GHGT-11

A Study of Mass transfer Kinetics of Carbon Dioxide in (Monoethanolamine + Water) by Stirred Cell
Ying Jirua, Dag A. Eimerb*

aTel-Tek, Porsgrunn 3918, Norway
bTelemark University College, Porsgrunn 3901, Norway

Abstract

The gas phase resistance in a stirred cell was investigated to understand and avoid its influence on the measurement of the reaction kinetics. To validate the influence of gas phase resistance and the experimental conditions of pseudo first order reaction for Monoethanolamine (MEA) + CO₂ system, low CO₂ partial pressure under various inert gas pressure were employed for CO₂ the absorption into 0.5, 1, 3 and 3.6 M MEA solutions with H₂O and ethyleneglycol as solvents, respectively. The absorption was investigated with the stirred cell based on a fall-in-pressure technique.

© 2013 The Authors. Published by Elsevier Ltd.
Selection and/or peer-review under responsibility of GHGT

Keywords: Monoethanolamine; CO₂; Stirred cell; Mass transfer kinetics; Gas phase resistance

1. Introduction

So-called stirred cells are classical tools for studying reaction and mass transfer kinetics for gas-liquid systems with or without chemical reactions. Despite of such equipment having been in use for such purpose for several decades, there are still issues worth discussing. Stirred cells are less complicated than the classic tools including wetted walls, single spheres and laminar jets in the sense that less supporting equipment are needed. Hence the flowsheet and as a consequence the temperature control becomes much easier. Another convenient property is that less liquid is needed to do measurements, and there is no chemical analysis needed for the liquid. The structure of the stirred cell is simple and easy to operate. The only challenge with respect to construction is to arrange for the stirring, but this is in practice easily dealt with. If operated in batch fashion, the rate of reaction may be derived from pressure measurements. Semi-batch operation with gas flow-through will also involve flow measurements. In this work the focus in on batch operation. Danckwerts [1], Blauwhoff and Versteeg [2][3], Sandall [4], Vaidya [5] and other research groups have employed stirred cells to perform a large number of studies on mass transfer of gas-liquid. Recently, Kucka [6] discussed the analysis of rate data based on pressure measurements. He

* Corresponding author. Tel.: +47 95230506
E-mail address: Dag.A.Eimer@tel-tek.no.
analysed and compared five analytical and numerical methods for the estimation of reaction rate constants from dynamic experiments in stirred cell reactors, and a reference method was developed and suggested. However, the methods II, III and IV summarized in his review are actually the same method from the perspective of data numerical treatment. The reference method takes the load of the liquid bulk phase into account and thus offers the opportunity to perform several experiments in series, without time-consuming purification of the liquid phase. This is a good idea for the usage of a stirred cell when the load of the liquid bulk is a little high. However, it is found that the reference method is too complex in practise and not necessary if the liquid amount is large or the load of the liquid bulk is low.

The gas phase resistance during the absorption of a gas into a liquid in the stirred cell was not investigated in the present literature, and it was always neglected in the measurements. Actually, as the gas phase in the stirred cell includes liquid vapours and inert gases such as N₂, it is impossible to completely remove non-reacting gas from the stirred cell. If the partial pressure of the reactant gas is very low and the gas absorption rate is high, the influence of the gas phase resistance on the result is significant. For instance, with respect to the aqueous MEA+CO₂ system, the CO₂ partial pressure was set very low, to about 3 – 5 kPa, to meet the pseudo first order reaction regime requirements, but the partial pressure of the inert gas (MEA, H₂O vapor and N₂) is normally higher than this value for CO₂, about 3 – 12 kPa. The typical absorption curve and gas, liquid statuses are shown in Figure 1.

![Schematic diagram of the gas and liquid status of the typical gas-liquid absorption in the stirred cell absorber.](image)

- ①: solution and its vapors before gas introduction, ②: reactant gas is introduced and absorption starts,
- ③: gas is absorbing in liquid, ④: reactant gas is absorbed fully in liquid

Monoethanolamine (MEA) was one of the alkanolamines introduced for CO₂ absorption already in the 1930s and has been industrially important since then. There is, however, still potential for improvement of the much-used absorption process using MEA in spite of all the development work done over these years. To this end stirred cells will be important as a part of the arsenal of scientific methods to study the kinetics of gas-liquid reactions that are key issues in CO₂ capture. Efficient use of stirred cells might be a better line of investigation to follow than some of the semi-quantitative so-called screening tests in the sense that specific quantitative information would be produced.

In this work, to study the influence of the gas phase resistance in the stirred cell, this parameter was investigated in the absorption of CO₂ in 1 M and 3 M MEA solutions with various solvents (water and
ethylene glycol) at 303.15 K under various inert gas pressures, respectively. The mass transfer kinetics of aqueous MEA+CO₂ with 0.5 and 3.6 M MEA concentrations were studied at the temperature 298.15 K to validate the analytical and numeric methods, and the experimental conditions needed to obtain pseudo first order reaction conditions. An “integral method” is employed to determine the kinetics parameters which are measured by a stirred cell based on the fall-in-pressure technique.

2. Experimental Section

2.1. Experimental Equipment and Procedure

A schematic diagram of the stirred cell absorber is shown in Figure 2. The stirred cell absorber comprises an inner diameter 12.5 cm chamber with a water jacket which is connected to a water bath. Deionised water is used in the double jacket to provide isothermal operating conditions. The entire assembly was proven to have no leak. The gas phase stirrers were two fan turbines with six blades each mounted in the gas phase while the liquid phase stirrer with two blades placed halfway down the liquid's depth. Both the gas and liquid phase stirrers were driven by the same shaft at speeds 0 - 2500 rpm that can be adjusted electronically within an accuracy of ± 1 rpm. Eight baffles inside the reactor are designed to prevent vortex formation during the stirring of the liquid phase and also to ensure a flat horizontal interface. A pressure transducer (Druck, PTX1400, U.K., 0-100kPa abs.) with accuracy 0.15%, was mounted on the flange and coupled with a data acquisition system to record the total pressure inside the reactor. A metal pipe with 10 cm³ volume was used for storage gas. It was wound around the metal flange which was temperature controlled by an independent controller based on an electric heater. This equipment unit is used to provide the required temperature for the gas. Both the upper and bottom metal flanges and the storage gas pipe are thermally insulated to improve the accuracy of the temperature control.

For the kinetics measurements of absorption runs, the stirred tank absorber was operated batchwise with respect to both the gas phase and the liquid phase. For each experimental run, 500 - 600 cm³ volume of the freshly prepared (0.5 or 3.6 M) MEA solution is fed into the chamber and degassed under vacuum
for approximately 0.5 - 1 hour. Once the degassing process is complete, the liquid is kept under vacuum (i.e. approx. 3.1 kPa at 298.15 K) in preparation for the experimental run and data collection. The storage gas pipe is filled with the gas to be studied (CO₂) at 500 kPa (gauge) and then heated to the specified temperature. The temperature of metal flange was kept a little higher (+0.3 K) than that of the liquid to avoid condensation on the surface of the metal flange. After approximately 1 hour, the equilibria of both temperature and gas-liquid are reached, CO₂ is introduced into the chamber in 5 s and the absorption starts immediately. The total gas pressure, the temperatures of the liquid and gas phases and the agitation speed (rps) in the reactor are recorded using a data acquisition system (data logger, Agilent BenchLink 34972A). The partial pressure of the gas A at the experimental condition was corrected for the vapor pressure of the solution as follows.

\[ P_A = P_{\text{total}} - \left( P_{N_2} + x_{H_2O} P_{H_2O}^v + x_{MEA} P_{MEA}^v \right) \]  \tag{1}

where \( P_{N_2} \) is the partial pressure of nitrogen, \( P_{H_2O}^v \) is the water vapor pressure, \( P_{MEA}^v \) is the vapor pressure of MEA, \( x_{H_2O} \) and \( x_{MEA} \) are the mole fraction of water and MEA, respectively.

For each experiment with CO₂ absorption in MEA solution, and the initial partial pressure of CO₂ was low, 3 - 5 kPa, to satisfy the criterion for a pseudo-first-order reaction, as given by Danckwerts [7] as follows:

\[ 3 < H_a \ll E^\infty \]  \tag{2}

here \( H_a \) is Hatta number [8] and \( E^\infty \) is the limiting case of absorption, the infinite enhancement factor, for a single irreversible reaction. \( E^\infty \) is defined as the enhancement factor given instantaneous conversion of reactants. The rate of absorption is thus completely being limited by the diffusion of the governing components. This is approximated by Higbie [9] as

\[ E^\infty = \sqrt{\frac{D_{CO_2,L}}{v_{MEA}}} + \sqrt{\frac{D_{MEA,L}}{v_{CO_2,L}}} \]  \tag{3}

Here \( v_{MEA} \) is the stoichiometric coefficient of MEA, \( H_{CO_2} \) is the Henry’s constant, \( D_{CO_2,L} \) and \( D_{MEA,L} \) are the diffusivities of CO₂ and MEA in the liquid, respectively. According to equation (3), if \( C_{MEA} \) is large enough or \( P_{CO_2}/H_{CO_2} \) small enough, \( E^\infty \) will be large enough to satisfy the criterion given by equation (2). In practice, to meet the pseudo first order reaction criterion, the requirement for the \( P_{CO_2} \) is different for different reaction systems. For example, the CO₂ partial pressure is not required to be as low to meet one of the criterion conditions (\( H_a \ll E^\infty \)) for methyldeithanolamine (MDEA) + CO₂ reaction system. But for MEA + CO₂, it is required that the CO₂ partial pressure is low because of the high \( H_a \) value (or high reaction rate).

The influence of the CO₂ liquid loading on the rate of the reverse reaction is only 1% at the maximum as checked by Cornelisse et al. [10]. In this work, about 3 – 5 kPa CO₂ (1.4 L) was used for the absorption measurement in 0.5 L MEA solution.

To check the influence of gas phase resistance on the measurement of chemical absorption, the reaction rate constants of MEA+CO₂ were measured under different inert gas pressures at 303.15 K. The experimental concentrations of MEA were 1 and 3 M with H₂O as a solvent and 3 M with ethyleneglycol as a solvent, respectively. The gas and liquid stirrer speed was 1 rps.

2.2. Reagent and Solution Preparation
Reagent grade MEA with mass fraction purity $\geq 99.5\%$ was obtained from Merck and used without further purification. Deionized water (was purified with a mini-Q system (Millipore), 18.2 MΩ cm) and MEA were degassed by applying vacuum and then mixed to prepare various concentrations of the aqueous MEA solutions using an analytical balance and a 500ml volumetric flask. The whole preparation process was protected by a nitrogen atmosphere. The purity of CO$_2$ was $\geq 99.995\%$, produced by AGA Gas GmbH.

3. Results and Discussion

3.1. Determination of Gas-liquid Reaction Kinetics

Kucka [6] suggested a “reference method” to take the CO$_2$ loading of the solution into account after one or more measurements. It is found that the reference method is too complex, in fact, when the quantity of MEA is large and the CO$_2$ loading is very low, it is safe to ignore the influence of CO$_2$ loading on the bulk and assume that $C_{\text{MEA}}$ is constant due to the amount of MEA being large compared to that of CO$_2$. An “integral method” of data analysis is suggested as follow,

$$
\ln P_A = \frac{R A T {k_2 C_{\text{MEA}} D_{\text{CO}_2}}}{H_A V_G} t + \ln P_{A,0}
$$

(4)

If plotting $\ln P_A$ vs. $t$ from the equations (4), the slope $b$ is given by

$$
b = \frac{R A T {k_2 C_{\text{MEA}} D_{\text{CO}_2}}}{H_A V_G}
$$

(5)

The slope $b$ can be determined by linear regression of the plot $\ln P_A$ vs. $t$, hence $k_2$ can be obtained as the value of $(D_{\text{CO}_2})^{1/2}/H_A$ is known. After the absorption is finished, the CO$_2$ loading is approximately $10^{-6}$ mol/mol, and the CO$_2$ back-pressure of the CO$_2$ loading in this solution is very small according to the measurement of equilibrium solubility by Jou et al. [11]. Therefore, it is safe to use the same solution more than once for the measurements with CO$_2$ without a need to worry about the very low initial loading.

3.2. Investigation of Gas Phase Resistance

It was investigated whether the gas phase resistance should be taken into account or not in the research of kinetics of MEA with CO$_2$ reaction by stirred cell. According to the film theory, penetration theory and surface-renewal theory, the mass transfer coefficient is a function of diffusivity as follows [12]

$$
k = D^\alpha
$$

(6)

where $\alpha$ is $0.5 - 1$. The typical order of magnitude of diffusion of gas is $10^{-9}$ m$^2$s$^{-1}$ in liquid phase and $10^{-5}$ m$^2$s$^{-1}$ in gas phase, respectively. Theoretically, the typical value of the mass transfer coefficient $k_G$ is $10^{-2}$ m s$^{-1}$ and $k_L$ is $10^{-5}$ m s$^{-1}$, respectively. Obviously, $k_G >> k_L$, the mass transfer of a gas in the gas phase is much higher than in the liquid phase if the gas solubility in liquid is not high (viz. $H_A$ is low). Since $H_A$ is high in the present case, almost all researchers ignored the influence of the gas phase resistance when they studied the reaction kinetics by stirred cell with batchwise operation on gas and liquid.
It is safe to neglect the gas phase resistance if the mass transfer in liquid phase is slow, (i.e. without chemical reaction or with slow chemical reaction). However, for the mass transfer with fast chemical reaction, the absorption rate could be high due to the enhancement by the chemical reaction, and the liquid side mass transfer resistance is \( H_A/k_L E \). In the present work, the values of \( k_L E \) were calculated, and the typical value is \( 10^{-2} \text{ m s}^{-1} \) for 3.6 M aqueous MEA solution + CO\(_2\) system. Then the mass transfer coefficient in liquid phase is of the same order of magnitude as that in the gas phase, and if the concentrations of MEA solution increase, the values could be higher and even \( k_G \leq k_L E \). Thus, the gas phase resistance cannot be neglected for the fast chemical reaction system.

![Figure 3](image-url)

**Figure 3** ln\( P_{CO_2} \) - t with different inert gas pressure (12 kPa and 4.5 kPa) and different initial CO\(_2\) pressures in 1 M aq. MEA solution at 303.15 K: (o, solution used 1st time; red line, the same solution used 2nd time) with \( P_{inert}=12 \text{ kPa and } P_{CO_2,ini}=10.7 \text{ kPa}; \) green line, the same solution used 3rd time with \( P_{inert}=12 \text{ kPa and } P_{CO_2,ini}=10.7 \text{ kPa}; \) blue line, the same solution used 4th time with \( P_{inert}=4.5 \text{ kPa and } P_{CO_2,ini}=7.7 \text{ kPa}. \)

Figure 3 shows that the relationship of ln\( P_{CO_2} \) - t with different inert gas pressure (12 kPa and 4.5 kPa) and different initial CO\(_2\) pressures were absorbed in 1 M aq. MEA solution at 303.15 K. It can be seen that the absorption rate of CO\(_2\) under the inert gas pressure of 12 kPa is almost same as that of 4.5 kPa when \( P_{CO_2} \) is higher than 3 kPa (seeing the time range in 0 - 80 s), but lower than that of 4.5 kPa when \( P_{CO_2} \) is lower than 3 kPa (see the time range is 100 - 270 s). This result shows that the CO\(_2\) partial pressure, \(<3 \text{ kPa}\), is the region where the pseudo 1st order reaction criterion for calculating the reaction rate constant of the MEA + CO\(_2\) system will apply. At the same time, the results show that the gas phase resistance affects the measurement of the kinetics parameter. This is although the \( P_{CO_2} \) is lower than 3 kPa, the pressure of inert gas is about 3.2 kPa at 298.15 K and 12 kPa at 323.15 K, which is nearly equal to the \( P_{CO_2} \) and even higher if the temperature is higher. It is noted that the slope \( b \) is almost the same when the solution was used three times, this means that the low CO\(_2\) loading in the solution has negligible influence on the result.

Figure 4 shows the slope \( b \) as a function of the \( P_{inert} \) in 3 M MEA+CO\(_2\) reaction system with the solvents H\(_2\)O and ethyleneglycol at 303 K, respectively. It is obvious that the absorption rate of CO\(_2\) in MEA solution increases with a decrease of the pressure of the inert gas. The absorption rate increases significantly when the inert gas pressure drops to less than 10 kPa. The minimum \( P_{inert} \) of the experiment with H\(_2\)O as solvent at 303 K is 4 kPa due to the vapor pressure of a 3 M solution being 4 kPa at this temperature. To reduce the \( P_{inert} \) further, ethyleneglycol was investigated as a solvent since its vapor pressure is lower, and the minimum \( P_{inert} \) can be decreased to 2 kPa at 303 K. The result of ethyleneglycol as a solvent shows that the absorption rate increases slightly as \( P_{inert} \) decreases from 4 kPa to 2 kPa.
slope and the estimated reaction rate constants are listed in Table 1. The results manifest that the influence of the gas phase resistance cannot be ignored, because of the high chemical reaction speed in the mass transfer of the CO₂ in the solution.

To resolve this problem and simplify the measurement with a stirred cell, a simple method was employed in the present study, viz. to speed up the stirrer to increase the mass transfer in the gas phase. In this work, due to the gas stirrer and the liquid stirrer being mounted on the same shaft, the number of fan turbines is increased to two and each turbine is mounted with six blades (39 mm × 14 mm × 2 mm) to increase the stirring. Then, the gas phase resistance can be reduced and neglected for the conditions investigated.

![Graph](image)

Figure 4 The slope \( b \) versus the partial pressure of inert gas of 3 M MEA+CO₂ at 303.15 K, 1 rps with different solvent: □, H₂O; ●, ethyleneglycol

Table 1 The slope \( b \) and \( k_2 \) of 3 M aq. MEA+CO₂ under various inert pressure at 303.15 K. (The initial Pressure of CO₂ is approx. 4 kPa)

<table>
<thead>
<tr>
<th>( P_{\text{inert}} ) (kPa)</th>
<th>4.09</th>
<th>7.01</th>
<th>10.11</th>
<th>20.09</th>
<th>30.01</th>
<th>39.86</th>
</tr>
</thead>
<tbody>
<tr>
<td>slope ( b )</td>
<td>0.03823</td>
<td>0.02856</td>
<td>0.02404</td>
<td>0.02047</td>
<td>0.01845</td>
<td>0.01794</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>8420</td>
<td>4699</td>
<td>3329</td>
<td>2414</td>
<td>1961</td>
<td>1854</td>
</tr>
</tbody>
</table>

3.3. Kinetics of Chemical Reaction of CO₂ Absorbed in Aqueous MEA Solution

To validate further the experimental conditions of pseudo first order reaction for aqueous MEA+CO₂ system, low CO₂ partial pressure were used for the absorption into 0.5 M and 3.6 M aqueous MEA solutions respectively under low inert gas (the vapor of the solution) and a high gas stirred speed. The results are that, at 298.15 K, \( H_a \) is 88, \( E^\circ \) is 492 and \( k_2 \) is 3728 dm\(^3\) mol\(^{-1}\) s\(^{-1}\) for 0.5 M MEA solution, and \( H_a \) is 304, \( E^\circ \) is 3734 and \( k_2 \) is 7666 dm\(^3\) mol\(^{-1}\) s\(^{-1}\) for 3.6 M MEA, respectively. In the determination, the physical solubility and diffusivity data of CO₂ in solutions were obtained from previous work [13][14]. It can be seen that the \( k_2 \) values measured in this work are in agreement with literature values [15]. Furthermore, it can be seen that the experimental conditions of both 0.5 M and 3.6 M aqueous MEA solutions satisfy the criterion of pseudo first order reaction, equation (2). Thus, 3 kPa CO₂ partial pressure was used to ensure the reaction is in the range when pseudo first order reaction may be assumed.
4. Conclusions

The absorption of a gas in a liquid was determined with a stirred cell from the fall in pressure and the liquid-side mass transfer coefficient and the reaction rate constant were determined by an integral method. The kinetics of the reaction of carbon dioxide with aqueous MEA solutions was studied using the stirred cell with a plane gas-liquid interface to validate the influence of gas phase resistance on the results and the experimental conditions of the pseudo first order reaction. The results show that the gas phase resistance cannot be neglected if the resistance is not under control. It is found that to keep a low inert gas pressure and speed up the stirrer is a good and simple method to reduce the gas phase resistance. An upper limit of 3 kPa CO₂ partial pressure was suggested to ensure the reaction is in the range where the pseudo first order reaction assumption may be made.

Acknowledgements

This work was supported by Norwegian Research Council and Statoil ASA, Norway (project No.188936).

References