

## Reactive Absorption of CO<sub>2</sub> into Aqueous Solutions of N,N-Diethylethanolamine

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The kinetics of the reaction of CO<sub>2</sub> with aqueous solutions containing N,N-diethylethanolamine (DEEA) was studied in a stirred cell reactor with a plane, horizontal gas-liquid interface, in the temperature range of 298 to 308 K. The DEEA concentration in the aqueous solutions was varied in the range of 2 to 3 kmol/m<sup>3</sup>. DEEA, which is a tertiary alkanolamine linked with 2 alkyl groups, has a base-catalytic effect on CO<sub>2</sub> hydrolysis. The investigated reaction was found to be of the first order with respect to both CO<sub>2</sub> and DEEA. A combined parameter involving the reaction rate constant and the solubility and diffusivity of CO<sub>2</sub> in DEEA solutions was estimated. Besides, the effect of addition of piperazine as possible activator of the absorption rate was studied and it was found that even with a small amount of piperazine (0.1 kmol/m<sup>3</sup>) added, the CO<sub>2</sub> absorption rate increased.

### 1. Introduction

The reaction of CO<sub>2</sub> with alkanolamines is of considerable industrial importance, e.g., in treating natural/associated gas streams, in the manufacture of hydrogen via steam reforming of natural gas, in ammonia plants to make the gaseous streams free of CO<sub>2</sub>, and in thermal power stations to meet the discharge limits for CO<sub>2</sub> in flue gas. Industrially important alkanolamines for CO<sub>2</sub> removal are the primary amine *monoethanolamine* (MEA), the secondary amine *diethanolamine* (DEA) and the tertiary amine *methyldiethanolamine* (MDEA).

Primary and secondary alkanolamines react rapidly with CO<sub>2</sub> to form carbamates. However, the heat of absorption associated with the carbamate formation is high. Consequently, this results in high solvent regeneration costs. Further, the CO<sub>2</sub> loading capacity of such alkanolamines is limited to 0.5 mol of CO<sub>2</sub> / mol of amine. In tertiary alkanolamines, which have a low reactivity with respect to CO<sub>2</sub>, there is no hydrogen atom attached to the nitrogen atom, as in case of MEA and DEA, and thus the carbamation reaction cannot take place. Instead, tertiary amines promote the CO<sub>2</sub> hydrolysis reaction forming bicarbonates. The reaction heat associated with bicarbonate formation is lower as compared to the heat associated with carbamate formation, thus resulting in lower solvent regeneration costs. Moreover, tertiary amines have a high CO<sub>2</sub> loading capacity of 1 mol of CO<sub>2</sub> / mol of amine.

In this work, the reaction of CO<sub>2</sub> with one such tertiary alkanolamine, namely, *N,N-diethylethanolamine* (DEEA) is investigated. It comprises two ethyl groups replacing

the hydrogen atoms of the amino group in MEA. Diethylamine (obtained from ethanol) and ethylene oxide (obtained from the oxidation of ethylene which, in turn, can be prepared by dehydration of ethanol) react to form DEEA. Ethanol, which is the major raw material for the manufacture of this alkanolamine, can be prepared from agricultural products and/or residues. Thus, DEEA is a potentially attractive absorbent for sour gas purification, as it can be prepared from renewable resources. However, up to now, there is practically no information available to provide fundamental understanding of the reaction of  $\text{CO}_2$  with DEEA in aqueous solutions. The  $\text{CO}_2$  absorption rate of an aqueous DEEA solution can be enhanced by the addition of an activator. *Piperazine* (PIP), a cyclic amine, was selected as a possible activator for this study, and the reactive absorption of  $\text{CO}_2$  into formulated aqueous solutions of N,N-diethylethanolamine containing piperazine (DEEA + PIP +  $\text{H}_2\text{O}$ ) was investigated, too.

## 2. Experimental

A glass stirred cell reactor (Fig. 1) with a plane, horizontal gas-liquid interface was used for the absorption rate measurements (cf. Kucka et al., 2002). This easy-to-use experimental device was operated batchwise and equipped with a data acquisition system. A series of experiments was conducted at different temperatures (298-308 K) and DEEA concentrations (2-3  $\text{kmol/m}^3$ ). In each experiment, the decrease in system pressure due to reaction was monitored by a pressure transducer and the “pressure vs. time” data were recorded. This measurement method based on the fall-in-pressure technique enabled a simple and straightforward estimation of the absorption rates. Further, no analysis of the liquid phase was required and the pressure decrease was the only factor for the evaluation of the kinetic parameters. The reproducibility of experiments was checked and the error in all experimental measurements was found to be less than 3%.

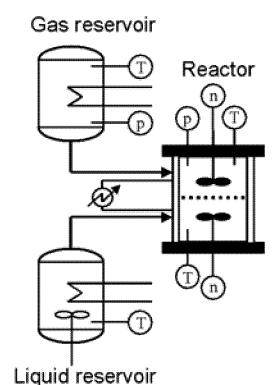
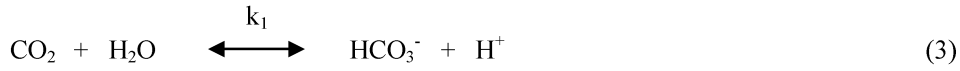
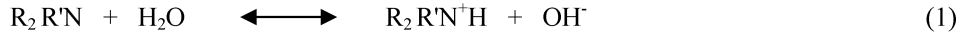


Figure 1. Experimental setup according to Kucka et al. (2002).

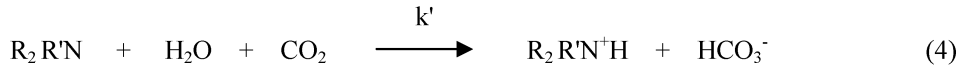
## 3. Results and Discussion

### 3.1 Reaction mechanism

Mahajani and Joshi (1988) discussed the reaction between  $\text{CO}_2$  and tertiary alkanolamines. The following reactions may take place in an aqueous DEEA solution (here DEEA is denoted as  $\text{R}_2\text{R}'\text{N}$ , where  $\text{R} = -\text{C}_2\text{H}_5$  and  $\text{R}' = -\text{CH}_2\text{CH}_2\text{OH}$ ):



The amine dissociation reaction (Eq. 1) is almost instantaneous. The reaction between  $CO_2$  and  $OH^-$  (Eq. 2) is also fast. Donaldson and Nguyen (1980) earlier reported that tertiary alkanolamines cannot react directly with  $CO_2$ . Such amines have a base catalytic effect on the hydration of  $CO_2$ . This could be represented as follows:



$k_{OH^-}$ ,  $k_1$  and  $k'$  denote the forward reaction rate constants in Eqs. 2, 3 and 4 respectively. The total rate of all  $CO_2$  reactions in the solution is therefore given by the sum of the reaction rates given by Eqs. 2 to 4:

$$r = [k_1 + k_{OH^-}(OH^-) + k'(R_2R'N)](CO_2) = k_{obs}(CO_2) \quad (5)$$

where  $k_{obs}$  denotes the observed reaction rate constant that can be measured and  $(CO_2)$ ,  $(OH^-)$  and  $(R_2R'N)$  denote the concentrations of  $CO_2$ , hydroxyl ions and DEEA respectively. Eq. 5 does not account for the water concentration. The apparent reaction rate constant,  $k_{ap} = k'(R_2R'N)$ , which is used for the analysis of experimental data, can be obtained from  $k_{obs}$  as follows:

$$k_{ap} = k_{obs} - [k_1 + k_{OH^-}(OH^-)] \quad (6)$$

The base catalysis reaction could also be explained by a zwitterion mechanism earlier proposed by Yu and Astarita (1985):



Eq. 7 represents a reaction of DEEA with  $CO_2$  to form an unstable complex. Eq. 8 describes the homogeneous hydrolysis reaction. Water reacts with the zwitterion-type complex, which results in a bicarbonate formation.

### 3.2 Reaction kinetics

Knowledge on the reaction kinetics is essential in design and operation of gas treatment units. When the  $CO_2$  partial pressure in the bulk liquid is negligible, it can be shown based on the two-film theory of mass transfer (Danckwerts, 1970) that the following relation holds:

$$\frac{P_{\text{CO}_2}}{R_{\text{CO}_2} a} = \frac{1}{k_G a} + \frac{1}{k_L a H_{\text{CO}_2} E} \quad (9)$$

where  $P_{\text{CO}_2}$ ,  $R_{\text{CO}_2}$  and  $a$  denote partial pressure of  $\text{CO}_2$  in bulk gas phase, specific rate of absorption of  $\text{CO}_2$  and gas-liquid interfacial area respectively. The mass transfer coefficients on the gas- and liquid-side are denoted by  $k_G$  and  $k_L$ , respectively.  $E$  is the enhancement factor due to chemical reaction and  $H_{\text{CO}_2}$  is the Henry's law constant ( $\text{kmol}/(\text{m}^3 \text{ kPa})$ ). To determine the kinetic parameters, it is necessary that the system belongs to the fast reaction regime, without depletion of the amine at the gas-liquid interface (Danckwerts, 1970; Doraiswamy and Sharma, 1984). The necessary conditions are:

$$10 < \sqrt{M} < q \quad (10)$$

$$\sqrt{M} = \frac{\sqrt{[2 / (m+1)] D_{\text{CO}_2} k_{mn} (\text{CO}_2)^{m-1} (\text{DEEA})_0^n}}{k_L} \quad (11)$$

$$q = \frac{(\text{DEEA})_0}{z (\text{CO}_2)} \frac{D_{\text{DEEA}}}{D_{\text{CO}_2}} \quad (12)$$

where  $k_{mn}$  is reaction rate constant for an  $m, n^{\text{th}}$  order reaction and  $D_{\text{CO}_2}$  and  $D_{\text{DEEA}}$  are diffusivities of  $\text{CO}_2$  and DEEA in the liquid phase ( $\text{m}^2/\text{s}$ ).  $(\text{DEEA})_0$  denotes the initial DEEA concentration and  $z$  the stoichiometric reaction coefficient. In the fast reaction regime ( $E = \sqrt{M}$ ), the rate of absorption is independent of  $k_L$  and hence it should not depend on the agitation speed. We studied this effect experimentally and found practically no change in the absorption rate while varying the stirring speed in the range of 50 to 100 rpm at 303 K. Hence, it could be concluded that this system belongs to the fast reaction regime systems. All further experiments were conducted at a speed of 70 rpm. The  $\text{CO}_2$  absorption rates into aqueous DEEA solutions at various temperatures are shown in Table 1. All previous studies on the reactions of  $\text{CO}_2$  with alkanolamines suggest that the reaction order with respect to  $\text{CO}_2$  is equal to one:  $m = 1$ . For the case  $n = 1$ , Eq. 9 can be rewritten as:

$$\frac{P_{\text{CO}_2}}{R_{\text{CO}_2}} = \frac{1}{k_G} + \frac{1}{H_{\text{CO}_2} \sqrt{D_{\text{CO}_2} k_2 (\text{DEEA})_0}} \quad (13)$$

where  $k_2$  is the second order reaction rate constant ( $\text{m}^3/(\text{kmol s})$ ). A plot of  $(P_{\text{CO}_2}/R_{\text{CO}_2})$  vs.  $1/\sqrt{(\text{DEEA})_0}$  is shown in Fig. 2. Indeed, this plot confirms that the reaction is of the first order with respect to DEEA ( $n = 1$ ). Since the range of concentrations studied is not large,  $D_{\text{CO}_2}$  and  $k_2$  are assumed to be constant. From the slope of this graph, the value of the combined parameter,  $H_{\text{CO}_2} \sqrt{D_{\text{CO}_2} k_2}$ , at 303 K was found to be  $1.3 \times 10^{-7} \text{ kmol}^{1/2}/(\text{m}^{1/2} \text{ s kPa})$ . The gas-side mass transfer resistance is negligible, as can be concluded from Fig. 2.

Table 1. CO<sub>2</sub> absorption rates into aqueous DEEA solution

| Temperature<br>K | (DEEA) <sub>0</sub><br>kmol/m <sup>3</sup> | P <sub>CO2</sub><br>kPa | R <sub>CO2</sub> × 10 <sup>6</sup><br>kmol/(m <sup>2</sup> s) |
|------------------|--|-------------------------|---|
| 298              | 2.25                                       | 15.62                   | 1.86  |
|                  | 2.50                                       | 14.10                   | 2.49  |
|                  | 3.0  | 14.26                   | 2.79  |
| 303              | 2.0  | 4.54                    | 0.77  |
|                  | 2.0  | 6.36                    | 0.90  |
|                  | 2.0  | 7.58                    | 1.30  |
|                  | 2.0  | 12.74                   | 1.84  |
|                  | 2.25                                       | 5.30                    | 0.98  |
|                  | 2.25                                       | 7.73                    | 1.47  |
|                  | 2.25                                       | 10.46                   | 1.80  |
|                  | 2.25                                       | 15.62                   | 2.58  |
|                  | 2.50                                       | 2.27                    | 0.48  |
|                  | 2.50                                       | 4.99                    | 1.22  |
|                  | 2.50                                       | 8.94                    | 2.19  |
|                  | 2.50                                       | 13.19                   | 2.98  |
|                  | 3.0  | 3.94                    | 0.98  |
|                  | 3.0  | 6.82                    | 1.91  |
| 3.0              | 10.16                                      | 2.66                    |   |
| 3.0              | 14.41                                      | 3.52                    |   |
| 308              | 2.0  | 16.38                   | 3.19  |
|                  | 2.25                                       | 15.62                   | 3.47  |
|                  | 2.50                                       | 14.86                   | 4.17  |

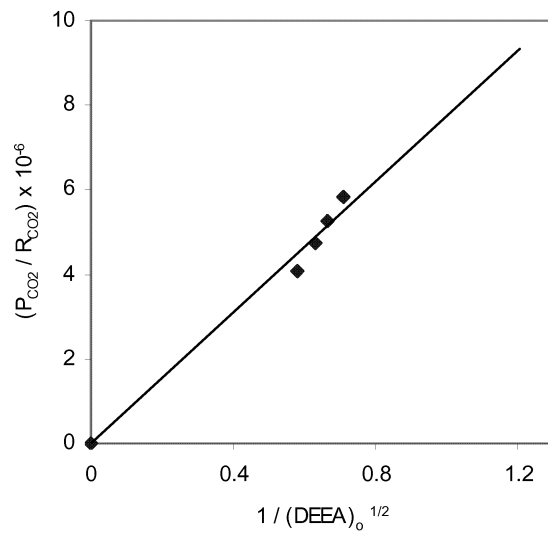
Figure 2. Estimation of the parameter  $H_{CO_2} \sqrt{D_{CO_2} k_2}$  at 303 K

Table 2. CO<sub>2</sub> absorption rates into aqueous DEEA solutions activated with PIP (303 K)

| (DEEA) <sub>0</sub><br>kmol/m <sup>3</sup> | Without PIP                        |  | With PIP (0.1 kmol/m <sup>3</sup> ) |  |
|--|------------------------------------|--|-------------------------------------|--|
|  | P <sub>CO<sub>2</sub></sub><br>kPa | R <sub>CO<sub>2</sub></sub> × 10 <sup>6</sup><br>kmol/(m <sup>2</sup> s) | P <sub>CO<sub>2</sub></sub><br>kPa  | R <sub>CO<sub>2</sub></sub> × 10 <sup>6</sup><br>kmol/(m <sup>2</sup> s) |
| 1.5  | 14.26                              | 1.62   | 12.77                               | 2.78   |
| 2.0  | 12.74                              | 1.84   | 14.57                               | 3.03   |
| 2.5  | 13.19                              | 2.98   | 14.02                               | 3.40   |

### 3.3 Effect of piperazine

The effect of addition of piperazine as possible activator of the absorption rate was studied. The CO<sub>2</sub> absorption rate was enhanced when a small amount of PIP (0.1 kmol/m<sup>3</sup>) was added into the aqueous DEEA solution (see Table 2). The reactions that may take place in presence of PIP (here denoted by R" (NH)<sub>2</sub>) can be explained by the homogeneous activation mechanism (Xu et al., 1992; Zhang et al., 2001):



Reaction described by Eq. 14 occurs simultaneously with that described by Eq. 7. Hence, CO<sub>2</sub> could be transferred by R" (NHCOO)<sub>2</sub> to DEEA as follows:



### Conclusions

The kinetics of the reaction of CO<sub>2</sub> with aqueous solutions containing DEEA as well as the effect of addition of piperazine as possible absorption activator was studied. DEEA reacts relatively slowly with CO<sub>2</sub> due to its tertiary amine characteristics and has a base catalytic effect on the hydration of CO<sub>2</sub>. It was found that the investigated reaction is of the first order with respect to both CO<sub>2</sub> and DEEA, whereas piperazine acts as an effective absorption activator in aqueous DEEA solution.

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