

Kinetics of CO₂ Absorption in Aqueous AMP (2-amino-2-methyl-1-propanol) Solutions

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The reaction rate of CO₂ with 2-amino-2-methyl-1-propanol (AMP), MEA monoethanolamine (MEA) and diethanolamine (DEA) in aqueous solutions has been determined using a stirred vessel with a plane gas-liquid interface over a wide range of concentrations of amines at different temperatures. The results show that the overall reaction rate is first order with respect to both CO₂ and amine. The reaction rate constant varies with temperature according to the relationship which agrees with the experimental data. The proposed interpretation is that the kinetic rate determining step is a reaction of CO₂ with amine to form carbamic acid which is then totally and immediately ionized.

Key words: 2-amino-2-methyl-1-propanol (AMP), reaction rate constant, carbamic acid, stirred vessel

1. Introduction

Recently CO₂ has been given careful attention since it is believed to be one of the main greenhouse gases which cause global warming. Its accumulation in the atmosphere is growing rapidly. As a countermeasure to this environmental problem, research on the separation of CO₂ from industrial waste gases has been given primary importance. For this purpose several processes are already being used at the industrial scale or are still under development at the laboratory level for better separation efficiency.

So far, one of the conventional processes used for CO₂ separation is based on the chemical absorption method. The best performances of this method rely mainly on the development of solvents exhibiting high solubilities and absorption rate with regard to CO₂, together with easy regeneration capabilities. Among others commonly used solvents consist of alkanolamines such as

MEA (monoethanolamine), DEA (diethanolamine) and TEA (triethanolamine). In addition, recent development in the field of chemical absorbents for CO₂ separation have led to a new group of alkanolamines; termed sterically hindered amines.

These amines exhibit attractive advantages over conventional ones, since they provide high stoichiometric capacities and relatively high absorption rates comparable to those obtained with the commonly used primary or secondary alkanolamines at high CO₂ loadings (Satori, 1983).

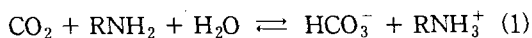
2-amino-2-methyl-1-propanol (AMP) is one of these sterically hindered amines. Although the kinetics of the reaction of AMP with CO₂ has been widely investigated (Chakraborty, 1986 ; Yih, 1988 ; Alper, 1990 ; Sharma, 1965 ; Caplow, 1968), both the reaction rate constants obtained and the parameters ($\sqrt{D_A}/H_A$) required for the analysis have been found to be subject to a large discrepancy (Xu, 1991). Then the absorption of CO₂ into aqueous solution of AMP was measured

at various temperatures and concentrations using a stirred tank absorber with a plane gas-liquid interface. The validity of the reaction rate constants is checked by simulation of CO₂ absorption into loaded AMP solutions, using the film model with reversible reaction.

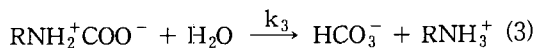
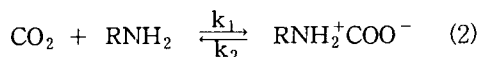
2. Materials and Methods

2.1. Theory

It has been reported (Chakraborty, 1986; Yih, 1988) that the overall reaction between CO₂ and AMP in aqueous solutions is



This reaction is believed to take place according to the zwitterion path (Sartori, 1983; Yih, 1988) as follows,



This zwitterion path is an extension of the zwitterion mechanism for carbamate formation first proposed by Caplow (1968). Yih and Shen postulated that the formation of the zwitterion is slow and hence the reaction rate can be expressed by

$$r = k_{11} [\text{CO}_2(\text{aq})][\text{RNH}_2] \quad (4)$$

By assuming the steady-state for the zwitterion, the reaction rate can be derived as

$$r = \frac{k_1 k_3}{k_2 + k_3} [\text{CO}_2(\text{aq})][\text{RNH}_2] \quad (5)$$

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

$$N_A = k_L C_{Ai} \frac{\sqrt{M} \left(\frac{\phi_\infty - \phi}{\phi_\infty - 1} \right)^{\frac{n}{2}}}{\tanh \left[\sqrt{M} \left(\frac{\phi_\infty - \phi}{\phi_\infty - 1} \right)^{\frac{n}{2}} \right]} \quad (6)$$

The relationship 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 ϕ due to the chemical reaction which is produced in the liquid phase and also of the mass transfer coefficient of the liquid film k_L by eq. (7)

$$\phi = \frac{N_A}{k_L C_{Ai}} \quad (7)$$

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

$$N_A = \left[\frac{2}{m+1} D_A k_{m,n} (C_{Ai})^{m+1} (C_{B0})^n \right]^{1/2} \quad (8)$$

D_A is the diffusivity of A in the liquid phase. C_{B0} is the concentration of reactant B participating in the chemical reaction. D_B is the diffusivity B, the region with a pseudo-order of (m,n) is characterized by eq. (8)

2.2. Experimental Apparatus and Procedures

A cylindrical glass vessel of inside diameter 6.51cm and a height of 11.86cm 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 the gas

phase and such a system enables a steady state operation. The volume of absorbent liquid in the vessel was 200cm² without soluble gases. The gas mixture were fed with a constant flow rate and composition adjusted by using the mass flow controller through the saturator contained water. The absorption temperature was controlled by water bath and the total system was operated in an air chamber with constant temperature. And flow rates of outlet were measured by a soap-bubble meter. The absorbent liquid was mixed by an 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 cm³/min, those of composition of CO₂ in feed gases of CO₂-N₂ 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, and absorption experiments were carried out at 25°C and atmospheric pressure.

3. Results and Discussion

Physical properties such as the liquid-phase diffusivity and solubility of CO₂ in aqueous solutions, reaction rate constant and mass transfer coefficients, which were used for analysis about the transport phenomena in this system, were obtained as followings.

Because the diffusivity and solubility of a gas in an aqueous phase were dependent of the ionic strength in the electrolyte aqueous solutions (Danckwerts, 1970), these values were obtained from the empirical equation suggested by Messaoudi and Sada (1996), which expressed a relationship between the combined parameter and concentration of AMP.

$$\log \left(\frac{\sqrt{D_{AW}}/H_{AW}}{\sqrt{D_A}/H_A} \right) = c C_{Bo}^d \quad (9)$$

Subscript w indicates water, C_{Bo}, initial concentration of AMP, and c and d, empirical constants. D_{AW} and 1/H_{AW} were obtained from the reference (Danckwerts, 1970; Hikita, 1976) as 1.97 × 10⁻⁵ cm²/s, 3.05 × 10⁻⁵ mol/atm · cm³, at 25 °C, respectively. The constants, c and d in eq. (9) were obtained as 0.11 and 0.36, respectively from reference (Messaoudi, 1996).

The reaction rate of CO₂ with AMP in the range of fast reaction region can be expressed (Doraiswamy, 1984).

$$N_A = C_{Ai} \sqrt{k_{11} D_A C_{Bo}} \quad (10)$$

The mass transfer rate of CO₂ into AMP aqueous solutions were obtained from the measured absorption rate of CO₂ with the same stirred vessel used in the study (Park, 1997) at speed of agitation, 200 rev/min. The results given in Table 1 were obtained by the property ($\sqrt{D_A}/H_A$) of CO₂ in aqueous AMP solutions with various temperatures. The influence of AMP concentration on the absorption rate was examined by plotting $N_A / (\sqrt{D_A}/H_A)$ versus $\sqrt{C_{Bo}}$ as shown in Fig. 1. The reaction rate constant (k₁₁) was evaluated to be 9.89 × 10⁴ cm³/mol · s obtained from the slope of the linear relationship between $N_A / (\sqrt{D_A}/H_A)$ and $\sqrt{C_{Bo}}$ at 25°C as shown in Fig. 2. The energy of activation deduced from Fig. 3 and this curve is:

$$E_a = 10.911 \times 10^3 \text{ cal/mol}$$

thus, the reaction rate of CO₂ with AMP is:

$$r = k_{11} [\text{CO}_2(\text{aq})][\text{RNH}_2]$$

with

$$\log k_{11} = - \frac{10.911 \times 10^3}{T(^{\circ}\text{K})} + 13.79$$

and to confirm to the fast reaction region, the requirement $\sqrt{k_{11} D_A C_{B_0}} / k_L^0 < C_{B_0} / C_{A_i}$ (Doraiswamy, 1984) must be fulfilled. This is satisfied when AMP concentration is greater than 0.5 mol/ℓ.

Table 1. Mass transfer rate of CO₂ in aqueous AMP solutions at various temperature and C_{B₀}.

Temp. (°C)	C _{B₀} (mol/ℓ)	N _A × 10 ⁷ (mol/cm ² ·s)	√D _A /H _A × 10 ⁷	√C _{B₀}	N _A / (√D _A /H _A)
20	0.5	6.236	1.2752	0.0224	4.890
	1.0	7.079	1.2059	0.0316	5.870
	1.5	9.091	1.1588	0.0387	7.845
	2.0	10.390	1.1223	0.0447	9.254
25	0.5	7.779	1.2752	0.0224	6.100
	1.0	10.250	1.2059	0.0316	8.501
	1.5	13.020	1.1588	0.0387	11.240
	2.0	14.590	1.1223	0.0447	13.001
30	0.5	10.510	1.2752	0.0224	8.240
	1.0	12.350	1.2059	0.0316	10.241
	1.5	13.910	1.1588	0.0387	12.002
	2.0	19.080	1.1223	0.0447	17.003
40	0.5	13.061	1.2752	0.0224	10.239
	1.0	15.680	1.2059	0.0316	13.001
	1.5	20.860	1.1588	0.0387	18.002
	2.0	21.830	1.1223	0.0447	19.448

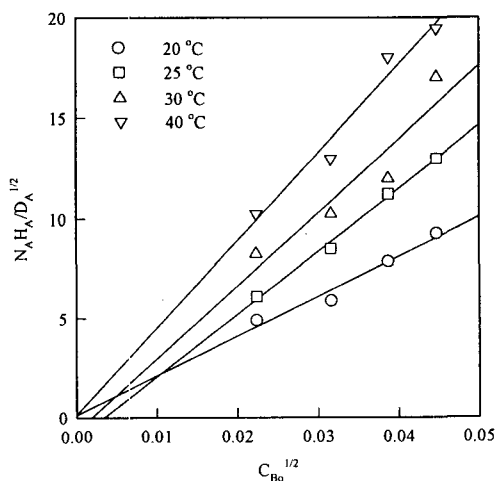


Fig. 1. Effect of AMP concentration on $N_A H_A / D_A^{1/2}$ at different temperatures.

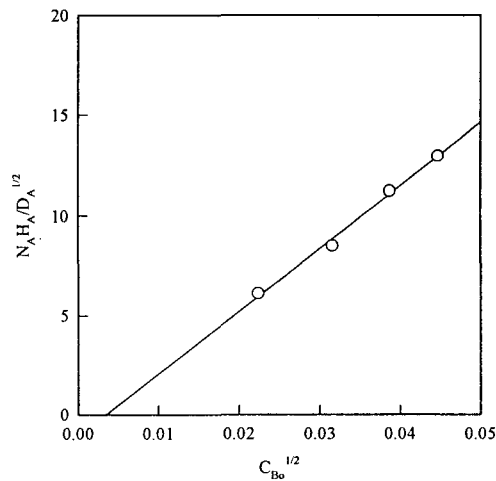


Fig. 2. Effect of AMP concentration on $N_A H_A / D_A^{1/2}$ at 25°C.

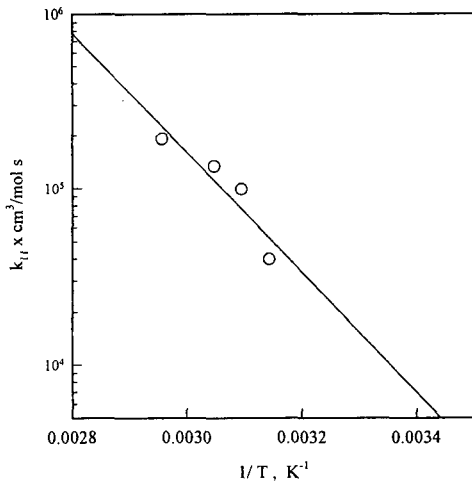


Fig. 3. Arrhenius plot for CO₂-AMP system.

4. Conclusion

The rate of carbon dioxide absorption into aqueous AMP solutions were measured using a semi-batch stirred tank with a plane gas-liquid interface at 25°C. The absorption rates under the fast reaction regime were analysed by the chemical absorption theory incorporating the reaction mechanism via a zwitterion. The reaction was found to be first order with respect to both CO₂ and the amine. The second-order forward rate constant had a value of $9.89 \times 10^4 \text{ cm}^3/\text{mol} \cdot \text{sec}$ within the amine concentration range 0.5~2.0 mol/ℓ at 25°C, 200rpm. the activation energy(E_a) is $10.911 \times 10^3 \text{ cal/mol}$.

Nomenclature

- C_{Ai} : solubility of CO₂ in liquid, [mol/ℓ]
 C_{B0} : initial concentration of AMP, [mol/ℓ]
 $[CO_2(aq)]$: concentration of CO₂ dissolved in amine solution, [mol/ℓ]
 D_A : diffusivity of CO₂ in AMP aqueous solution, [cm²/s]

- D_B : diffusivity of AMP in aqueous solution, [cm²/s]
 D_{AW} : diffusivity of CO₂ in water, [cm²/s]
 E : enhancement factor defined by $\sqrt{k_{11}D_A C_{B0}}/k_L^0$
 E_a : activation energy, [cal/mol]
 E_i : enhancement factor in instantaneous reaction
 H_A : Henry constant of CO₂ in liquid, [atm · cm³/mol]
 H_{Aw} : Henry constant of CO₂ in water, [atm · cm³/mol]
 k_L : liquid-side mass transfer coefficient, [cm/s]
 k_1 : forward reaction rate constant in eq. (2), [cm³/mol · s]
 k_2 : backward reaction rate constant in eq. (2), [cm³/mol · s]
 k_3 : forward reaction rate constant in eq. (3), [s⁻¹]
 k_{11} : second order reaction rate constant in eq. (5), [cm³/mol · s]
 k_{mn} : (m+n)th order reaction rate constant, [cm^{3(m+n-1)}/mol^(m+n-1) · s]
 M : function of the reaction diffusion modulus
 N_A : mass transfer rate of CO₂, [mol/cm² · s]
 $[RNH_2]$: concentration of amine, [mol/ℓ]

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