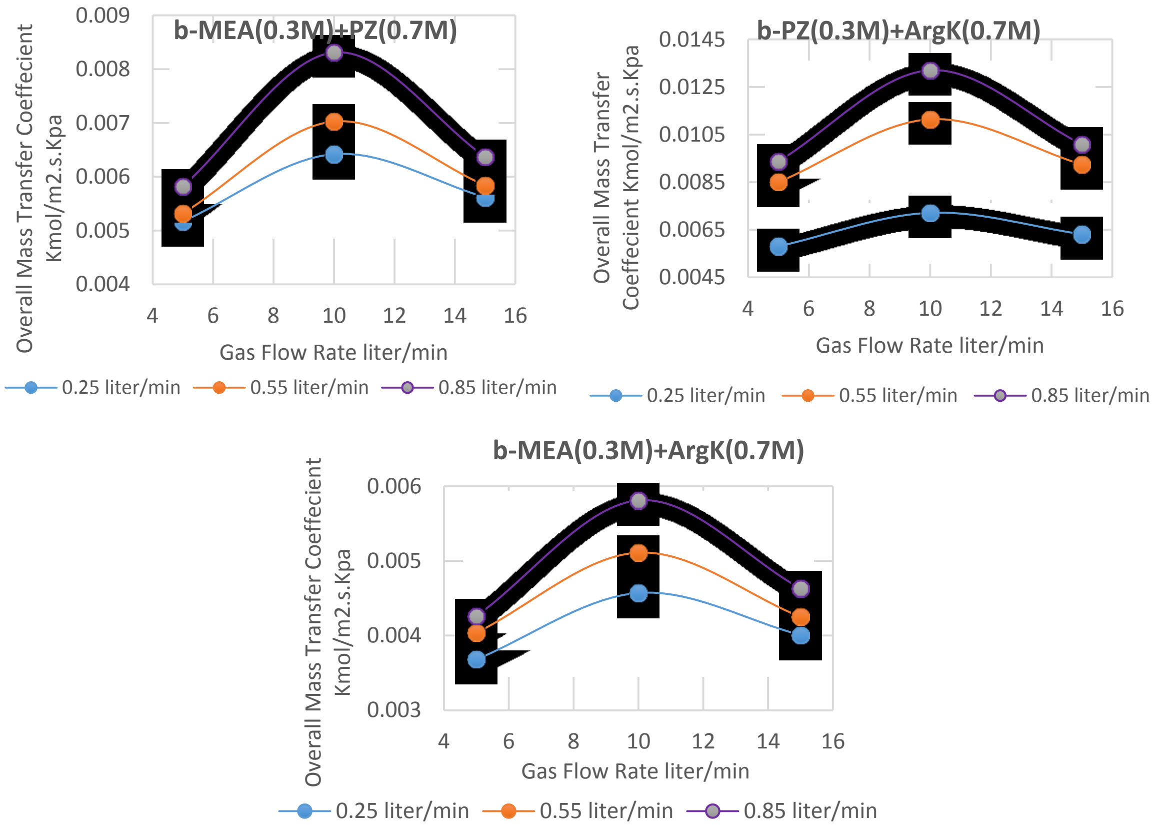
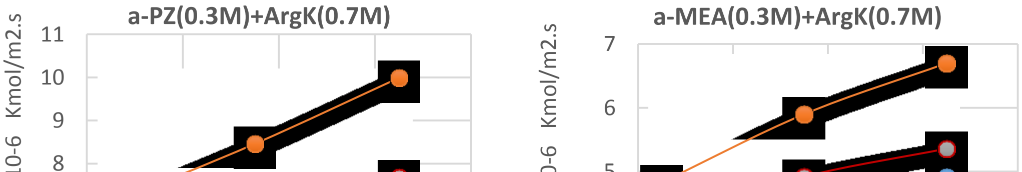


**Figure 4: a-Absorption rate of CO2, b- Overall mass transfer coefficient of CO2 vs gas flow rate for promoted NH3 solution as a function of liquid flow rate, at 10Kpa initial CO2 partial pressure and various blended promoters.**

According to the variation of the overall mass transfer coefficient in Figure 4, it is proposed that the gas flow rate should attain a certain value to reduce the gas-side resistance i.e. the gas flow rate should be kept suitable value. Similar behavior was showed by Xu et al., [33] and Li et al., [51].

*III. Effect of Liquid Flow Rate.*

Figures 4 and 5 show effects of liquid flow rate on the absorption rate ($\varphi_{CO_2}$) and overall mass transfer coefficient ($K_{G,CO_2}.a_v$). It could be noticed from those figures, the increase in the fluid flow rate from 0.25 to 0.85 liter/min would result in a significant increase in the value of the $K_{G,CO_2}.a_v$. A similar trend has also resulted by previous studies of Zeng et al., [36], Ma et al., [58], Jeon et al., [59], Koronaki et al., [61] and Xu et al., [33].



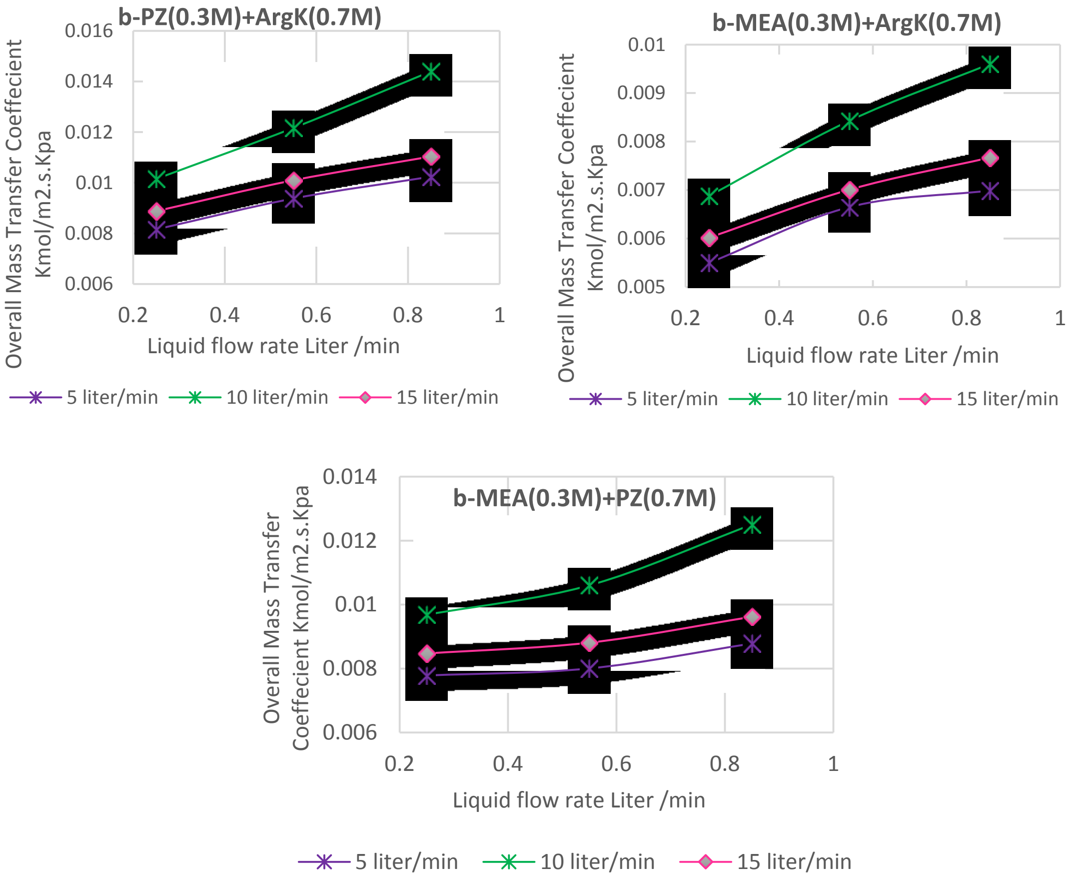


**Figure 5: a-Absorption rate of $CO_2$, b- Overall mass transfer coefficient of $CO_2$ vs liquid flow rate for promoted $NH_3$ solution as a function of gas flow rate, at 15 Kpa initial $CO_2$ partial pressure and various blended promoters.**

This may be described to the following explanations: firstly, increasing the liquid flow rate, leading to more packing surface would be wetted by liquid, and thereby cause an improvement in the gas-liquid effective interfacial area. Secondly, according to the two-film theory, the turbulence degree at gas–liquid interface is increased at a higher liquid flow rate which leads to an increase of liquid side mass transfer coefficient where it has a positive impact on the overall mass transfer coefficient in the case of liquid-phase controlled mass transfer according to Eqs. (15 and 17).

### *IV. Effect of blended promoters (types and concentration).*

Figures 3 and 6 shows the $CO_2$ absorption rate behavior into aqueous promoted ammonia solutions with (MEA+PZ), (MEA+ potassium argininate (ArgK)), and (PZ+ aqueous potassium argininate (ArgK)) at different promoter concentration. The absorber was operated at a temperature of 25 °C, a gas flow rate of 10 Liter/min, liquid flow rate 0.85 Liter/min and a $CO_2$ inlet partial pressure 15 KPa. It is worthwhile to note that the absorption rate ($\varphi_{CO_2}$) in the aqueous promoted $NH_3$ solution and overall mass transfer coefficient ($K_{G,CO_2}.a_v$) increases significantly resulting of the addition of a small amount of all blended promoter and concentration compared with the un-promoted ammonia solution. This confirmed that the addition of a combination of promoters has a better-enhanced effect on the absorption rate. As can be seen from Figure 6, introducing a small amount of MEA (0.3M) +PZ additives with various PZ(0.1,0.5,0.7M) concentration can enhance and accelerate absorption characteristics of absorption process from 48.14 to 99.095 % over than the un-promoted-$NH_3$ solution (i.e., blank solution). Furthermore, the addition (PZ (0.3M) + potassium argininate (ArgK) (0.1,0.5,0.7M)) shows excellent and greatest activity as a favorable promoter, which can accelerate the rate of absorption attaining from 66.166 to 123.23 % over than the unpromoted-$NH_3$ solution. In addition, adding (MEA (0.3M) + potassium argininate (ArgK) (0.1,0.5,0.7M)) to the $NH_3$ solution, it rose absorption rate to reach a value of 11.11 to 42.28 % over the $NH_3$ solution blank as evidence in Figure 6. Shen et al., [49] reported that an increase of $CO_2$ absorption rate was attained to about 87.5% for arginine promoter in 30% potassium carbonate while Xu et al., [33] reported values from 41.5 to 72.2% for PZ promoter in $NH_3$ solution.

The promising results of the mass transfer coefficient and absorption rate have been gained by using combination promoters of (MEA + PZ) and (PZ+ potassium argininate (ArgK)). This can be described by two different chemicals mechanizes for the MEA promotion effect. The first one was the shuttle mechanism which explained catalytic activity of MEA promoters, at ambient temperature, where the promoter works as a carrier to offer alternative pathway for the moving of the $CO_2$ absorbed from the interface to the bulk of liquid [42]. The homogenous catalytic mechanism was another way to describe the MEA catalytic activity where the amine(MEA) behave as a homogenous catalyst in the reaction between $CO_2$ and $NH_3$ of reaction shown in Eq. (2) by creating an intermediate (Eq. (6)) with the absorbed $CO_2$ then the intermediate is deprotonated to produce the final product by a very fast reaction Eq. (7).

The progress of $CO_2$ absorption by PZ-promoter is owing to the structure feature of PZ with two secondary amine sites. This can be applied to explain the reason exhibits a relatively higher absorption rate and capacity [24,31,33]. Additionally, the improved mass transfer absorption rate can be explained through chemical interactions where the intermediates of zwitterions changes proton with a base namely, PZ , MEA or $NH_3$ . It is well-known that the role of $NH_3$ is that it acts as a proton acceptor over the over PZ and MEA since $NH_3$ is present at high concentrations and receives a larger quantity of the protons. This permits extra free PZ to exist in the solution enhancing mass transfer compared to PZ alone. Furthermore, aqueous $NH_3$ solution works as pH buffer which providing a higher pH as CO2 absorbed. For amino acid salts, potassium argininate (ArgK) shows excellent performance and can speed up $CO_2$ absorption rate over the $NH_3$ alone. Two probable reasons are taken into account for potassium argininate as a preferable promoter in $NH_3$ solutions. One is that of their basic side chains (R groups) mainly amino group which has indicated to have fast rate of reaction with $CO_2$ [49]. The zwitterion mechanism of reaction is recognized and the formation of carbamate is a key step. The other is because of its side chain (guanidinium group) of argininate, which owns a pKa of 12.5. Fast deprotonation by the basic guanidinum group from the $CO_2$ amino acid salts complex is expected to result in the formation of carbamates.

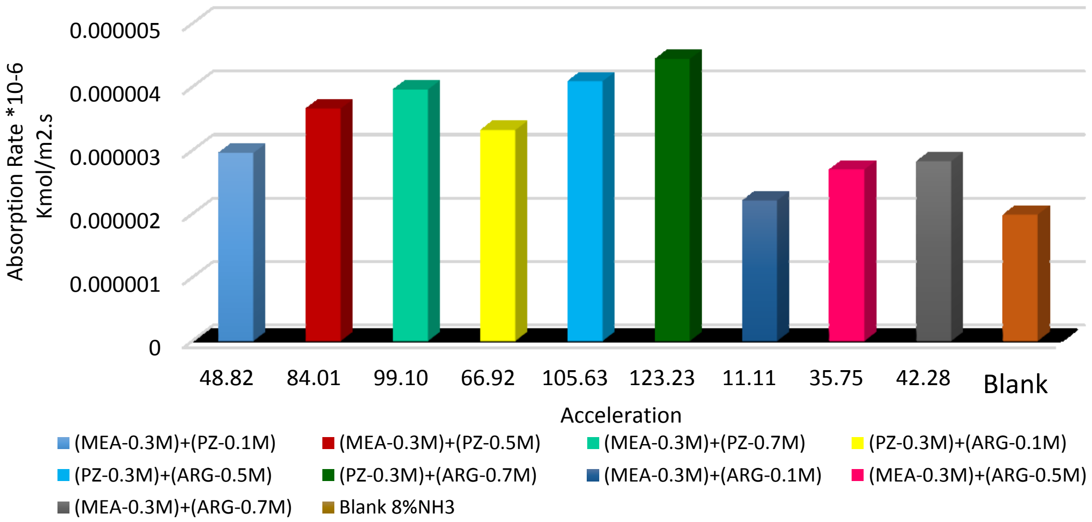


**Figure 6: Acceleration % Vs. Absorption rate of CO2 for promoted NH3 solution at 10 Kpa initial partial pressure of CO2, gas flow rate (15liter/min), liquid flow rate (0.25liter/min) and various blended promoters concentration.**

## 5. Conclusions.

The absorption of $CO_2$ from a gas mixture containing 5-15Kpa initial partial pressure by absorption in a packed column using aqueous ammonia solution promoted with different types of blended amine and amino acid salts was studied. The experimental results indicated the following points: -

1- The absorption rate ($\varphi_{CO_2}$) and overall mass transfer coefficient ($K_{G,CO_2}.a_v$) increases significantly with the increasing initial partial pressure and liquid flow rate.

2- The increased gas flow rate lead to increases absorption rate and overall mass transfer coefficient and then have a tendency to decline when the gas flow rate > 10 liter/min, this indicate that the resistance to mass transfer mainly lies in the gas film between 5-10 liter/min gas rate and liquid film when gas rate >>10 liter/min.

3- Adding a small amount of blended promoters of MEA +PZ, PZ+ ArgK and MEA + ArgK at various concentration can to some extent promote and accelerate absorption of $CO_2$ in $NH_3$ solution.

4- The absorption rate and overall mass transfer coefficient for PZ+ ArgK promoter were observed to be at least .

5- 123.23% higher than that of MEA +PZ and MEA +ArgK, indicating that the PZ+ ArgK promoter was superior to the other promoters to possess a larger catalytic activity at the same concentration for $CO_2$ absorption.

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