Reaction Kinetics of Carbon Dioxide in Aqueous Blends of N-Methyldiethanolamine and L-Arginine Using the Stopped-Flow Technique

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Abstract: Reduction of carbon dioxide emission from natural and industrial flue gases is paramount to help mitigate its effect on global warming. Efforts are continuously deployed worldwide to develop efficient technologies for CO2 capture. The use of environment friendly amino acids as rate promoters in the present amine systems has attracted the attention of many researchers recently. In this work, the reaction kinetics of carbon dioxide with blends of N-methyldiethanolamine and L-Arginine was investigated using stopped flow technique. The experiments were performed over a temperature range of 293 to 313 K and solution concentration up to one molar of different amino acid/amine ratios. The overall reaction rate constant (kω) was found to increase with increasing temperature and amine concentration as well as with increased proportion of L-Arginine concentration in the mixture. The experimental data were fitted to the zwitterion and termolecular mechanisms using a nonlinear regression technique with an average absolute deviation (AAD) of 7.6% and 8.0%, respectively. A comparative study of the promoting effect of L-Arginine with that of the effect of Glycine and DEA in MDEA blends showed that MDEA-Arginine blend exhibits faster reaction rate with CO2 with respect to MDEA-DEA blend, while the case was converse when compared to the MDEA-Glycine blend.

Keywords: Reaction; kinetics; carbon dioxide; N-methyldiethanolamine; L-Arginine; stopped flow technique

1. Introduction

The rapid growth of world economies associated with increased fossil fuel consumption for energy needs resulted in the generation of large amounts of greenhouse gases accumulated in the atmosphere. Carbon dioxide (CO2) is a major contributor to greenhouse gases accountable to the observed climate change and associated environmental problems. Reducing CO2 concentration in the atmosphere to an acceptable level is necessary for future generation’s well-being. Different options are available to capture CO2; however, amine based reactive solvents is one of the most mature and successful technology used in the industry, especially from large point sources, such as natural gas treatment units and power generation plants [1–6]. Large variants of amine based solvents are available in the market, many of which contain proprietary additives to enhance their absorption performances. Amine based solvents are known by their high absorption capacities and their ability to selectively absorb CO2/H2S from natural and flue gases. Conventional amine solvents, such as primary monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP), secondary
diethanolamine (DEA), tertiary amine N-methyldiethanolamine (MDEA) and polyamines (such as piperazine (PZ), 2-(2-aminoethylamino) ethanol (AEEA) are efficient for capturing CO\textsubscript{2} from various industrial processes and are still the choice in the industry because of the well-known absorption-regeneration process. However, several drawbacks like low absorption rate, periodic solvent make up to compensate for solvent losses, high regeneration energy requirement and severe equipment corrosion are still associated with their use [7–11].

Liquid tertiary amines, such as MDEA have higher theoretical sorption capacity with a ratio of 1:1 mol [12] but the reaction rate is much slower. To overcome this drawback, blended amines have been suggested [7]. To take advantage of their high loading capacity, low degradation rate and low energy for regeneration, tertiary amines are mixed with faster reacting primary/secondary amines or piperazine to develop new solvents with better CO\textsubscript{2} capture performance such as high absorption and cyclic capacity, fast reaction kinetics, low corrosion, degradation and less heat duty requirement [13,14].

Amino acids, usually called alkaline salts of amines, have recently drawn attention to CO\textsubscript{2} capture due to their exceptional properties [15]. The structure of amino acids consists of two important functional groups, namely amine (-NH\textsubscript{2}) and carboxylic acid (-COOH) or a sulfonic acid group [16]. Their salt nature makes their volatilities negligible which results in low solvent losses [17]. Their low environmental impact and high biodegradability [18] make them more environmentally friendly [19]. In addition, amino acids have high resistance to oxidative degradation making them a right choice for CO\textsubscript{2} capture from flue gases containing large amounts of oxygen [20]. However, at high concentration or at high CO\textsubscript{2} loading, they tend to precipitate resulting in lower mass transfer [21], which is a major drawback.

Nevertheless, several studies has reported on CO\textsubscript{2} capture using amino acids [22–25]. Siemens developed an amino acid based process and claim it has a reduced energy consumption of about 73% compared to the conventional MEA process [26]. Aqueous solutions of sodium glycinate were proposed for CO\textsubscript{2} absorption [27,28]. Shen et al. [29,30] used potassium salts of lysine and Histidine for CO\textsubscript{2} absorption and concluded that histidine reactivity towards CO\textsubscript{2} was comparable to that of MEA. Portugal et al. [31] used potassium glycinate and potassium threonate for CO\textsubscript{2} absorption purposes [32]. Huang et al. [33] and Wei et al. [34] determined the reaction rate constant of taurate carbamate formation during the absorption of CO\textsubscript{2} into CO\textsubscript{2}-free and CO\textsubscript{2}-loaded taurate solutions using a wetted-wall column at a temperature range of 293–353 K. The properties necessary for mass transfer evaluation, such as density, viscosity, CO\textsubscript{2} diffusivity, N\textsubscript{2}O solubility were reported for several amino acids under different conditions [35–40].

In a previous study on reaction kinetics of amino acids with CO\textsubscript{2}, it was observed, that L-Arginine, an amino acid, showed faster reaction rate compared to that of Glycine and Sarcosine when used as a single solvent [41]. Another study on the promoting effect of Glycine in MDEA blends showed that the reaction rate of MDEA with CO\textsubscript{2} could be significantly increased by the presence of an amino acid promoter [42]. However, the promoting effect of L-Arginine in MDEA blends remain unknown. In this work, the reaction kinetics of CO\textsubscript{2} with aqueous mixtures of MDEA and L-Arginine were determined using the stopped flow technique. The temperature was varied from 298 to 313 K and the amine total concentration was varied from 0.25 to 1 mol of different proportions of Arg/MDEA. Our findings provide a new insight to the use of Arg as rate promoter for CO\textsubscript{2} capture blended tertiary amines. The molecular structure of MDEA and L-Arginine are shown in the figure 1.

![Molecular Structure of MDEA (N-methyldiethanolamine) and L-Arginine.](image-url)
2. Reaction models

2.1. Reaction of CO$_2$ with MDEA

It is widely accepted that the reactions of CO$_2$ with primary amines results in formation of a carbamate and a bicarbonate products. However, in case of tertiary amines, only bicarbonates are formed during the reaction with CO$_2$. Therefore, MDEA being a tertiary amine will also not form any carbamates and the reaction of CO$_2$ in aqueous solution is as follows [21]:

$$\text{CO}_2 - H_3CN(C_2H_4OH)_2 + H_2O \xrightarrow{k_{\text{MDEA}}} H_3CNH^+(C_2H_4OH)_2 + \text{HCO}_3^-$$ (1)

Its pseudo-first-order reaction rate is:

$$r_{\text{CO}_2-MDEA} = -k_{\text{MDEA}}[\text{CO}_2][\text{MDEA}]$$ (2)

In addition to this reaction, the formation of bicarbonates in aqueous systems may be considered:

$$\text{CO}_2 + \text{OH}^- \xrightarrow{k_{\text{OH}}} \text{HCO}_3^-$$ (3)

Its rate of reaction was given as [43]:

$$r_{\text{CO}_2-\text{OH}} = -k_{\text{OH}}[\text{CO}_2][\text{OH}^-]$$ (4)

2.2. Reaction of CO$_2$ with amino acid

2.2.1. Zwitterion Mechanism

This mechanism was first coined by Caplow to comprehend the reactions of primary or secondary amines with CO$_2$ [44]. Amino acid [NHR$_1$R$_2$COO$^-$] has a molecular structure similar to that of primary or secondary amines. Its reaction pathway with CO$_2$ is considered to be similar to that of CO$_2$-amines and usually yields the formation of carbamate ion through two successive steps: (i) the formation of an intermediate zwitterion according to Reaction 5, (ii) proton removal by any base present in the solution according to Reaction 6 [22].

$$\text{CO}_2 + \text{NHR}_1\text{R}_2\text{COO}^- \xrightarrow{k_{\text{bi}}} \text{OOCN}^-\text{R}_1\text{R}_2\text{COO}^-$$ (5)

$$\text{OOCNH}^-\text{R}_1\text{R}_2\text{COO}^- + \text{B} \xrightarrow{k_{\text{bi}}^-} \text{OOCNR}_1\text{R}_2\text{COO}^- + \text{BH}^-$$ (6)

The corresponding reaction rate is given as [20]:

$$r_{\text{CO}_2-\text{Arg}} = -k_2[\text{Arg}][\text{CO}_2]/\left(1 + \left(\frac{1}{\sum_i k_{b_i}[B_i]}\right)\right)$$ (7)

Where the term ‘$k_{bi}$’ represents the deprotonation rate constant of the zwitterion by any base. The reaction rate constant can be written as:

$$k_{\text{Arg}} = k_2[\text{Arg}]/\left(1 + \left(\frac{1}{\sum_i k_{b_i}[B_i]}\right)\right)$$ (8)

The analysis of this model reveals two asymptotic cases, namely, $1 >> \frac{k_{-1}}{\sum_i k_{b_i}[B_i]}$ and $1 << \frac{k_{-1}}{\sum_i k_{b_i}[B_i]}$.

When the formation of the zwitterion carbamate following Reaction 5 is the rate limiting step. The first case prevails, thus, Equation (7) reduces to:

$$k_{\text{Arg}} = -k_2[\text{Arg}]$$ (9)

In the opposite case, when $1 << \frac{k_{-1}}{\sum_i k_{b_i}[B_i]}$, the proton removal from the zwitterion intermediate according to Reaction 6 is the rate limiting step; Equation (7) then becomes:

$$k_{\text{Arg}} = k_2[\text{Arg}]/\left(\sum_i k_{b_i}[B_i]\right)/k_{-1}$$ (10)
In the latter case, the reaction order dependency on the amino acid concentration varies from one to two. This phenomenon is commonly observed in CO$_2$ reaction with primary and secondary amines [26,27] and was proved to prevail in other salts of amino acids [28].

2.2.2. Termolecular Mechanism

Crooks and Donnellan [45] proposed an alternative single-step termolecular mechanism, which involves only one-step in the reaction process as shown in the Figure 2 below.

![Figure 2. Termolecular Mechanism.](image)

This mechanism was further investigated by Silva and Svendson [46], based on which they suggested that the reaction progresses through the bonding of the CO$_2$ molecule with the amine, which is stabilized by solvent molecules with hydrogen bonds. This in turn results in the formation of loosely bounded complex. They also added that the carbamate will be formed only when the amine molecule is in the vicinity of zwitterion. An analysis of the rate expression of the termolecular mechanism shows that the reaction of CO$_2$ with amine is second order with respect to amine. Therefore, in this case, Equation (7) becomes:

$$r_{CO_2} = k_{ov}[CO_2] = [CO_2][Arg]\sum k_{bi}[B_i]$$ (11)

Regardless of the mechanism employed, a carbamate and a protonated base are the generally accepted products of the CO$_2$ reaction with amine.

2.3. Reaction of CO$_2$ with Mixtures of MDEA and L-Arginine

For blends of MDEA and L-Arginine, the overall reaction rate with CO$_2$ is considered as the sum of reaction rates of CO$_2$-MDEA and CO$_2$-L-Arginine, hence:

$$r_{CO_2} = r_{CO_2, Arg} + r_{CO_2, MDEA} + r_{CO_2, OH}$$ (12)

Which can be written as:

$$r_{CO_2} = \left( k_2 [Arg] \frac{1}{1+k_1 \sum k_{bi}[B_i]} \right)[MDEA][CO_2]$$ (13)

Or

$$r_{CO_2} = \left( k_{Arg} + k_{MDEA} [MDEA] \right)[CO_2] = k_{ov}[CO_2]$$ (14)

In case of aqueous solution of L-Arginine, water molecules, ‘H$_2$O’; hydroxyl ions, ‘OH$^-$’ and deprotonated amino acid, ‘L-Arginine,’ act as bases. Therefore, if the reaction is expected to proceed via the zwitterion mechanism, then based on Equation (8), the term ‘$k_{Arg}$’ can be defined as follows:

$$k_{Arg} = \frac{k_2 [Arg]}{1+k_1 \left( k_{Arg}[Arg] + k_{OH}^{-} [OH^-] + k_{MDEA}[MDEA] + k_{H_2O}[H_2O] \right)}$$ (15)

Which can be written as:
\[
\begin{align*}
\frac{k_{\text{Arg}}}{k_2} &= \frac{[\text{Arg}]}{1 + \frac{1}{k_2} \left\{ \frac{k_{2k_{\text{Arg}}} k_{\text{Arg}}}{k_{-1}} + \frac{k_{2k_{\text{OH}^-} \text{OH}^-}}{k_{-1}} + \frac{k_{2k_{\text{MDEA}}} \text{MDEA}}{k_{-1}} + \frac{k_{2k_{\text{H}_2\text{O}} \text{H}_2\text{O}}}{k_{-1}} \right\}} \\
\end{align*}
\]

By defining new constants, \(k_a, k_{\text{hyd}}, k_b\) and \(k_w\) as:
\[
\begin{align*}
\frac{k_{\text{Arg}}}{k_2} &= \frac{k_{2k_{\text{Arg}}} k_{\text{Arg}}}{k_{-1}} + \frac{k_{2k_{\text{OH}^-} \text{OH}^-}}{k_{-1}} + \frac{k_{2k_{\text{MDEA}}} \text{MDEA}}{k_{-1}} + \frac{k_{2k_{\text{H}_2\text{O}} \text{H}_2\text{O}}}{k_{-1}} \\
\end{align*}
\]

and \(k_w = \frac{k_{2k_{\text{H}_2\text{O}} \text{H}_2\text{O}}}{k_{-1}}\). Equation (13) becomes:
\[
\begin{align*}
\frac{k_{\text{Arg}}}{k_2} &= \frac{[\text{Arg}]}{1 + \frac{1}{k_2} \left\{ k_a [\text{Arg}] + k_{\text{hyd}} [\text{OH}^-] + k_b [\text{MDEA}] + k_w [\text{H}_2\text{O}] \right\}} \\
\end{align*}
\]

However, if the reaction is expected to proceed via the termolecular mechanism, the term \('k_{\text{Arg}}'\) can be redefined as follows:
\[
\begin{align*}
\frac{k_{\text{Arg}}}{k_2} &= [\text{Arg}] \left\{ k_a [\text{Arg}] + k_w [\text{H}_2\text{O}] + k_{\text{hyd}} [\text{OH}^-] \right\} \\
\end{align*}
\]

3. Materials and methods

3.1. Materials

Reagents used in this work were analytical grade N-methyldiethanolamine (MDEA) with a mass purity of 99% obtained from Sigma-Aldrich and L-Arginine with purity of 99% purchased from Fluka (St. Louis, MS, USA). All chemicals were used as received without further purification. CO\(_2\) solutions were prepared by bubbling analytical grade CO\(_2\) (99.99%) for at least half an hour in deionised water. Deionised water was used as solvent throughout the experiments.

3.2. Methods

Pseudo first-order kinetics of CO\(_2\) reaction with different aqueous mixtures of L-Arginine in MDEA were measured using stopped-flow apparatus (Hi-Tech Scientific Ltd., and Model SF-61DX2, Bradford-on-Avon, Wiltshire, UK) with a dead time of 1 ms. The apparatus essentially consists of working syringes immersed in water bath, where the reacting solutions are loaded. It also contains a pneumatically controlled drive plate to load the reacting solutions into a mixer and the conductivity of the mixed solution is measured within the conductivity cell. Finally, the mixed solution is collected in a stopping syringe. A schematic diagram of the Stopped-Flow Apparatus has been presented in Figure 3 below.
Processes 2019, 7, 81

Figure 3. A Schematic Diagram of the Stopped-Flow Apparatus.

An external water bath (Alpha RA8, Lauda, Delran, NJ, USA) was used to control the temperature of the sample flow circuits within ±0.10 K. Depending on the applied temperature, the run time of the experiment was varied from 0.05 to 0.2 seconds. Freshly saturated solutions of CO$_2$ were prepared by bubbling CO$_2$ in deionized water. Concentration of CO$_2$ in the bubbled solution was measured with gas chromatography (GC-6890 from Agilent, Santa Clara, CA, USA) following Shell method®-SMS 2239-04. Fresh water used to dilute the solution in order to maintain the concentration ratio of the amine/amino acid solution 20 times higher than that of the CO$_2$ solution. This was done to ensure that the reaction conditions with respect to [CO$_2$] fall within the pseudo first order regime [47]. The amine/amino acid solutions were also prepared using deionized water. For each run, the CO$_2$ and amine/amino acid solutions were loaded in two separate syringes. Equal volumes of aqueous solutions of amine/amino acid and CO$_2$ were mixed in the stopped-flow apparatus. The reaction was monitored by measuring the conductivity change as function of time. The change in the conductivity, $Y$, with respect to time as described by Knipe et al [48] was fitted to an exponential equation resembling a first-order kinetics equation:

$$Y = -A \cdot \exp(-k_{ov} \cdot t) + Y_{\infty}$$

Where, ‘$k_{ov}$’ is the pseudo first-order reaction rate constant. The averages of three experimental runs were considered to obtain a reproducible and consistent $k_{ov}$ value for the whole range of the tested concentrations and temperatures. The reproducibility error of $k_{ov}$ was found to be less than 3% in all experiments. The experimental results were obtained in the provided ‘Kinetic Studio’ Software (Bradford-on-Avon, Wiltshire, UK). A screenshot of typical conductivity profile is presented in Figure 4.
4. Results and discussion

4.1. Reaction of CO$_2$ with MDEA and L-Arginine

The obtained pseudo first order rate constants, $k_{ov}$, were plotted against temperature for one molar total concentration (see Figure 5). The overall rate constants ($k_{ov}$) increased with increasing solution temperature as well as with increased [Arg] proportion in the total mixture. Similarly, the plot of the overall rate constants against different Arg/MDEA ratios for a total concentration of 1 mol is shown in Figure 6.

Figure 4. Typical Experimental run for MDEA-Arg at 303 K.

Figure 5. Rate constant, $k_{ov}$, vs. temperature for total 1 M solution.
Upon applying the power law kinetics to plot the overall rate constants against the concentrations of L-Arginine, an average exponent of 0.98 was obtained, which affirms that the pseudo first order regime prevails. Therefore, within the range of the experimental conditions, the reaction can be analysed via the zwitterion mechanism [49]. Additionally, the possibility of using the termolecular mechanism to interpret the obtained data was also verified by plotting $k_{ov}$/[ARG] against [ARG]. The plots show a satisfactory linear relationship indicating that the termolecular mechanism can also be applied to interpret the obtained experimental kinetics data [49,50]. A typical plot is shown in Figure 7. Hence, obtained experimental kinetics data were analysed using both the zwitterion and termolecular mechanisms.
4.2. Zwitterion Mechanism

The experimental data of the rate ($k_{ov}$) of the CO$_2$ reaction with methyldiethanolamine (MDEA) and L-Arginine (Arg) were obtained by fitting the conductivity-time curves to Equation (19). Zwitterion mechanism was used to interpret the obtained experimental data and the obtained overall rates along with apparent and predicted $k_{Arg}$ rates are presented in Table 1.

**Table 1. Rate constants at different temperatures and (MDEA+Arg) concentrations.**

| ARG | MDEA | OH $\times 10^9$ | H$_2$O | $k_{ov}$ | $k_{Arg-exp}$ | $k_{Arg-pred}$ | AAD% |
|-----|------|------------------|--------|----------|-------------|----------------|------|
| mol L$^{-1}$ | mol L$^{-1}$ | mol L$^{-1}$ | mol L$^{-1}$ | s$^{-1}$ | s$^{-1}$ | s$^{-1}$ |      |
| 298 K |
| 0.025 | 0.975 | 2.07 | 49.16 | 99.17 | 93.30 | 80.50 |      |
| 0.050 | 0.950 | 2.07 | 49.14 | 177.47 | 171.70 | 166.90 |      |
| 0.100 | 0.900 | 2.07 | 49.08 | 312.35 | 306.90 | 356.00 |      |
| 0.025 | 0.475 | 1.46 | 52.35 | 82.40 | 79.50 | 70.60 | 7.60 |
| 0.050 | 0.450 | 1.46 | 52.32 | 152.55 | 149.80 | 148.10 |      |
| 0.100 | 0.400 | 1.46 | 52.26 | 320.43 | 318.00 | 321.80 |      |
| 0.025 | 0.225 | 1.03 | 53.94 | 60.75 | 59.40 | 65.00 |      |
| 0.050 | 0.200 | 1.03 | 53.91 | 125.47 | 124.30 | 137.50 |      |
| 0.075 | 0.175 | 1.03 | 53.88 | 214.23 | 213.20 | 216.90 |      |
| 303 K |
| 0.025 | 0.975 | 2.21 | 49.13 | 124.65 | 116.50 | 104.30 |      |
| 0.050 | 0.950 | 2.21 | 49.11 | 226.15 | 218.20 | 216.20 |      |
| 0.100 | 0.900 | 2.21 | 49.05 | 410.33 | 402.80 | 460.40 |      |
| 0.025 | 0.475 | 1.56 | 52.33 | 107.15 | 103.20 | 91.00 | 6.30 |
| 0.050 | 0.450 | 1.56 | 52.31 | 195.64 | 191.90 | 190.80 |      |
| 0.100 | 0.400 | 1.56 | 52.25 | 423.84 | 420.50 | 414.30 |      |
| 0.025 | 0.225 | 1.10 | 53.93 | 78.32 | 76.40 | 83.50 |      |
| 0.050 | 0.200 | 1.10 | 53.90 | 165.36 | 163.70 | 176.50 |      |
| 0.075 | 0.175 | 1.10 | 53.88 | 281.52 | 280.00 | 278.40 |      |
| 308 K |
| 0.025 | 0.975 | 2.35 | 49.11 | 171.38 | 160.20 | 136.10 |      |
| 0.050 | 0.950 | 2.35 | 49.08 | 294.32 | 283.40 | 281.40 |      |
| 0.100 | 0.900 | 2.35 | 49.03 | 532.24 | 521.90 | 596.90 |      |
| 0.025 | 0.475 | 1.66 | 52.32 | 149.90 | 144.40 | 117.60 | 8.20 |
| 0.050 | 0.450 | 1.66 | 52.29 | 234.18 | 229.00 | 246.00 |      |
| 0.100 | 0.400 | 1.66 | 52.24 | 496.55 | 491.90 | 532.50 |      |
| 0.025 | 0.225 | 1.17 | 53.92 | 101.41 | 98.80 | 106.90 |      |
| 0.050 | 0.200 | 1.17 | 53.90 | 231.21 | 228.90 | 225.80 |      |
| 0.075 | 0.175 | 1.17 | 53.87 | 357.73 | 355.70 | 355.80 |      |
| 313 K |
| 0.025 | 0.975 | 2.49 | 49.09 | 213.71 | 198.40 | 167.80 |      |
| 0.050 | 0.950 | 2.49 | 49.07 | 357.97 | 343.10 | 347.80 |      |
| 0.100 | 0.900 | 2.49 | 49.02 | 625.84 | 611.70 | 740.80 |      |
| 0.025 | 0.475 | 1.76 | 52.31 | 188.23 | 180.80 | 145.90 | 8.40 |
| 0.050 | 0.450 | 1.76 | 52.29 | 310.72 | 303.70 | 306.10 |      |
| 0.100 | 0.400 | 1.76 | 52.24 | 632.39 | 626.10 | 665.10 |      |
| 0.025 | 0.225 | 1.24 | 53.92 | 130.31 | 126.80 | 133.50 |      |
| 0.050 | 0.200 | 1.24 | 53.90 | 302.60 | 299.50 | 282.50 |      |
| 0.075 | 0.175 | 1.24 | 53.87 | 451.29 | 448.50 | 445.90 |      |
| AAD% |            |      |      |      |      |      | 7.60 |
The rate constant $k_{\text{arg}}$ was calculated using Equation (17) by subtracting $k_{\text{MDEA}}$ and $k_{\text{OH}}$ values from $k_w$ values. The values of $k_{\text{MDEA}}$, $k_{\text{OH}}$, $k_a$, $k_s$ and $k_w$ were estimated from the previous works [41–43,51]. It is to be noted that, there was a typographical error within the power of the previously reported rate expression for $k_w$ ($1.23 \times 10^{12} \ e^{-\frac{4364.7}{T}}$ was reported instead of $1.23 \times 10^{9} \ e^{-\frac{4364.7}{T}}$) [41], this error has been revised in this work and the correct rate expression for $k_w$ along with the other expressions that were used in this work have been listed in Table 2.

**Table 2. List of rate expressions used for zwitterion mechanism.**

| Rate          | Equation                                      | References              |
|---------------|-----------------------------------------------|-------------------------|
| $k_{\text{MDEA}}$ (m$^3$ kmol$^{-2}$ s$^{-1}$) | $k_a = 2.56 \times 10^9 e^{-\frac{5922.0}{T}}$ | BENAMOR et al. [42]     |
| $k_{\text{OH}}$ (m$^3$ kmol$^{-2}$ s$^{-1}$)  | $k_{\text{OH}} = 4.33 \times 10^{10} e^{-\frac{6666.6}{T}}$ | Pinsent et al. [43]    |
| $k_s$ (m$^3$ kmol$^{-1}$ s$^{-1}$)            | $k_s = 2.81 \times 10^{10} e^{-\frac{4482.9}{T}}$ | Mahmud et al. [41]     |
| $k_w$ (m$^8$ kmol$^{-2}$ s$^{-1}$)            | $k_w = 1.23 \times 10^{9} e^{-\frac{4364.7}{T}}$ | Mahmud et al. [41]*    |

*Corrected value.

Experimental rate constants, ‘$k_{\text{arg}}$’ data were fitted to Equation (17) to extract the individual blocks of rate constants described in this equation. The concentrations of water molecules [H$_2$O] were calculated by mass balance while those of hydroxyl ions [OH$^-$] were estimated from the relation given by Astarita et al. [52]. The use of this relationship is justified since the CO$_2$ loading in the amine solution was very small as it was verified by Gas Chromatography throughout all experiments.

$$[\text{OH}^-] = \frac{k_w [\text{AM}]}{K_{\text{pi}}} \text{ for } \alpha \leq 10^{-3}$$

Using Equation (20), the total [OH$^-$] was taken to be the sum of [OH$^-$] ions produced by MDEA and those produced by Arg. The water dissociation constant, ‘$K_w$’ and protonation constant, ‘$K_{\text{pi}}$’ for MDEA and L-Arginine were expressed as a function of temperature according to the following equation:

$$\ln K_i = \frac{a_i}{T} + b_i \ln T + c_i T + d_i$$

Values of the constants $a_i$–$d_i$ are given in Table 3.

**Table 3. Values of different equilibrium constant used to estimate OH$^-$ in Equation (20).**

| Parameter           | $a_i$  | $b_i$  | $c_i$  | $d_i$  | validity range | source |
|---------------------|--------|--------|--------|--------|----------------|--------|
| $K_{\text{pi}}$(MDEA) | -8483.95 | -13.8328 | 0       | 87.39717 | 293–333 K     | [53]   |
| $K_{\text{pi}}$(Arginine) | -3268.3 | 0       | 0       | -9.9729 | 293–323 K     | [41]   |
| $K_w$               | -13445.9 | -22.4773 | 0       | 140.932 | 273–498 K     | [54]   |

Applying a nonlinear regression technique using Excel solver, experimental $k_{\text{arg}}$ values were fitted to Eq 17 taking into account the species concentrations, H$_2$O, Arg, OH$^-$ and MDEA previously calculated. Since the rate expressions for the terms $k_a$, $k_s$ and $k_w$ were already available from previous work [41]. The regression analysis was initially performed to generate the values of the term $k_b$ and $k_{\text{OH}}$ only. However, the obtained values for the $k_{\text{OH}}$ indicated no catalytic influence on the $k_{\text{arg}}$ values. This can be attributed to the fact that the concentration of the hydroxyl ions is very low compared to other bases in the system, which leads to the conclusion that there is no significant influence of catalytic hydroxyl ions on the kinetics. Furthermore, the reaction between hydroxyl and CO$_2$ exhibits slower kinetics which has been previously demonstrated by Gou et al. [55]. Hence, the final regression analysis were performed excluding the $k_{\text{OH}}$ term. The generated rate constant values for the $k_b$ term are summarized in Table 4.
Table 4. Reaction rate constants at different temperatures using Zwitterion mechanism.

| Temperature | 298 K | 303 K | 308 K | 313 K |
|-------------|-------|-------|-------|-------|
| Rate constant, $k_r$ (m$^6$ kmol$^{-2}$ s$^{-1}$) | 2321.0 | 3127.5 | 4400.5 | 5130 |

Using these generated rate constants, the overall reaction rate constant, $k_{Arg}$, values were predicted using Equation (17) and were plotted against real experimental data in a parietal plot as shown in Figure 8. It is very clear that the adopted rate model along with extracted individual rate constants represent very well the experimental results with an average absolute deviation, AAD, of 7.6%. Figure 8 validated the choice of the kinetics model used to interpret the data of the reaction of CO$_2$ with mixtures of MDEA and Arg represented in Equation (12). Furthermore, these results confirm the contribution of Arg and MDEA species in the base-catalytic formation of carbamate.

Figure 8. Parity plot of experimental and predicted $k_{Arg}$ values for Zwitterion mechanism.

The individual rate constants at different temperatures were plotted as a function of temperature according to Arrhenius equation as shown in Figure 9 and associated parameters are summarized in Table 5. The activation energy ($E_a$) of each reaction was derived from the Arrhenius plots along with the pre-exponential coefficient of each rate constant.

Table 5. Summarized kinetics rate constants for CO$_2$-MDEA-Arg reaction using Zwitterion Mechanism.

| Rate | $k_{ov} = k_{MDEA}[MDEA] + k_{OH}[-OH]$ |
|------|------------------------------------------|
| $k_{MDEA}$ (m$^3$ kmol$^{-2}$ s$^{-1}$) | 21.66 49.24 | $k_{MDEA} = 2.56 \times 10^6 e^{-\frac{5922.0}{T}}$ | Benamor et al. [42] |
| $k_{OH}$ (m$^3$ kmol$^{-2}$ s$^{-1}$) | 24.49 554.26 | $k_{OH} = 4.33 \times 10^6 e^{-\frac{66666.0}{T}}$ | Pinsent et al. [43] |
| $k_2$ (m$^3$ kmol$^{-2}$ s$^{-1}$) | 24.06 37.27 | $k_2 = 2.81 \times 10^{10} e^{-\frac{4482.9}{T}}$ | Mahmud et al. [41] |
| $k_a$ (m$^6$ kmol$^{-2}$ s$^{-1}$) | 25.10 38.28 | $k_a = 7.96 \times 10^{10} e^{-\frac{4603.8}{T}}$ | Mahmud et al. [41] |
| $k_b$ (m$^6$ kmol$^{-2}$ s$^{-1}$) | 24.83 42.27 | $k_b = 6.07 \times 10^{10} e^{-\frac{5083.8}{T}}$ | This Work |
| $k_w$ (m$^6$ kmol$^{-2}$ s$^{-1}$) | 18.63 36.29 | $k_w = 1.23 \times 10^6 e^{-\frac{4364.7}{T}}$ | Mahmud et al. [41]* |

$^*$Corrected expression.
From Table 5, it can be observed that the activation energy of L-Arginine (39.15 kJ mol\(^{-1}\)) is smaller than that of MDEA (49.24 kJ mol\(^{-1}\)), which shows that L-Arginine reacts faster with CO\(_2\) than MDEA. In fact, L-Arginine having a molecular structure similar to that of primary amines, have a faster reaction rate compared to tertiary amine MDEA. The \(E_a\) for Arg, MDEA and H\(_2\)O catalytic carbamate formation showed that the contribution of water to the overall formation of carbamate (36.29 kJ mol\(^{-1}\)) is the most important followed by that of L-Arginine (38.28 kJ mol\(^{-1}\)), while the contribution of MDEA to this reaction (42.27 kJ mol\(^{-1}\)) were found to be the least.

### 4.3. Termolecular Mechanism

Since the termolecular applicability tests revealed the possibility of applying this mechanism to interpret the experimental data, the kinetics of CO\(_2\)-MDEA-Arg were then further investigated via this mechanism. Similar to that of the zwitterion mechanism, the values of \(k_a\) and \(k_w\) were also estimated from previous work [41] and are listed in Table 6.

**Table 6. List of rate expressions used for Termolecular mechanism.**

| Rate         | Equation                        | References       |
|--------------|---------------------------------|------------------|
| \(k_a\) (m\(^6\) kmol\(^{-2}\) s\(^{-1}\)) | \(k_a = 5.72 \times 10^{10}e^{-\frac{4769.00}{T}}\) | Mahmud et al. [4] |
| \(k_w\) (m\(^6\) kmol\(^{-2}\) s\(^{-1}\)) | \(k_w = 9.41 \times 10^{7}e^{-\frac{4365.00}{T}}\) | Mahmud et al. [41] |

Using the \(k_a\) and \(k_w\) values, previously obtained \(k_{ Arg\text{-Arg}}\) values were then fitted in accordance to the Equation (18). Excel solver was then used to regress the experimental data to obtain the rate expressions. The apparent and predicted \(k_{ Arg\text{-Arg}}\) values obtained using the termolecular mechanism are presented in Table 7.
Table 7. Rate constants at different temperatures and (MDEA+Arg) concentrations.

| ARG | MDEA | OH | H₂O | k<sub>Arg-exp</sub> | k<sub>Arg-pred</sub> | AAD% |
|-----|------|----|-----|-----------------|-----------------|------|
| mol L<sup>−1</sup> | mol L<sup>−1</sup> | mol L<sup>−1</sup> | s<sup>−1</sup> | s<sup>−1</sup> |
| 298 K |
| 0.025 | 0.975 | 3.2 × 10<sup>4</sup> | 49.16 | 93.3 | 79.7 |
| 0.050 | 0.950 | 4.5 × 10<sup>4</sup> | 49.14 | 171.8 | 166.2 |
| 0.100 | 0.900 | 6.2 × 10<sup>4</sup> | 49.08 | 306.9 | 358.9 |
| 0.025 | 0.475 | 2.3 × 10<sup>4</sup> | 52.35 | 79.5 | 70.0 | 7.8 |
| 0.050 | 0.450 | 3.1 × 10<sup>4</sup> | 52.32 | 149.8 | 146.6 |
| 0.100 | 0.400 | 4.1 × 10<sup>4</sup> | 52.26 | 318.0 | 319.9 |
| 0.025 | 0.225 | 1.5 × 10<sup>4</sup> | 53.94 | 59.4 | 65.1 |
| 0.050 | 0.200 | 2.1 × 10<sup>4</sup> | 53.91 | 124.3 | 136.8 |
| 0.075 | 0.175 | 2.4 × 10<sup>4</sup> | 53.88 | 213.2 | 215.2 |
| 303 K |
| 0.025 | 0.975 | 3.0 × 10<sup>4</sup> | 49.16 | 116.5 | 103.4 |
| 0.050 | 0.950 | 4.2 × 10<sup>4</sup> | 49.14 | 218.2 | 215.3 |
| 0.100 | 0.900 | 5.8 × 10<sup>4</sup> | 49.08 | 402.8 | 465.2 |
| 0.025 | 0.475 | 2.1 × 10<sup>4</sup> | 52.35 | 103.2 | 90.0 | 6.9 |
| 0.050 | 0.450 | 2.9 × 10<sup>4</sup> | 52.32 | 191.9 | 188.7 |
| 0.100 | 0.400 | 3.8 × 10<sup>4</sup> | 52.26 | 420.5 | 411.9 |
| 0.025 | 0.225 | 1.4 × 10<sup>4</sup> | 53.94 | 76.4 | 83.4 |
| 0.050 | 0.200 | 1.9 × 10<sup>4</sup> | 53.91 | 163.7 | 175.4 |
| 0.075 | 0.175 | 2.2 × 10<sup>4</sup> | 53.88 | 280.1 | 276.0 |
| 308 K |
| 0.025 | 0.98 | 2.8 × 10<sup>4</sup> | 49.16 | 160.2 | 134.7 |
| 0.050 | 0.95 | 3.9 × 10<sup>4</sup> | 49.14 | 283.4 | 280.3 |
| 0.100 | 0.90 | 5.4 × 10<sup>4</sup> | 49.08 | 521.9 | 604.6 |
| 0.025 | 0.48 | 2.0 × 10<sup>4</sup> | 52.35 | 144.5 | 115.8 | 8.6 |
| 0.050 | 0.45 | 2.7 × 10<sup>4</sup> | 52.32 | 229.0 | 242.6 |
| 0.100 | 0.40 | 3.6 × 10<sup>4</sup> | 52.26 | 492.0 | 529.2 |
| 0.025 | 0.23 | 1.3 × 10<sup>4</sup> | 53.94 | 98.8 | 106.4 |
| 0.050 | 0.20 | 1.8 × 10<sup>4</sup> | 53.91 | 228.9 | 223.8 |
| 0.075 | 0.18 | 2.1 × 10<sup>4</sup> | 53.88 | 355.7 | 352.2 |
| 313 K |
| 0.025 | 0.98 | 2.6 × 10<sup>4</sup> | 49.16 | 198.5 | 164.8 |
| 0.050 | 0.95 | 3.6 × 10<sup>4</sup> | 49.14 | 343.1 | 343.9 |
| 0.100 | 0.90 | 5.0 × 10<sup>4</sup> | 49.08 | 611.8 | 745.2 |
| 0.025 | 0.48 | 1.8 × 10<sup>4</sup> | 52.35 | 180.8 | 143.3 | 8.8 |
| 0.050 | 0.45 | 2.5 × 10<sup>4</sup> | 52.32 | 303.7 | 301.0 |
| 0.100 | 0.40 | 3.3 × 10<sup>4</sup> | 52.26 | 626.1 | 659.5 |
| 0.025 | 0.23 | 1.3 × 10<sup>4</sup> | 53.94 | 126.8 | 132.6 |
| 0.050 | 0.20 | 1.7 × 10<sup>4</sup> | 53.91 | 299.5 | 279.6 |
| 0.075 | 0.18 | 1.9 × 10<sup>4</sup> | 53.88 | 448.6 | 441.0 |

Overall AAD% 8.0

Similar to the results obtained using the zwitterion mechanism, the obtained fitting results showed that hydroxyl ion (k<sub>OH</sub>) had a negligible effect for CO₂-MDEA-Arginine reaction using termolecular mechanism. Only L-Arginine, MDEA and water concentrations effects were found to be significant. The natural logarithm of the individual rate constants was plotted against T<sup>−1</sup> according to Arrhenius equation as shown in Figure 10. The generated rate constant values for the k<sub>b</sub> term are summarized in Table 8.
Figure 10. Arrhenius plots of CO₂-MDEA-Arg rate constants using termolecular mechanism.

Table 8. Reaction rate constants at different temperatures using termolecular mechanism.

| Rate constant | 298 K | 303 K | 308 K | 313 K |
|---------------|-------|-------|-------|-------|
| $k_b$ (m₆ kmol⁻² s⁻¹) | 1043.0 | 1397.0 | 1927.0 | 2240.0 |

The predicted rate constant values were compared to the experimental ones as via a parity plot shown in Figure 11, which displayed good agreement between both values with an AAD of 8.0%. Since the AAD% is very close to that obtained in case of zwitterion mechanism (7.60%), it can be suggested that termolecular mechanism can be also used to interpret the obtained experimental data. The obtained rate expressions using termolecular are summarized in Table 9.
Table 9. Summarized kinetics rate constants for CO$_2$-MDEA-Arg reaction using Termolecular Mechanism.

| Rate          | Expression | References |
|---------------|------------|------------|
| $k_{MDEA}$ (m$^3$kmol$^{-2}$ s$^{-1}$) | $k_{MDEA} = 2.56 \times 10^9 e^{-\frac{5922.0}{T}}$ | Benamor et al. [42] |
| $k_{OH}$ (m$^3$kmol$^{-2}$ s$^{-1}$) | $k_{OH} = 4.33 \times 10^9 e^{-\frac{66666.0}{T}}$ | Pinseit et al. [43] |
| $k_a$ (m$^6$ kmol$^{-2}$ s$^{-1}$) | $k_a = 5.72x \times 10^9 e^{-\frac{4769.0}{T}}$ | Mahmud et al. [41] |
| $k_b$ (m$^6$ kmol$^{-2}$ s$^{-1}$) | $k_b = 1.42 \times 10^{10} e^{-\frac{4888.6}{T}}$ | This Work |
| $k_w$ (m$^6$ kmol$^{-2}$ s$^{-1}$) | $k_w = 9.41 \times 10^7 e^{-\frac{4365.0}{T}}$ | Mahmud et al. [41] |

Upon evaluating the obtained rate expression for the ‘$k_w$’ term in both mechanisms, it is observed that activation energies in both models are comparable to each other ($E_a^Z = 42.27$ kJ mol$^{-1}$ and $E_a^T = 40.65$ kJ mol$^{-1}$). Furthermore, it is noticed that regardless of the model used catalytic effect of L-Arginine ($E_a^Z = E_a^T = 38.28$ kJ mol$^{-1}$) is higher than the catalytic effect of MDEA. Based on this, it can be concluded that the CO$_2$-MDEA-Arg reactions can be effectively interpreted using both zwitterion and termolecular mechanisms.

5. Comparison with other amine systems.

5.1. Comparison with secondary, tertiary and sterically hindered amine

The obtained rate constants data for 1M MDEA-Arg (0.9M MDEA + 0.1M Arg) in this work were compared with those of DEA [56], MDEA [42] and AMP [57] as shown in Figure 12. It was observed that the rate constants of MDEA-Arg were much lower than that of secondary amine (DEA) and lower than that of sterically hindered amine (AMP). However, the rate constant of MDEA-Arg mixtures were always higher than those of the tertiary amine (MDEA). This elucidates the effect of L-Arginine presence in the MDEA-Arg blend which can enhance the overall kinetics of the CO$_2$-MDEA reaction and make it comparable to other secondary and hindered amines. Based on the above
an analysis, the overall rate constants of these amine systems with CO\(_2\) were found to be in the following order: DEA > AMP > MDEA-Arg > MDEA.

![Graph showing overall rate constants of different amine systems with CO\(_2\)](image)

**Figure 12.** Comparison of the obtained data with MDEA-Arg with other amine systems.

### 5.2. Comparison of the promoting effect of L-Arginine

The promoting effect of L-Arginine investigated in this work was also compared with that of the available data of MDEA-Glycine [42] and MDEA-DEA [58] systems at different temperatures and at the same overall concentration (1 M) as shown in Figure 13. For all three compared systems, the same 0.1 M of the promoter was added. It is observed that the addition of 0.1 M L-Arginine in the MDEA-Arg has resulted in higher overall rate constant compared to the addition of the 0.1 M DEA. However, the addition of 0.1 M Glycine in the MDEA blend has resulted in higher overall rate constant compared to that of 0.1 M L-Arginine. Although the previous study [41] revealed that the kinetics of L-Arginine alone with CO\(_2\) is higher than that of the Glycine, Guo et al. [55] observed that the Glycine at higher pH exhibits faster kinetics. Since the presence of MDEA can increase pH of the solution, it triggers the base form of Glycine to react with the CO\(_2\) resulting in a higher overall rate constant in the MDEA-Glycine blend as observed in the work of Benamor et al. [42]. The presence of MDEA has more significant catalytic effect towards the formation of zwitterion intermediate in MDEA-Glycine (E\(_a\) = 24.67 kJ mol\(^{-1}\) [42]) compared to that of MDEA-Arg (E\(_a\) = 42.27 kJ mol\(^{-1}\)). Furthermore, activation energy for the reaction of zwitterion intermediate formation of Glycine in the MDEA-Gly is 22.95 kJ mol\(^{-1}\) [42] is also lower than that of L-Arginine (E\(_a\) = 37.27 kJ mol\(^{-1}\)) in the MDEA-Arg blend. Therefore, based on this analysis, the rate constants of the three blended amine systems with CO\(_2\) were found to be in the following order: MDEA-Gly > MDEA-Arg > MDEA-DEA.
6. Conclusions

The kinetics of the reaction of CO$_2$ with MDEA + Arginine in aqueous solutions was studied using the stopped-flow technique for the first time. The measurements were performed for a concentration range from 0.25 M to 1 M and a temperature range from 298 to 313 K. The rate constants were well correlated by Arrhenius equation type. The activation energies for the rate constants were estimated. Both of the adopted zwitterion and termolecular models were very accurate in representing the experimental data over a range of five different temperatures from 293 to 313 K with an AAD of 7.6% and 8.0%, respectively. The contribution of L-Arginine, MDEA and H$_2$O to the catalytic carbamate formation pathway was assessed using rate constants generated from the reaction of arginine alone with CO$_2$. The results showed that the contribution of arginine to the overall formation is more significant followed by the contribution of water in both models, while the contribution of MDEA molecules was found to be the least. Based on the regression results, rate expression for the catalytic formation of zwitterion was to be $k_b = 6.07 \times 10^{10} e^{-\frac{5003.8}{T}}$ for the zwitterion mechanism and $k_b = 1.42 \times 10^{10} e^{-\frac{4888.0}{T}}$ for the termolecular mechanism. A comparison of the obtained overall rate constant with other amine systems revealed the MDEA-Arginine-CO$_2$ reaction was faster than that of MDEA-CO$_2$ but slower than that of secondary and stERICALLY hindered amine. A further comparison with MDEA-promotor blends showed that the reaction of MDEA-Arginine with CO$_2$ is slower than MDEA-Glycine but faster than MDEA-DEA. This was attributed to the fact that the catalytic contribution of L-Arginine for the formation of zwitterion intermediate is lower compared to Glycine in MDEA blends. Furthermore, presence of MDEA can significantly catalyse the formation zwitterion intermediate in MDEA-Glycine blend ($E_a = 24.67$ kJ mol$^{-1}$ [43]) than that of MDEA-Arg blend ($E_a = 42.27$ kJ mol$^{-1}$). Consequently, a faster reaction kinetics was observed in MDEA-Glycine-CO$_2$: reactions than MDEA-Arg-CO$_2$: reactions.

Nomenclature

MDEA N-methyldiethanolamine
Arg L-Arginine
Gly Glycine
MEA Monoethanolamine
DEA Diethanolamine
AMP 2-Amino-2-Methyl-1-Propanol

\( r_{CO2-MDEA} \) (l mol\(^{-1}\) s\(^{-1}\)) Reaction rate of CO\(_2\) with MDEA

\( r_{CO2-OH} \) (l mol\(^{-1}\) s\(^{-1}\)) Reaction rate of CO\(_2\) with hydroxyl ions

\( r_{CO2-Arg} \) (l mol\(^{-1}\) s\(^{-1}\)) Reaction rate of CO\(_2\) with L-Arginine

\( r_{CO2} \) (l mol\(^{-1}\) s\(^{-1}\)) Reaction rate of CO\(_2\) with MDEA-Arginine

\( k_{MDEA} \) (s\(^{-1}\)) Overall reaction rate of CO\(_2\) and MDEA

\( k_{OH} \) (s\(^{-1}\)) Overall reaction rate of CO\(_2\) and Hydroxyl ion

\( k_{Arg} \) (s\(^{-1}\)) Overall reaction rate of CO\(_2\) and L-Arginine

\( k_r \) (m\(^3\) kmol\(^{-1}\) s\(^{-1}\)) Reaction rate constant of the formation of the intermediate Zwitterion

\( k_{MDEA} \) (m\(^3\) kmol\(^{-1}\) s\(^{-1}\)) Reaction rate constant of CO\(_2\) and MDEA reaction.

\( k_{OH} \) (m\(^3\) kmol\(^{-1}\) s\(^{-1}\)) Reaction rate constant of CO\(_2\) and hydroxyl ion reaction.

\( k_1 \) (s\(^{-1}\)) Reaction rate constant of the consumption of the intermediate Zwitterion

\( k_{0,1} \) (s\(^{-1}\)) Individual reaction rate constants according to zwitterion mechanism

\( T \) (K) Temperature

\( t \) (s) Time

\( K_w \) (mol l\(^{-1}\)) Water dissociation constant

\( K_{eq} \) (mol l\(^{-1}\)) Protonation constant for MDEA and L-Arginine

\( k_{Arg-exp} \) (s\(^{-1}\)) Experimental apparent rate constant of CO\(_2\) and L-Arginine.

\( k_{Arg-pred} \) (s\(^{-1}\)) Predicted apparent rate constant of CO\(_2\) and L-Arginine.

\( E_a \) (kJ mol\(^{-1}\)) Activation energy

\( E_a^z \) (kJ mol\(^{-1}\)) Activation energy obtained in zwitterion mechanism

\( E_a^l \) (kJ mol\(^{-1}\)) Activation energy obtained in termolecular mechanism

\( k_z \) (m\(^6\) kmol\(^{-2}\) s\(^{-1}\)) Catalytic contribution of L-Arginine in the reaction rate according to zwitterion mechanism

\( k_{OH} \) (m\(^6\) kmol\(^{-2}\) s\(^{-1}\)) Catalytic contribution of hydroxyl ion in the reaction rate according to zwitterion mechanism

\( k_s \) (m\(^6\) kmol\(^{-2}\) s\(^{-1}\)) Catalytic contribution of MDEA in the reaction rate according to zwitterion mechanism

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