Kinetics of carbon dioxide capture into aqueous potassium carbonate promoted by glutamic acid salt

Rana Esam Ahmed¹, Ahmed Daham Wiheeb², Sanaa Rabie Saleh³ { <u>eng.ranaesam1993@gmail.com¹</u>, <u>chahmed@tu.edu.iq²</u>, <u>sanaarabie85@gmail.com³</u>}

Chemical Engineering Division, Entirety of Engineering, Tikrit University, Tikrit, Sallahaddin, Iraq, 07708482517¹, Chemical Engineering Division, College of Engineering, University of Diyala, Baqubah, Diyala, Iraq², North Refinery Company, Ministry of Oil, Baiji, Sallahaddin, Iraq³

Abstract. In this research, potassium carbonate (K₂CO₃) aquatic solution reinforcement by glutamic sour salt utilized to capturing carbon dioxide (CO₂) from Gaseous fuel in a stuffed absorber pillar at room temperature and at atmospheric pressure. Effect of glutamic sour salt concentrations on the CO₂ absorption rates into carbonate solutions and glutamic acid salt were investigated. The outcome exhibit that the interaction of CO₂ with K₂CO₃ aquatic solution promoted by glutamic acid salt was second-order and the rate constant (k₂) was calculated from the experiments. The interaction of CO₂ with glutamic sour salt was a depiction utilized zwitterionic self-acting. The aggregate interaction pragmatic stationary (k_{ov}) robustly augmentation with the augmentation of glutamic sour salt concentricity based on the pseudo-first-arrange regime.

Keywords: , Kinetics, CO2 capture, up taking, potassium carbonate, glutamic acid.

1 Introduction

The augmentation of CO_2 subtract to the atmosphere is the prime benefactor to international weather variation. up taking of CO_2 is one of favorable pathway to minify the CO₂ subtract from scorbutic fuel- release power plants. In the bygone years, numerous manner has been offered for yet- blaze CO_2 up take [1-2]. sucking with chemical aqueous solution is extreme vastlv elaborate and handy picking to considerable-calibrate the enforcement . The capturing of CO_2 with amines or carbonate aquatic solution have obtained spread alertness inter alia absorptive [3]. Hot potassium carbonate process, recognized as Benfield process, has been hired tardily for curing sour gas influx for plentiful years [4]. In rapprochement to the benchmark amine-based aquatic solutions in private monoethanolamine (MEA)), potassium carbonate has a grist of trait-like little of up taking, little price, minus virulent and aquatic solutions minus, no thermal and oxidative ebb, outwardly the figuration of heat-firm pressing [2]. The confront correlating with hire K_2CO_3 is the tardy interaction rate of up taking, bring about in pauper CO_2 mass transfer [5-6]. Furthermore, for yet- blaze uptake, the up taking process is wanted to turn on at flue gas conditions like naturalistic pressure and comparatively little temperature [7]. The up taking rate would be worst than that in Benfield process. subsequently, the potency of rate growing by the use of developer is of worthy avails to recover the CO₂ mass convey rates. Lately, piperazine has been inspected vastly in carbonate aquatic solutions and theorize as a favorable developer inter alia the amine set in order to of prompt up taking rate and adequate evenness demeanor [8]. however although, for yet-blaze flue gas curing in the extremely oxygenated milieu and elevation temperature restoration, amines similar MEA and piperazine might not be of considerable benefit in order to oxidative

and thermal retrogression, elevation dispersal, elevation energy request, attrition and ecological influence [9-10]. Lately, alkaline salts of amino sours have been offered as adequate elect aquatic solutions for CO_2 up taking in order having congruent handy set as alknolamines. presently, there is a freshen benefit in the hire of amino sours salt for CO_2 up take from flue gas influx. comparatively studies once upon a time announce concerning the up taking of CO_2 in diverse amino sour salt aquatic solutions like potassium salts of glycine, taurine, threonine, sarcosine, proline and alanine [13]. Van Holst et al. [16] candida ridding treatise for the kinetics of CO_2 up taking into aquatic solutions of sundry amino sour salts. The salts of sarcosine and proline with altitude interaction rate stationary at CO_2 have been announcing in recently viewed [14]. Otherwise, the interaction of CO_2 with diverse alkaline salts of amino sours has been qualified by zwitterionic mechanization and has been taken apart hire pseudo-first seek [15].

In this work, Glutamic acid salt has been offered as a rate- developer in carbonate aquatic solutions. Glutamic sour salt embarrasses a incipient amino bracket in an addendum to a two carboxyl groups in its side chain can be foreseeable to interact with CO_2 in a analogous modality with an amine. Its reactivity and strength are prospective analogous to amines of the united layers and simple rejuvenation of absorptive is also prospective . however although, its kinetic reference in this scope is exceptional in urbanity and poverty to be evidence. In the sitting work, the up taking rate of CO_2 into glutamic sour salt- corroborative aquatic carbonate solution were utterly hiring a Packed bed pillar at 30wt.% K₂CO₃.

2 Reaction mechanism

The average of interaction is a remarkable laborer in remission the bulk of the pillar and the magnitude of solvent and subsequently minify the capital charges of the absorber, whilst a weakened value of acid dissociation constant (Pka) is requisite to minify the energy poverty for CO_2 restoration [11].

2.1 Hydration of CO₂ into an aquatic solution of K₂CO₃

The interactions of CO_2 with an aquatic solution of K_2CO_3 can be described as follows [17]:

$$CO_{2} + OH^{-} \stackrel{K_{OH}^{-}}{\longrightarrow} HCO_{3}^{-}$$
(1)
$$CO_{2} + H_{2}O \stackrel{K_{H_{2}O}}{\longrightarrow} HCO_{3}^{-} + H^{+}$$
(2)

In requisite aquatic solutions (pH > 8), the interaction of CO₂ with H₂O (equation (2) can be ignored . As a result, the reaction of CO₂ with OH⁻ (equation (1)) is the victorious interaction and the average- shackle interaction in requisite aquatic solution . The average of fore reaction qualified by equation (1) is given by [18]:

$$r_{CO_2-K_2CO_3} = k_{OH^-}[CO_2][OH^-]$$
(3)

the second seek average stationary \mathbf{k}_{0H} - with hydroxide ion is fully realize in the typecast [19, 20] and can portend as a duty of ionic intensity.

2.2 Reaction of CO₂ with Glutamic acid salt

The molecular structure of Glutamic acid $(C_5H_9O_4N)$ can be perform as [HOOC-CH(NH₂)-(CH₂)₂-COOH] with two carboxyl set (⁻COOH) and one (mainly) amino set (⁻NH₂). subsequently, glutamic sour would be in prospect to interact with CO₂ by its mainly amino set. The interaction of CO₂ with amino sour is a qualified setup on zwitterionic mechanization [21]. Deprotonation of the zwitterionic amino sours is carried out by joining a twice molar compensate of a potent rule like potassium hydroxide (KOH) which perfectly untangle in water [22]. This deprotonation follows in his footsteps is essential due to make the amino set interact with CO₂.

Many studies [31-33] have been offered that the interaction CO_2 and the deprotonated amino sours income utilizing a zwitterionic carbamate moderate :

$$^{-}OOC - CH(NH_{3}^{+}) - (CH_{2})_{2} - COO^{-} + CO_{2} \underset{k_{-1}}{\leftrightarrow} ^{-}OOC - CH(NH)(COO^{-}) - (CH_{2})_{2} - COO^{-}$$
(4)

Where: k_2 , is the forward second seek average stationary evenness and k_{-1} , is the zwitterion mechanization average stationary.

The above interaction is follow up by the elimination of a proton from the zwitterionic carbamate hiring any rule B, to form an indifferent carbamate (the base-catalyzed deprotonation) as offered in neutralization (5). In this labor, water (H₂O), carbonate ions $(CO_3^{2^-})$, bicarbonate ions (HCO_3^{-}) and the deprotonated amino sour (AA) all can performance as rule [26].

$$^{\circ}COOC - CH(NH)(COO^{-}) - (CH_2)_2 - COO^{-} + B \stackrel{k_b}{\leftrightarrow} ^{\circ}COOC - CH(N)(COO^{-}) - (CH_2)_2 - COO^{-} + BH^+$$
(5)

Where: kb : kinetic constant represents deprotonation of the zwitterions.

acting as if a quasi- stationary-case constrain for the zwitterion concentricity and the second proton relocate interaction can be reckoned not to reverse, (the average of the interaction of CO_2 in an aquatic glutamic acid salt aquatic solution can be in any event express as:

$$r_{CO_2,GLu_s} = -\frac{k_2[CO_2][AA]}{1 + \frac{k_{-1}}{\sum k_b[B]}}$$
(6)

$$r_{CO_{2,GLu_{s}}} = -\frac{k_{2}[CO_{2}][AA]}{1 + \frac{k_{-1}}{k_{AA}[AA] + k_{H_{2}O}[H_{2}O] + k_{CO_{3}^{-2}}[CO_{3}^{-2}] + k_{HCO_{3}^{-}}[HCO_{3}^{-1}]}}$$
(7)

Two prime similar stance $\frac{\mathbf{k}_{-1}}{\sum \mathbf{k}_{b}[B]} \ll 1$ and $\frac{\mathbf{k}_{-1}}{\sum \mathbf{k}_{b}[B]} \gg 1$ are considered simplifying the interaction kinetic paradigm of amino sour corn, which is wholly qualified in letters [11, 23,27]. The preceding outcome in modest second-seek kinetics. The outcome in a ganglion interaction average express (e.g. third-seek kinetics if the deprotonation is fundamentally by amine). mainly amines like MEA ordinarily interact with CO₂ next a second seek interaction

kinetics which wherewithal that the deprotonation of the zwitterion is comparatively quickly when contrast to the invert average of CO_2 and first amines . Subsequently, the confined stipulation, $\frac{\mathbf{k}_{-1}}{\sum \mathbf{k}_{b}[B]} \ll 1$ (the average of zwitterion deprotonation is prompt than the invert average of CO_2 and glutamic acid) leads to a straightforward interaction average express as follows [11, 24]:

$$r_{CO_2,GLu_s} = k_2[CO_2][Glus]$$
(8)

Indicating that the interaction is the first seek of jointly the CO_2 and the amino acid corn, and hence, totally of the second seek.

2.3 Interaction rate for CO_2 absorption into the K_2CO_3 aquatic solution with a glutamic acid salt

When aquatic K_2CO_3 promoted by glutamic acid salt, it is fundamental to gather together CO_2 hydration with OH^- and zwitterionic interaction with glutamic acid into reckoning in the translation of the up taking average tests. The CO_2 up taking average can be offered by [21]:

$$r_{ov} = k_{ov} [CO_2] = r_{CO_2, K_2CO_3} + r_{CO_2, GLu_s}$$
(9)

Where: k_{ov} , is the inclusive pseudo-first-seek interaction average stationary.

subrogate the interaction average from equation (3) and equation (8) into equation. (9), k_{ov} can then be expressed as [17]:

$$r_{ov} = k_{OH^{-}}[CO_2][OH^{-}] + k_2[CO_2][Glus]$$
(10)

$$k_{ov} = k_{OH} - [OH^{-}] + k_2[Glus]$$
 (11)

3 Experimental work

3.1 Chemicals and tools

In this treatise, K_2CO_3 (99%) and Glutamic acid (Glu) were procured from Scharlau/ Spain. Potassium hydroxide (KOH) with 85% was purchased from Fluka. Hydrochloric acid (HCl) with 37% pureness procured from Merck Germany . CO_2 (99.99%) and N_2 (99.99%) used in the absorption tests were together furnished from SDI Samarra, Iraq. Stuffed pillar synthetic from glazier with an interior diameter of 4.2 cm and elevation of 140 cm was hired in the up taking tests of CO_2 . The stuffing elevation interior the pillar was 88 cm with a stuffing substance of attaining gang (0.3 cm extrinsic diameter) . whilst, glazier receptacle of 100 ml was hired in the desorption tests of CO_2 . For perfect allocation of aquatic solutions during the stuffing, fluid dispenser was conformed in the elevation fraction . The gas blend (CO_2 and N_2) pushed during to the stuffed pillar through the cribriform dish stationary in under most of the pillar to shore the stuffing substances . However although, a rotameters linked with gas rollers and fluid pump were hired to take control of the gas flowing average and solvent flowing average, respectively.

3.2 Experimental procedure

 CO_2 up taking tests brought about by following our previous experimental procedure [2]. Figure 1 exhibit the empirical intrigue of the up taking process . The CO_2 capacity was computed in the existent aquatic solution paradigm possessed at stationary times utilizing the procedure of acidification titration (Chittick device) [2]. Pending the mensuration of CO_2 loading, 1 M HCl was a supplement to the aquatic solution paradigm till changeful the evidence tint [1]. So, CO_2 gas was emitted in order to the neutralization interaction and gather in a surpass roller encompass the offer tint aquatic solution . Overabundant quantity of HCl was a supplement to assure the perfectly emitted of CO_2 . The CO_2 loading expressed as mol CO_2 per mol aquatic solution was computed by rebating the complete magnitude of HCl from the magnitude of CO_2 , as an offering in eq. (12) :

$$\alpha_{\rm CO_2} = \frac{\left(V_{\rm CO_2} - V_{\rm HCl}\right) \times (P) \times (273K)}{C_{\rm solution} \times V_1 \times A \times (760 \text{ mmHg}) \times (T)}$$
(12)

Where α_{CO_2} : CO₂ loading (mole CO₂/mole solvent), V_{CO_2} is the magnitude of CO₂ composed in the graduated gas cylinder (ml), V_{HCl} : is the magnitude of HCl adjust midst the titration process (ml), T: is the laboring temperature (K), P: is the atmospheric pressure (mmHg), V₁: is the magnitude of aquatic solution paradigm (ml) and A: is the convertibility factor (22.41 L/mol). Then the equipoise was proven one-day frequent readings of pH exhibit just a trivial variance. Next, pass into the first hour of up taking the test, CO₂ loading was frequent per 15 min.



Fig. 1. Silhouette of the up taking process.

The aquatic solution up taking process was deem following up before time authenticated labor [1]. Figure 2 offers the test put-up of the rejuvenation process. The efficiency of rejuvenation can be calculated using equation (13) [29].

Regeneration efficiency =
$$(1 - (\alpha_{CO_{2 \text{ lean}}} / \alpha_{CO_{2 \text{ rich}}})) \times 100$$
 (13)



Fig. 2. Silhouette of the rejuvenation process.

3.3 Kinetics measurement

Reaction rate is calculated from the change of CO_2 concentration obtained from experimental results with absorption time (d[CO_2]/dt). After that, the calculated reaction rates were plotted against CO_2 concentrations to prove the order of the reaction from the curve shape. The k_{ov} was calculated from equation (14):

$$\mathbf{r}_{\rm ov} = \mathbf{k}_{\rm ov} [\mathrm{CO}_2] \tag{14}$$

Where: r_{ov} : CO₂ kinetic average (mol L⁻¹ s⁻¹), k_{ov} : pseudo-first-rank interaction average stationary (s⁻¹), [CO₂]: concentricity of CO₂, (mol L⁻¹). Then, the average constants k_{OH} - and k_2 were calculated from the experimental results using equation (15):

$$k_{ov} = k_{OH^-}[OH^-] + k_2[Glus]$$
 (15)

Where: k_{OH^-} and k_2 are the rate constants (L mol⁻¹ s⁻¹), [OH⁻], [Glus] are the molar concentrations (mol L⁻¹). deeming the donating of average enhancement and the addendum of glutamic acid salt, the interaction average stationary for Glus, \mathbf{k}'_{ov} , is realized as follow up :

$$k'_{ov} = k_{ov} - k_{OH^{-}}[OH^{-}]$$
 (16)

The interaction average (k'_{ov}) rise linearly with [Glu_s]. The slopes of this line were represented the rate constant (k_{glu}) .

4 Results and discussion

Figure 3. appears the affluent and scrawny CO₂ tautology for K_2CO_3 aquatic solution and Glus at 1M concentricity, air pressure and temperature. It very well may be noticed that Glus has better CO₂ affluent tautology analyzed than various solvents. whilst, the CO₂ scrawny tautology of Glus was lower than various solvents. These outcomes can be clarified that the absorption tautology of CO₂ was diminished with increasing carbon series length thanks to a rise in molecular weight which suggests that the answer contains a lower molecule of the absorbent [30, 31]. The CO₂ tautology for K₂CO₃ and Glus appears to be acceptable concurrence with aftereffects of past work [6, 32]. The low CO₂ tautology for K₂CO₃ is thanks to the troublesome crumbling of the bonds and discharged CO₂ [23]. Likewise, it is seen that K₂CO₃+Glus dissolvable have lower CO₂ scrawny tautology. The assimilation of CO₂ in K₂CO₃ is obviously improved when promoted with a few measures of amino acid salts. This was because of the reduction of the carbamate stability which prompts increment the CO₂ tautology in affluent dissolvable as a result of the expansion in the substituent attached to nitrogen particle[33].



Fig. 3. Rich and lean CO₂ loading of K₂CO₃, Glu_s, and K₂CO₃ +Glu_s solvents at atmospheric pressure, 298 K and 15% CO₂ balanced with N₂.

The identical revelation competence for every solvent at desorption temperature of 363 K is introduced in **Figure 4**. It is obviously observed that K_2CO_3 has the least recovery effectiveness of all the examined solvents. While Glus offered the very best regeneration performance contrasted with different solvents. Glus has kept up the very best regeneration efficiency thanks to discharge CO_2 from carbamate in all the single solvents was higher contrasted and bicarbonate in Glus. What's more, Glus has molecular structure that makes it effectively recover and acquaint incredible debasement obstruction examination with other solvents [34, 35]. the rise of bicarbonate concentration profoundly influences the CO_2 scrawny tautology thanks to the simplest heat breaking of bicarbonate than carbamate. Including of Glus increment the regeneration competence above that of other promoters as indicated by their tendency and the mix impact with K₂CO₃. Glus kept the very best regeneration efficiency thanks to the opposite solvent. While, other solvent required a high measure of vitality for revelation [26, 36].



Fig. 4. Regeneration efficiency of K₂CO₃, Glu_s, and K₂CO₃ +Glu_s solvents at atmospheric pressure, 298 K and desorption temperature of 363 K.

Figure 5 presents the rate reaction of CO_2 in K_2CO_3 aquatic solution advanced by 15 vol.% of Glus. It tends to be seen that the relationship was nonlinear and expanding the response rate with the concentration of CO2 reactant. The R² from the bent fitting was equivalent to 1 with a second request connection between the rate response of CO_2 with dissolvable concentrations. In this manner, the reaction is second order. Two potential reasons were considered for glutamic corrosive to be the best advertiser in K_2CO_3 for CO_2 retention. To begin with, the glutamic acidulous contains a principally amino gathering which has a quick response rate with CO_2 [19, 20]. Second, the zwitterion response instrument is commonly acknowledged and the carbamate development is a crucial step.



Fig. 5. Rate reaction of CO₂ with K₂CO₃ solution promoted by 15 vol.% of Glus.

Figure 6 presents the impact of absorption time on the general reaction rate constant (kov) determined from condition (14) for K_2CO_3 solution advanced by 15 vol.% Glus. It very well may be seen that the kov dropped pointedly. Toward the start of absorption, concentrations of hydroxide ion and Glus have been at a significant level, and afterward, quick absorption rates were found. With increasing the absorption time, the concentration of HCO⁻₃ and deprotonated zwitterions from Glus in solution expanded and afterward the concentration of hydroxide ion and dynamic Glus segment diminished [21, 37].



Fig. 6. Overall reaction rate constant with absorption time for K_2CO_3 solution promoted by 15 vol.% of Glu_s at 298K.

In light of the pseudo-first-request system and zwitterionic component for the response of CO₂ and glutamic acidulous, the second-order response rate consistent, k_2 , (determined from condition (15), is 21282.16 L mol-1 s-1 and the second-order response rate steady with hydroxide particle, (determined from condition (15), is 7265.6 L mol-1 s-1. The low warmth of absorption related with K₂CO₃ arrangement and K₂CO₃₊ Glus frameworks might decrease vitality costs in CO₂ catch process. Higher CO₂ tautology and quick retention energy demonstrate that this amino acidulous can be a decent alternative solvent [1]. An examination between rate constants of varied promoters at 1 M and 25oC appears in Table 1. The way that the rate consistent of Glus is higher than those of some ordinary amines, yet lower than those of the cyclic diamine PZ. Notwithstanding Glus offering lower rate advancement when contrasted with PZ, glutamic acidulous is less harmful and earth amicable and in this way might be considered as a promising advertiser for carbonate-based solvents [17, 38].

Table 1. Rate constants of K₂CO₃ solution with various promoters at 1M and 298 K.

Solvent	Rate constant (s ⁻¹)	Ref.
K ₂ CO ₃ +MEA	5900	[47]
K ₂ CO ₃ +TEA	50	[48]
K ₂ CO ₃ +MDEA	4.4	[51]
K ₂ CO ₃ +Piperazine	53700	[49]
K ₂ CO ₃ +DEA	1300	[48]
K ₂ CO ₃ +Boric acid	45	[50]
K ₂ CO ₃ +Glutamic acid	24541.48	This work

5 Conclusions

The kinetics of CO₂ response with K_2CO_3 solution promoted by 15 vol.% of Glus were explored in a packed bed absorber at room temperature. The CO₂ absorption rate of K_2CO_3 solution was upgraded by including a modest quantity of Glus. The pseudo-first-order system and zwitterionic component were applied to portray the energy of CO₂ connection with K_2CO_3 arrangement advanced by 15 vol.% of Glus. It was discovered that the response is a second order. The got second-order response rate consistent (k_2) is 21282.16 L mol-1 s-1 and the second-order response rate steady with hydroxide ion is seen as 7265.595 L mol-1 s-1. Glus contains a fundamentally amino gathering which has been appeared to have a quick reaction rate with CO₂. Glus is a promising advertiser to K_2CO_3 solution for catching of CO₂.

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