Research Article

Absorption Kinetics and Mass Transfer Coefficient for Carbon (IV) Oxide Sequestration by Ammonia Solution

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Abstract Mass transfer coefficient and kinetic studies of CO_2 sequestration into aqueous ammonia was carried out to reveal the extent of the effect of the CO_2 and CO capture for the reactions which is an important characteristic in determining the efficiency of absorption. Experimental parameters for concentration of solution were 2 to 10 mol/dm^3, process duration of 20 to 100 seconds and volume of solvent 40 to 200 millilitres with ambient temperature and atmospheric pressure as the conditions during the work. Data for kinetics of CO_2 sequestered were obtained via numerical differential formula, absorption of CO_2 into the ammonia solution conformed to the first-order reaction as the calculated values of the Hatta Number as shown were all above 100 and the regression coefficient, R^2, value obtained from is greater than 0.9 with good linearity. An empirical volumetric mass transfer coefficient K_GA_V correlation for the system was proposed, K_GA_V was found to increase with an increase in concentration of solvent and volume of solvent.

Keyword: Kinetics, Mass transfer coefficient, CO_2 sequestration, absorption, ammonia, concentration, volume, time, reaction pathways, environment

1. Introduction

The emission of CO_2 by fossil-fuel power plants is generally described as the major source of global warming and by extension the cause of greenhouse effect as a result of the gases therein. Post Combustion Capture (PCC) with ammonia solution is currently regarded as the most feasible technology to reduce the CO_2 and CO emission from fossil fuel and natural gas fired power plants [1]. CO_2 is the major greenhouse gas in the world that needs to be reduced in essence there are various technologies used to separate CO_2 from flue gas. This includes chemical solvent methods, physical absorption methods, cryogenic method, membrane systems, biological fixation and the O_2/CO_2 combustion process. Compared with chemical plant, power plant has a large flue gas flow and relatively low CO_2 concentration. Chemical solvent absorption methods have been studied and are considered as a reliable and relatively low cost method for reducing CO_2 emission from fossil fuel power plants [2]. The ammonia solvent is also an excellent reagent for removing SO_2 and HCl from waste gas streams and has the capacity to scrub all acid pollutants.

The focus on the above literature is on the determination of the removal efficiency and absorption. The motivation of this paper focuses on the mass transfer performance of the CO_2 absorption process using wetted wall column and ammonia solution. The wetted wall column was evaluated experimentally under various conditions to reveal the effect of process parameters including concentration, time, volume, liquid flow rate.

2. Materials and Methods

2.1 Materials

The ammonia solvent (analytical grade) was purchased at the chemical market whereas the all glassware prototype absorption column was designed and fabricated to aid the carbon (IV) oxide sequestration. The equipment has an absorption column, flask containing the ammonia solution, reservoir to house the content of the mixture in the aftermath of the reaction, openings for flue gas entrant and exit point after the reaction, non-heat sensitive pipe connected to the entry point of the absorption column and the exhaust pipe of the gasoline generating set.

2.2 Methodology

Absorption method was used for this research, due to the nature of the equipment made of glassware and in order to control the experiment, standard conditions of ambient temperature and atmospheric pressure were adopted for the process and also for the flow rate of the solution into the absorption column. Three parameters/independent variables were used which are Concentration of solvent, Contact time and Volume of solvent. Experimental parameters for concentration of solvent were 2 to 10 mol/dm^3, process duration of 20 to 100 seconds and volume of solvent 40 to 200 millilitres. The chemical solution is charged into the column from the top and is evenly distributed across the inner surface of the column while in contact with the plates. Gas enters through an opening at the base of the column, counter-currently contacting with the liquid as it flows up and reacts with the ammonia solution as it is beneficial to make CO_2 and aqueous contact and react vigorously [3]. A gas analyzer is used to determine all combustion and emission test data and analyzer parameters.

3. Results and Discussions

Before the experiment in the absorption column was carried out, the gas analyzer was used to ascertain the initial conditions from the flue gas source (petrol electricity generating set).

The values obtained are:

- Average amount of CO initially present in the flue gas: 703.33ppm (0.0703%)
- Average amount of CO_2 initially present in the flue gas: 6.02%
- Average amount of other gases: 85.2%

To ascertain the removal efficiency:

$$\% \text{ Removal Efficiency} = \frac{\text{Amount of gas leaving the column}}{\text{Amount of gas initially present in the flue gas source}} \times 100$$

3.1 Reaction rate for CO_2 absorption into aqueous ammonia

On the basis of all considerations concerning the various reactions with CO_2 in aqueous ammonia, the reaction rate for CO_2 absorption into aqueous ammonia solution can be described by equation (1) and equation (2) as follows:

$$r_{CO_2-NH_3} = k_2[NH_3][CO_2] \tag{1}$$

$$r_{CO_2-OH^-} = k_{OH^-}[OH^-][CO_2] \tag{2}$$

The overall reaction rate from equation (1) and (2) can be described as

$$r_{ov} = r_{CO_2-NH_3} + r_{CO_2-OH^-}$$
$$= k_2[NH_3][CO_2] + k_{OH^-}[OH^-][CO_2] \tag{3}$$

Where the values for rate constant k_2 for reaction between CO_2 and ammonia is calculated using Numerical Differential Formula at ambient temperature of the experimental process. Also the kinetic rate constant k_{OH^-} can be described in terms of temperature used for the research using the expression stated in equation (4) [4] as follows.

$$\log_{10}(K_{OH^-}) = 13.635 - \frac{2895}{T} \tag{4}$$

The value of kOH$^-$ is calculated with equation 4 while substituting for ambient temperature. The hydroxyl ion concentration and the pH value of aqueous ammonia are estimated by the following relations:

$$[OH^-] = \sqrt{K_b\sqrt{[NH_3]}} \tag{5}$$

$$p^H = -\log_{10}[H^+] = -\log_{10}\frac{K_w}{[OH^-]} \tag{6}$$

Where:

K_b represents the ionization equilibrium constant of the aqueous ammonia

Kw is the dissociation constant of water with respect to the constant temperature

From equation (3), the overall reaction rate can be approximately described as:

$$r_{ov} = r_{CO_2-NH_3} = k_2[NH_3][CO_2] \tag{7}$$

The reaction between NH_3 and CO_2 is very fast, and the CO_2 concentration in the liquid phase can be assumed to be zero in the fast pseudo-first-order reaction regime [4].

To verify whether the absorption of CO_2 into aqueous ammonia occurs in the fast first-order reaction regime, Hatta Number must be greater than or equal to 100

$(H_a \geq 100)$, [4].

Where the Hatta Number is expressed as:

$$H_a = \sqrt{\frac{K_2[NH_3]D_{CO_{2L}}}{K_l}} \tag{8}$$

Where:

K_2 represents the rate constant for reaction between CO_2 and aqueous ammonia

D_{CO2} is the diffusivity of Carbon (iv) oxide

K_L is the dissociation constant of water

The mass transfer coefficient in the liquid phase is expressed as:

$$H_a = \sqrt{\frac{\pi}{4}t_c k_2[NH_3]} \tag{9}$$

Where tc is the contact time (seconds)

3.2 Determination of Overall Mass Transfer Coefficient

The overall mass transfer coefficient is affected by three factors namely; there is the interfacial area between gas phase and liquid phase, the resistance in the gas phase, and the resistance in the liquid phase. In the derivation of the overall mass transfer coefficient, it is assumed that the liquid flow rate is unchanged [4]. So, the interfacial area between gas phase and liquid phase is unchanged. Then, the overall mass transfer coefficient is unchanged about the interfacial area between gas phase and liquid phase. The mass balance can be given as follows:

$$dm_A = \Omega G_B dY = N_A a_V \Omega \, dh \tag{10}$$

Where

$$G_B dY = K_G P a_v (y - y^*) dh \tag{11}$$

Where m_A represents the amount of carbon (IV) oxide absorbed per unit time in kmol/h,

    Y is the mole ratio of CO_2 gas,

    h is column height in m, G_B is gas flow rate in kmol/(m^3.h),

    y is the mole fraction of CO_2 in the gas stream.

From Equation 10, the element of column dh can be determined as

$$dh = \frac{G_B}{K_G P a_v}\frac{dY}{(y-y^*)} \tag{12}$$

When used for the chemical absorption, y* in Equation (12) is assumed to be zero since the chemical reaction is fast (Lin, Liu and Tan, 2003). Thus, Equation (12) is expressed as

$$dh = \frac{G_B}{K_G P a_v}\frac{dY}{y} \tag{13}$$

and

$$y = \frac{Y}{1+Y} \tag{14}$$

Therefore,

$$\int_o^h dh = \frac{G_B}{K_G Pa_v} \int_{Y_2}^{Y_1} \frac{1+Y}{Y} \, dY \tag{15}$$

and

$$h = \frac{G_B}{K_G Pa_v} In \frac{Y_1}{Y_2} + (Y_1 - Y_2) \tag{16}$$

In this work, the CO_2 concentration at the top and bottom of the column was measured and used for evaluating the $K_G A_V$ value according to Equation (16).

In the derivation of the overall mass transfer coefficient, it is assumed that the liquid flow rate is unchanged [4]. So, the interfacial area between gas phase and liquid phase is unchanged. Then, the overall mass transfer coefficient is unchanged about the interfacial area between gas phase and liquid phase. In the process of absorption, the total gas flow rate is constantly changing due to CO_2 absorption into aqueous ammonia solution.

4. Kinetics, Mass transfer coefficient and ANOVA analysis

The kinetic study reveals the potential rate of reaction for carbon sequestration and explains the nature of gas-liquid interaction for aqueous ammonia reaction with carbon (IV) oxide and carbon (II) oxide.

4.1 ANOVA analysis of the carbon (iv) oxide capture

Table 1: Optimization Results for the Capture of CO_2 on Ammonia Solution

Std	Concentration of Solvent (Mol/dm³)	Contact Time (Seconds)	Volume of Solvent (ml)	Amount of CO_2 captured (%)	Removal Efficiency (%)
1	4	40	80	3.13	50.33
2	8	40	80	3.31	54.98
3	4	80	80	2.27	37.71
4	8	80	80	2.96	49.17
5	4	40	160	2.15	35.71
6	8	40	160	1.72	28.57
7	4	80	160	2.59	43.02
8	8	80	160	2.67	44.35
9	2	60	120	1.82	30.23
10	10	60	120	2.08	34.55
11	6	20	120	1.39	23.09
12	6	100	120	1.48	24.58
13	6	60	40	2.60	43.19
14	6	60	200	1.33	22.09
15	6	60	120	5.0	83.06
16	6	60	120	5.06	84.05
17	6	60	120	4.74	78.73
18	6	60	120	5.14	85.38
19	6	60	120	5.02	83.39
20	6	60	120	4.79	79.57

Design Expert 10.0.6 trial version was used to analyze the results. The results were shown in Table 2 to 4. In Table 2, the summary of P-values for CO_2 captured indicated that a quadratic model fitted the ANOVA analysis because the adjusted R-squared value was very close to the value obtained for the predicted R-squared, also the P-value obtained in Lack of Fit was close to unity and hence it was suggested. The linear and 2FI models were not suggested, the cubic model was always aliased because the CCD does not contain enough runs to support a full cubic model. A significance level of 95% was used hence sequential P-value terms that are less than 0.05 are considered significant. In Table 3, quadratic model was suggested because of the closeness of the adjusted R-squared and predicted R-squared, with the cubic model aliased as a result of the CCD not having enough runs for a

full cubic model. In Table 4, quadratic model was suggested because the p-value is close to unity and there is a good relationship between the sum of squares and mean square.

A quadratic regression equation that fitted the data is:

$$Y\ CO_2\ captured = 4.96 + 0.065A + 0.022B + 0.32C + 0.13AB - 0.15AC + 0.33BC - 0.75A^2 + 0.88B^2 + 0.75C^2$$

(17)

Where Y is the response variable (amount of $CO_{2\ captured}$) and A, B and C are the coded values of the independent variables. The above equation represents the quantitative effect of the factors (A, B and C) upon the response (Y). Coefficients with one factor represent the effect of that particular factor while the coefficients with more than one factor represent the interaction between those factors. Positive sign in front of the terms indicates synergistic effect while negative sign indicates antagonistic effect of the factor.

Table 2: Summary of P-values for CO_2 captured

Source	Sequential p-value	Lack of Fit p-value	Adjusted R-Squared	Predicted R-Squared	Remark
Linear	0.8537	< 0.0001	-0.1325	-0.3656	Not suggested
2FI	0.9280	< 0.0001	-0.3954	-0.5428	Not suggested
Quadratic	< 0.0001	0.9998	0.9934	0.9947	Suggested
Cubic	1.0000	0.7742			Aliased

Table 3: Model Summary Statistics for CO2 captured

Source	Std. Dev.	R-Squared	Adjusted R-quared	Predicted R-Squared	PRESS	Remark
Linear	1.47	0.0463	-0.1325	-0.3656	49.75	Not suggested
2FI	1.61	0.0782	-0.3472	-0.3428	56.21	Not suggested
Quadratic	0.11	0.9965	0.9934	0.9947	0.19	Suggested
Cubic	0.15	0.9965	0.9889	0.9982	< 0.65	Aliased

Table 4: Lack of Fit Test for CO_2 captured

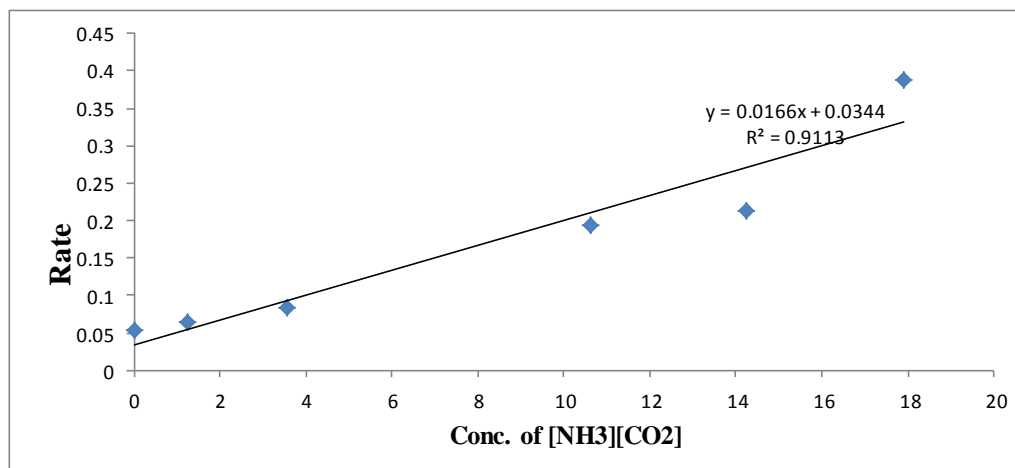| Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remark
Linear	34.62	11	3.15	126.01	< 0.0001	Not suggested
2FI	33.46	8	4.18	167.45	< 0.0001	Not suggested
Quadratic	2.292E-003	10	4.582E-004	0.018	0.9998	Suggested
Cubic	2.292E-003	1	2.292E-003	0.092	0.7742	Aliased
Pure Error	0.12	5	0.025			

4.2 First-order kinetic model

Figure 1: First-order plot for the absorption of CO_2 on aqueous ammonia

Table 5: Kinetic Data for the absorption of CO_2 in ammonia solution

Using Ionization equilibrium constant of aqueous ammonia, $K_b = 1.710 \times 10^{-5}$ [3]

NH_3 mol/dm³	KOH^- dm³ mol⁻¹s⁻¹	OH mol/dm³	$[KOH^-][OH]$ s⁻¹	$K_2(NH_3)$ mol.secs/dm³
2	12161.86	0.00585	71.1468	606
4	12161.86	0.00827	100.5786	1212
6	12161.86	0.01013	123.1996	1818
8	12161.86	0.01169	142.1721	2424
10	12161.86	0.01308	159.0771	3030

The **$K_2(NH_3)$** values were obtained from interaction of ambient temperature (30°C) and concentration of ammonia solution. From Table 5, the value of **KOH [OH⁻]** is much smaller than that of **$K_2(NH_3)$** as the reaction has a very low hydroxyl ion concentration.

Table 6: Data required for obtaining kinetics of CO_2 (Calculated using Numerical Differential Formula)

NH_3 mol/dm³	$[CO_2]$ %	$[CO_2]$ mol/dm³	t s⁻¹	$[NH_3][CO_2]$ mol/dm³ (x)	r (mol.secs/dm³) (Y)
0	0	0	0	0	0.05250
2	1.82	0.63	20	1.26	0.06475
4	3.35	0.89	40	3.56	0.0830
6	5.18	1.79	60	10.74	0.19325
8	5.16	1.78	80	14.24	0.2135
10	5.14	1.77	100	17.70	0.3880

Table 7: Concentration of solvent against Hatta Number

Conc. of solvent (mol/dm³)	Hatta Number
2	169.98
4	238.98
6	292.70
8	337.98
10	377.87

The kinetic data for the absorption of CO_2 into aqueous ammonia solution are presented in Table 5, the first-order kinetic model was investigated by plotting the calculated values from Numerical Differential Formula denoted as r against Conc. of $[NH_3][CO_2]$ as seen in Figure 1 and Table 5. The rate constant was calculated from the slope of the plot in Figure 4.10 while the correlation coefficient R^2 is also displayed on the graph. Absorption of CO_2 into aqueous ammonia solution follows first order if calculated values of the Hatta Number ($H_A \geq 100$) and R^2 value for the plot is greater than 0.9 and attains good linearity (Zeng et. al., 2011). It is observed from our work that as the values of the Numerical Differential Formula is increasing, concentration of $[NH_3][CO_2]$ increases. This observed trend is due to the increased fast absorption rate of ammonia and the ability of ammonia to diffuse through the gas-liquid interface while reacting favourably with the dissociated CO_2 in the reaction.

4.3 Mass Transfer Coefficient results

The effect of independent variables on the overall mass transfer coefficient was investigated by plotting the values of the overall mass transfer against the sequestrated carbon as shown in Table 8.

4.3.1 Effect of Concentration of solvent on the Mass Transfer Coefficient for CO_2

Table 8: K_GA_V against Conc. of Sol. for CO_2

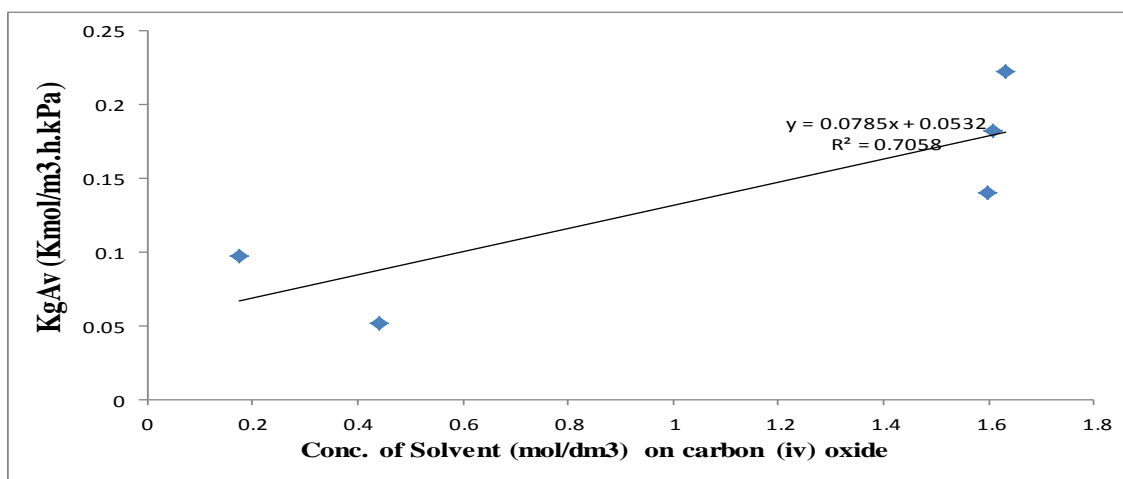| K_GA_V (kmol/(m³.h.kPa))	Conc. of Sol. for CO_2 (%)
0.0520	0.4430
0.0970	0.1746
0.1404	1.5961
0.1819	1.6076
0.2224	1.6311

Figure 2: Effect of Conc. of Solvent for K_GA_V on CO_2

Figure 2 and Table 8 elucidates the effect of ammonia concentration (2 to 10 mol/dm^3) on the percentage of CO_2 removal and K_GA_V. The percentage of CO_2 removal increases when ammonia concentration was increased from 2 to 10 mol/dm^3. This effect is due to the increased amount of active ammonia available to diffuse through the gas-liquid interface and react with dissociated CO_2. A reduction in K_GA_V will lead to an increase in the viscosity of the liquid solution which causes a reduction in the rate of molecular diffusion as reported in the work of De Montigny et al. [5]. In previous work, K_GA_V increasing as the ammonia concentration increases goes contrary to what has been observed about CO_2 absorption into solvents such as monoethanolamine in a packed column, this trend can be attributed to the fact that ammonia concentration and its active site has less effect on liquid viscosity unlike monoethanolamine concentration as reported in the work of Nair and Selvi [6]. For this research, increase in ammonia concentration creates room for the solvent to diffuse into the gas-liquid interface and reacts effectively with CO_2; this promotes an enhancement factor increase which leads to a higher mass transfer coefficient values. Furthermore, ammonia has large absorption capacity; it possesses small heat of reaction which helps CO_2 to evolve at atmospheric pressure.

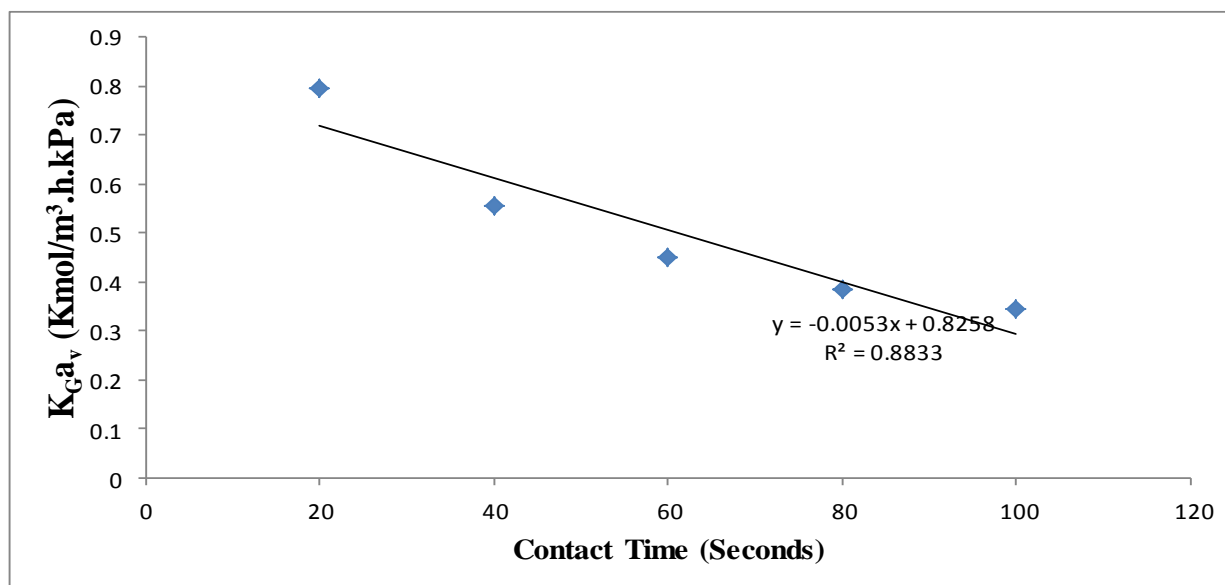**4.3.2 Effect of Contact Time on Mass Transfer Coefficient for CO_2**

Figure 3: Effect of Contact Time on K_GA_V for the captured gases

Table 9: K_GA_V against Contact Time

K_GA_V (kmol/(m³.h.kPa))	Time (secs)
0.794	20
0.554	40
0.449	60
0.386	80
0.344	100

Figure 3 and Table 9 show the effect of contact/operating time on gas removal and K_GA_V. It was observed that an increase in contact time of reaction between ammonia concentration and captured carbon molecules caused a decrease in the mass transfer coefficient, this goes to show that the higher the time assigned for the absorption/sequestration process the lesser the tendency of having increased amount of active ammonia in the liquid solution available to diffuse towards the gas-liquid interface for reaction with CO_2 which does not encourage efficient sequestration. Also an increase in contact time aid carbon molecule escapes while travelling from gas bulk to the gas-liquid interface which led to poor mass transfer performance. It is also well-known that gases are volatile compounds and do require limited time for a chemical reaction such as that of absorption. The trend in this research work agrees with the work of Halim et al. [7], on mass transfer performance of CO_2 absorption from natural gas using monoethanolamine (MEA) in high pressure operations.

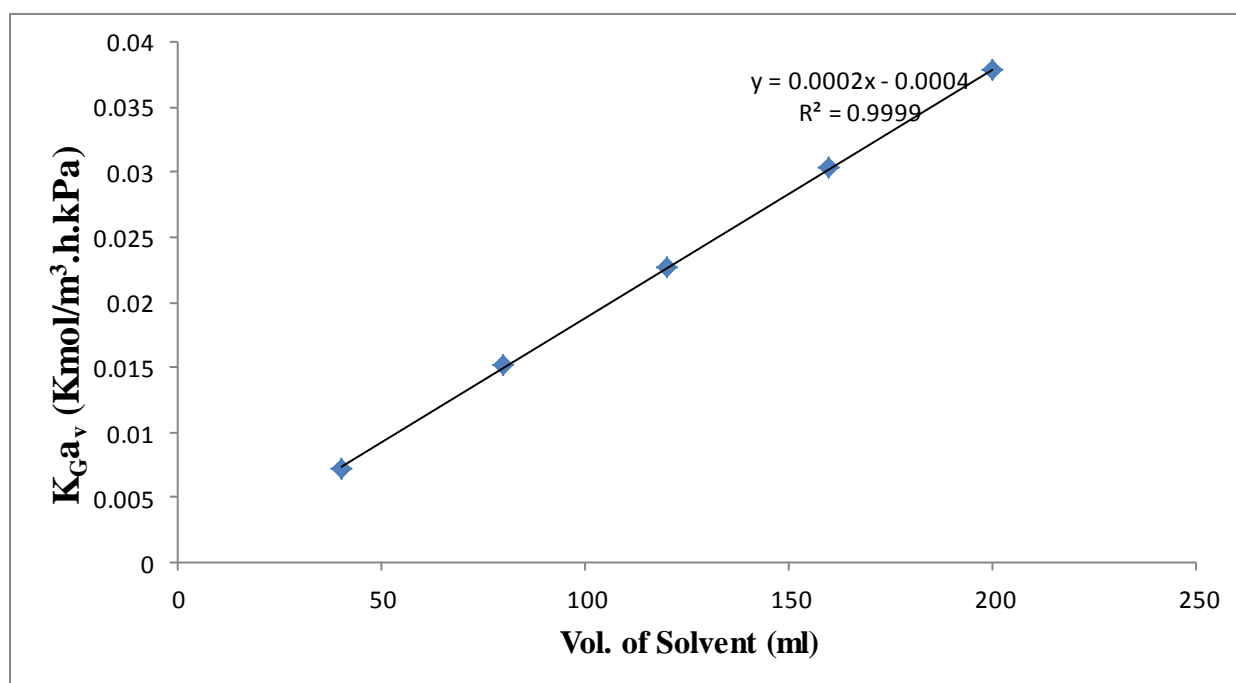**4.3.3 Effect of Volume of solvent on Mass Transfer Coefficient for CO_2**

Figure 4: Effect of Volume of Solvent on K_GA_V for the captured gases

Table 10: K_GA_V against Volume of Solvent

K_GA_V (kmol/(m³.h.kPa))	Volume (ml)
0.0075	40
0.0151	80
0.02272	120
0.03029	160
0.03787	200

Figure 4 and Table 10 elucidates the effect of volume of ammonia solvent on the mass transfer coefficient. As shown in figure 4, an increase in volume of solvent led to an increase in CO_2 (%) and K_GA_V values. By increasing the volume of solvent from 40 to 200 millilitres, a large amount of free amine molecules are available to come in contact with carbon molecules in the gas phase, thus enhancing the reaction of ammonia with the flue gas. Also the decrease in liquid film thickness led to an increase in the liquid-side mass transfer coefficient, this trend was reported in the work of Aroonwilas and Tontiwachwuthikal [8], Sema et al. [9] and Tan et al. [10]. Furthermore, as volume of ammonia solvent increased, more liquid was spread on the contact surface which led to an increased area per unit volume supporting carbon sequestration; this phenomenon was corroborated in the work of Zeng and Lin, [4].

5. Conclusion

In the study, the kinetic of absorption revealed the extent of the effect of the carbon capture for the reactions which was an important characteristic in determining the efficiency of absorption. The kinetic model revealed the mechanism of absorption by the results of mass transfer coefficient and results from the calculated Hatta Number, which is an essential parameter in determining that the reaction is first-order. The empirical K_GA_V correlation for this system was also proposed and it was shown that K_GA_V increased with increasing concentration of solvent with same phenomenon observed with the parameter for volume of solvent which was very rapid with good linearity buttressing that is appropriate to use K_G in the mass transfer process of the carbon sequestration by ammonia solution.

References

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