

## Absorption of Carbon Dioxide into Aqueous AMP Solutions

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(Manuscript received on 12 January, 1998)

The rates of absorption of carbon dioxide into aqueous solutions of 2-amino-2-methyl-1-propanol (AMP) were measured using a semibatch stirred vessel with a plane gas-liquid interface at 25°C. The absorption rates under the fast reaction regime were analysed using chemical absorption theory. The reaction was found to be first order with respect to both CO<sub>2</sub> and the amine.

Key words : absorption rate, 2-amino-2-methyl-1-propanol, stirred vessel, chemical absorption, reaction order

### 1. Introduction

Nowadays the global warming issue caused by greenhouse gases has become a matter of great concern, and carbon dioxide which is produced in enormous amounts has widely been recognized as one of the most influencing greenhouse gases. Industry is one of the major sources of CO<sub>2</sub>. Many plants such as fossil-fuel-fired power plants, iron and steel works, and cement works discharge a huge amount of CO<sub>2</sub> day after day. At present rates of emission, the CO<sub>2</sub> concentration in the atmosphere is expected to double by the middle of the next century. Since CO<sub>2</sub> emission will increase with increasing energy consumption, intensive efforts must be made toward energy conservation and promotion of energy efficiency.

As far as chemical absorption is concerned, the treatment of industrial gaseous streams has been dealt with using conventional absorbers consisting mainly of packed columns, bubble columns, spray towers and so on. This operation is in most cases conducted chemically in the presence of a

reactive absorbent in order to achieve high absorption rates. For this purpose, organic absorbents such as alkanolamines are widely used industrially. Those are conventionally classified as primary, secondary or tertiary amines such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), respectively and used extensively in aqueous solutions, because of their high solubility in water, low volatility, and their selectivity for removal of acid gases in the industrial gas purification plants.

In addition to conventional alkanolamines, a recently discovered group of so-called sterically hindered amines is also attractive since they provide high stoichiometric absorption capacities of 1.0 mol CO<sub>2</sub>/mol-amine (Sharma, 1965) because of the instability of their carbamates and show high absorption rates comparable to those obtained from the primary or secondary alkanolamines at high CO<sub>2</sub> loadings defined as the CO<sub>2</sub> total solubility per mole of amine. One example of the sterically hindered amine is 2-amino-2-methyl-1-propanol (AMP). The application of this type of amine was first suggested by Sharma (1965).

Later Sartori and Savage (1983) pointed out its high CO<sub>2</sub> loading capabilities in comparison to MEA, a non-hindered form of AMP. The first preliminary studies were reported by Chakraborty et al. (1986) and Zioudas and Dadach (1986). In these papers no information was given on the reaction mechanism and kinetic constants.

Bosch et al. (1990) evaluated the results of both Chakraborty et al. (1986) and Zioudas and Dadach (1986) with the aid of a numerically solved absorption model in which they assumed that the sterically hindered amine, AMP, reacted similar to conventional amines. However, in their simulations the value of the equilibrium constant,  $K_{eq}$ , was very low indicating that the carbamate species was very unstable. In their concluding remarks, they confirmed the validity of the zwitterion mechanism for the investigation of the absorption of CO<sub>2</sub> into aqueous solutions of AMP.

Yih and Shen (1988) and Alper (1990) also investigated the kinetics of the reaction between CO<sub>2</sub> and AMP in aqueous solution using absorption technique. Since Alper used a stopped flow method, if the reaction of CO<sub>2</sub> and AMP was in substantial conversion level, it was not affected by reversibility. Alper (1990) found a reaction order in AMP which was higher than one (~1.15) but interpreted the data as an overall second order reaction. His results at 298K are in good agreement with those of Bosch et al. (1990). At 313K the extrapolated rate constant of Alper coincides with the results of Yih and Shen (1988), 1.16m<sup>3</sup>/(mol.sec) vs. 1.27m<sup>3</sup>/(mol.sec) respectively. This latter result is somewhat surprising, since Yih and Shen (1988) ignored the possible influence of the reversibility of the reaction even at higher experimental CO<sub>2</sub> partial pressures. However, it is possible that their experiments were carried out in the pseudo first order reaction regime because they used a wetted wall column as a model reactor where higher mass transfer,

$k_L$ , can be obtained.

Xu et al. (1991) studied the absorption of CO<sub>2</sub> in a mixture of AMP-H<sub>2</sub>O-sulfolane over the temperature range 288-318K for one AMP concentration. They found that the pseudo first order reaction rate constant was of the same magnitude as for an aqueous solution of a similar AMP concentration.

In this present study, as the first part of gas separation using various amine solutions, a diffusion model of gas absorption into aqueous AMP solution in a stirred vessel was proposed and the reaction kinetics of CO<sub>2</sub> and AMP was examined.

## 2. Theory

The theory of gas-liquid absorption with chemical reaction is now sufficiently established and known: only the principal reactions which permit the interpretation of experimental results are recalled. The following chemical reaction between an initially gaseous constituent A and a reactant B in an aqueous solution is assumed ;



with a reaction rate

$$r = -\frac{dA}{dt} = -\frac{1}{z} \frac{dB}{dt} = k_{mn} C_A^m C_B^n \quad (2)$$

When one uses the film theory as a theoretical model, the basic differential equations for gas absorption with an irreversible (m,n)order reaction between a dissolved gas A and a liquid-phase reactant B can be represented as follows:

$$D_A \frac{\partial^2 C_A}{\partial x^2} = k_{mn} C_A^m C_B^n \quad (3)$$

$$D_B \frac{\partial^2 C_B}{\partial x^2} = z k_{mn} C_A^m C_B^n \quad (4)$$

Then the boundary conditions to be applied in order to solve the basic differential eq. (3), (4) are:

$$x=0 ; C_A = C_{Ai} \quad (5)$$

$$x \rightarrow \infty ; C_A = 0 \quad (6)$$

$$x=0 ; \frac{\partial C_B}{\partial x} = 0 \quad (7)$$

$$x \rightarrow \infty ; C_B = C_{Bo} \quad (8)$$

The theoretical expression for average absorption rate of solute gas A into liquid can be obtained by the following equation:

$$N_A = -D_A \left. \frac{\partial C_A}{\partial x} \right|_{x=0} \quad (9)$$

and following the usual procedure by using of eq.(3)~(8), we get

$$N_A = k_L C_{Ai} \frac{\sqrt{M} \left( \frac{E_i - E}{E_i - 1} \right)^{\frac{n}{2}}}{\tanh \left[ \sqrt{M} \left( \frac{E_i - E}{E_i - 1} \right)^{\frac{n}{2}} \right]} \quad (10)$$

Relationship(10) assumes that there is no gas phase resistance to mass transfer, and that the concentration of A in the bulk of the liquid is negligible. The flux is a function of the enhancement factor E due to the chemical reaction which is produced in the liquid phase and also to the mass transfer coefficient of the liquid film  $k_L$  by eq. (11)

$$E = \frac{N_A}{k_L C_{Ai}} \quad (11)$$

In a practical form, the variation of E as a function of the reaction diffusion  $\sqrt{M}$  which is expressed in the following form in the theory developed by Higbie (1935):

$$\sqrt{M} = \frac{1}{k_L} \sqrt{\frac{2}{m+1} D_A k_{mn} (C_{Ai})^{m-1} (C_{Bo})^n} \quad (12)$$

$D_A$  is the diffusivity of A in the liquid phase.  $C_{Bo}$  is the concentration of reactant B able to participate in the chemical reaction.

If the reaction instantaneous regime, the enhancement factor is expressed by:

$$E_i = 1 + \frac{D_B C_{Bo}}{z D_A C_{Ai}} \quad (13)$$

$D_B$  is the diffusivity of B the region with a pseudo-order of (m,n) is characterized by:

$$3 < \sqrt{M} = E \ll E_i \quad (14)$$

in this reaction regime, the flux  $N_A$  can be expressed by:

$$N_A = \sqrt{\frac{2}{(m+1)} D_A k_{mn} C_{Ai}^{(m+1)} C_{Bo}^n} \quad (15)$$

Herein, the concentration  $C_{Ai}$  and the partial pressure  $p_{Ai}$  of A at the interface are related to each other by Henry's law:

$$p_{Ai} = C_{Ai} H_A \quad (16)$$

### 3. Experimental Methods

A schematic diagram of the experimental apparatus was shown in Fig. 1. A cylindrical glass vessel of inside diameter 6.51cm and a height of 11.86 cm was used as the stirred tank

absorber. And the absorber was cross-shaped with four flat vertical blades. The absorber is of continuous-flow type in a gas phase and such a system enables steady state operation. The volume of absorbent liquid in the vessel was 200 cm<sup>3</sup> without soluble gases. The gas mixture was fed with constant flow rate and composition adjusted by using the mass flow controller through the saturator containing water. The absorption temperature was controlled by water bath and the total system was operated in an air chamber with constant temperature. The compositions of CO<sub>2</sub> at inlet and outlet of the vessel were analyzed by a gas chromatography (Shimadzu GC-8A, TCD, packing material: Porapak Q, detector temperature: 130 °C, the flow rate of carrier gas, He: 20 cm<sup>3</sup>/min), and flow rates of outlet were measured by a soap-bubble meter. The absorbent liquid was mixed by agitator, and the concentration of liquid was measured by HCl titration. All chemicals in this study were reagent grade (Acros Organics of Japan) and were used without further purification.

The ranges of flow rate of gas mixture were 20~50 cm<sup>3</sup>/min, those of composition of CO<sub>2</sub> in

feed gases of CO<sub>2</sub>-N<sub>2</sub> mixture, 5~40 mole %, those of concentration of AMP as absorbent agent, 0 ~ 2 mol/l, and those of agitation speed, 80~200 rev/min. Absorption experiments were carried out at 25°C and atmospheric pressure.

#### 4. Results and Discussion

In the present work, to confirm the resulting expression and evaluate the reaction rate constant, an (m, n)-th order reaction equation of the type ( $r_A = k_{mn} C_A^m C_B^n$ ) is considered. Both the order of reaction and the rate constant are determined from gas absorption rates in the fast reaction regime, according to the Hikita and Asai (1964).

A plot of  $N_A$  versus  $p_{Ai}$  in Fig. 2 for CO<sub>2</sub> · AMP solutions gives a slope of 1, which means that the order m with respect to CO<sub>2</sub> concentration is 1.

In this case, the equation (15) reduces to

$$N_A = C_{Ai} \sqrt{k_{1,n} D_A C_{B0}^n} \quad (17)$$

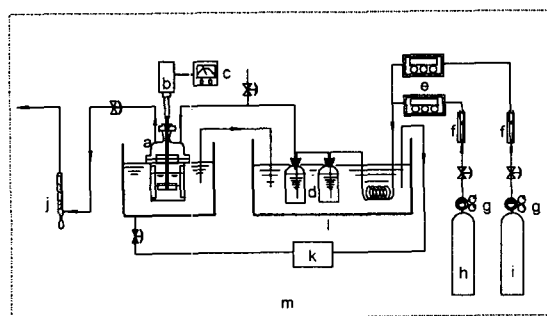


Fig. 1. Schematic diagram of experimental apparatus.  
 a: Agitated vessel      f: gas flow meter      k: Immersion circulator  
 b: Motor                      g: Gas regulator      l: Water bath  
 c: Motor controller      h: CO<sub>2</sub> cylinder      m: Air chamber  
 d: Saturation bottle      i: N<sub>2</sub> cylinder  
 e: Mass flow controller      j: Soap bubble meter

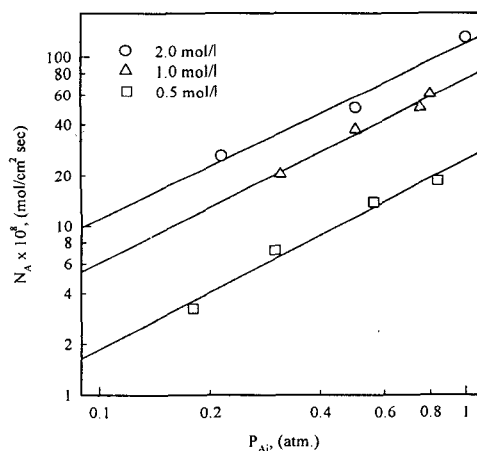


Fig. 2. Absorption rate of CO<sub>2</sub> into aqueous solution of AMP at 25°C.

The fast reaction regime is fulfilled by equation (14) and there in the enhancement factor  $E$  is equal to  $M^{1/2}$ . The reaction rate constant  $k_{1,n}$  in eq. (18) should depend on the amine concentration but, if the range of amine concentrations is not so wide,  $k_{1,n}$  may be regarded as constant. Plots of  $N_A / (C_{Ai} \sqrt{D_A})$  versus  $C_{B0}$  in Fig. 3 and Fig. 4 give a slope of 1/2, which means that the order  $n$  with the AMP is also 1.

Yih and Shen (1988), Sada et. al. (1996) and Hikita and Asai (1964) reported that the order of reaction with respect to  $CO_2$  and AMP in aqueous

solution was 1 and the order of overall reaction of  $CO_2$  with AMP was 2. Also, they concluded that these reactions occurred in the range of fast reaction regime.

## 5. Conclusions

The rate of carbon dioxide absorption into aqueous AMP solutions were measured using a semibatch stirred tank with a plane gas-liquid interface at 25°C. The absorption rates under the fast reaction regime were analysed by chemical absorption theory incorporating the reaction mechanism via a zwitterion. The reaction was found to be first order with respect to both  $CO_2$  and the amine.

## Nomenclature

- $C_A$  : concentration of  $CO_2$  in bulk body of liquid in a stirred vessel, [mol/ℓ]
- $C_{Ai}$  : solubility of  $CO_2$  in liquid, [mol/ℓ]
- $C_{B0}$  : initial concentration of AMP, [mol/ℓ]
- $C_B$  : concentration of reactant, [mol/ℓ]
- $D_A$  : diffusivity of  $CO_2$  in AMP aqueous solution, [cm<sup>2</sup>/s]
- $D_B$  : diffusivity of AMP in aqueous solution, [cm<sup>2</sup>/s]
- $D_{AW}$  : diffusivity of  $CO_2$  in water, [cm<sup>2</sup>/s]
- $E$  : enhancement factor defined by  $\sqrt{k_{11} D_A C_{B0}} / k_L$
- $E_i$  : enhancement factor in instantaneous reaction
- $H_A$  : Henry constant of  $CO_2$  in liquid, [atm · cm<sup>3</sup>/mol]
- $H_{AW}$  : Henry constant of  $CO_2$  in water, [atm · cm<sup>3</sup>/mol]

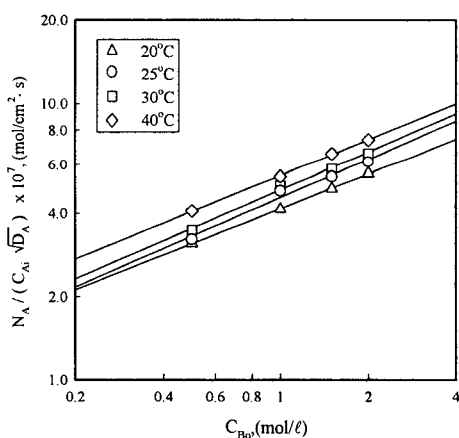


Fig. 3. Effect of AMP concentration on  $N_A / (C_{Ai} \sqrt{D_A})$  at different temperature.

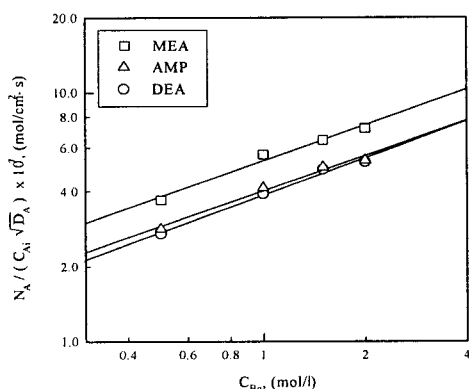


Fig. 4. Effect of amine concentration on  $N_A / (C_{Ai} \sqrt{D_A})$  at 150 rev/min., 25°C.

- $k_L$  : liquid-side mass transfer coefficient, [cm/s]  
 $k_{mn}$  : (m+n) order reaction rate constant, [cm<sup>3</sup>  
 (m+n-1)/mol<sup>(m+n-1)</sup> · s]  
 $M$  : function of the reaction diffusion modulus  
 $N_A$  : mass transfer rate of CO<sub>2</sub>, [mol/cm<sup>2</sup> · s]  
 $p_{Ai}$  : equilibrium partial pressure of CO<sub>2</sub>  
 equivalent to  $C_{Bo}$ , [atm]  
 $r$  : reaction rate of CO<sub>2</sub> with amine, [mol/cm<sup>3</sup> · s]  
 $T$  : temperature, [K]

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