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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Online publication date: 22 June 2010

To cite this Article Park, Sang-Wook , Park, Dae-Won , Oh, Kwang-Joong and Kim, Seong-Soo(2009) 'Simultaneous Absorption of Carbon Dioxide and Sulfur Dioxide into Aqueous 2-Amino-2-Methy-1-Propanol', Separation Science and Technology, 44: 3, 543 — 568

To link to this Article: DOI: 10.1080/01496390802634190

URL: http://dx.doi.org/10.1080/01496390802634190

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Separation Science and Technology, 44: 543–568, 2009

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390802634190

Simultaneous Absorption of Carbon Dioxide and Sulfur Dioxide into Aqueous 2-Amino-2-Methy-1-Propanol

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Abstract: Carbon dioxide and sulfur dioxide were simultaneously absorbed into aqueous 2-amino-2-methyl-1-propanol (AMP) in a stirred semi-batch tank with a planar gas-liquid interface within a range of 0–4.0 kmol/m^3 of AMP, 0.03–0.3 mole fraction of CO_2, 0.005–2 mole fraction of SO_2, and 298–318 K. Absorption data of each gas in the CO_2-AMP and SO_2-AMP systems are obtained to verify their reaction regimes, based on film theory, respectively, which are used to analyze the simultaneous absorption mechanisms of CO_2 and SO_2 in the CO_2-SO_2-AMP systems. The measured absorption rates of CO_2 and SO_2 are compared to those formulated by an approximate solution of the mass balances with simultaneous reactions.

Keywords: 2-Amino-2-methyl-1-propanol, carbon dioxide, simultaneous absorption, sulfur dioxide

INTRODUCTION

Carbon dioxide (CO_2) and sulfur dioxide (SO_2) in the flue gas generated from combustion of fossil fuel are the main cause of global, environmental problems such as air pollution and acid rain. The contents of CO_2 and

Received 13 January 2008; accepted 15 July 2008.

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SO_2 in the flue gas are 0.12–0.15% and below about 0.1–0.4% by volume (1), respectively. However, the produced volume of flue gas is so large globally that considerable amounts of CO_2 and SO_2 are introduced into the atmosphere.

Many studies have been done on the mechanisms and kinetics of the reaction of CO_2 with various alkanolamines, employing simple mass balance analysis and resulting in the zwitterion mechanism proposed by Caplow (2) and Danckwerts (3). Some discrepancies remained according to the reaction mechanism (4), particularly the types of amines, gas/liquid contactor, and analysis method used for the rate data, for example, the order of the overall reactions and the rate constants. Recently, a group of sterically hindered amines were developed (5), providing a high capacity of 1.0 mol of CO_2/mol of amine and a relatively high absorption rate, even at high CO_2 loading. One such example was 2-amino-2-methyl-1-propanol (AMP), a sterically hindered form of monoethanolamine.

The absorption of SO_2 into aqueous slurries of sodium, calcium, and magnesium compounds, serving as the absorbent (6–13), and alkaline solutions, has been studied for decades. The medium used in the alkaline solutions was typically alkaline salts (14–18), inorganic acids (19), organic acids (20–23), and amines for reversible reaction (24–28). Danckwerts (29) showed that SO_2 absorption in an alkaline solution is proceeded by an instantaneous reaction while Hikita et al. (30) proposed a penetration theory model based on the two-reaction model using approximate analytical solutions to investigate the kinetics of SO_2 with reactants in the liquid phase.

Gas mixtures containing more than two gases such as NO/SO_2 (31) or NO_2/SO_2 (32) emitted from stationary combustion acilities, and H_2S and SO_2 (33,34) from natural, coal, and refinery gases, have been separated by the simultaneous absorption into aqueous slurries or alkaline solutions. Most of this work has been done towards determing the mechanisms and kinetics of the reaction in the simultaneous absorption, proposed by Goetter and Pigford (35) and Hikita et al. (36).

In this present work, the simultaneous absorption data are analyzed in terms of chemical absorption theory under the reaction regime in the simultaneous absorption of CO_2 and SO_2 into aqueous AMP. To predict the absorption rates of CO_2 and SO_2, the film theory equation with the simultaneous absorption of both the gases was formulated and compared to an approximate solution previously described (36). This study will make the first attempt for removal of both the gases emitted from power plant flues and from the viewpoint of energy-efficient separation, it will hopefully become the preferred treatment over that of conventional, individual separation.

THEORY

The zwitterions mechanism originally proposed by Caplow (2) and later reintroduced by Danckwerts (3) and da Silva and Svendsen (4) is generally accepted as the reaction mechanism in the absorption of CO_2 into aqueous AMP as follows:

$$CO_2 + RNH_2 = RN^+H_2COO^- \tag{i}$$

$$RN^+H_2COO^- + H_2O \longrightarrow RNH_3{}^+ + HCO_3^- \tag{ii}$$

Overall reaction being:

$$CO_2(A) + RNH_2(C) + H_2O \longrightarrow RNH_3{}^+ + HCO_3^- \tag{iii}$$

The reactions of SO_2 in aqueous AMP, combined with the SO_2 reaction in an aqueous, alkaline solution (14), are as follows:

$$SO_2 + H_2O = 2H^+ + SO_3{}^{2-} \tag{iv}$$

$$RNH_2 + H^+ \longrightarrow RNH_3{}^+ \tag{v}$$

Overall reaction being:

$$SO_2(B) + 2RNH_2(C) + H_2O \longrightarrow 2RNH_3{}^+ + SO_3{}^{2-} \tag{vi}$$

The irreversible reactions between the dissolved species j and the reactant (C), as shown in reactions (iii) and (vi), may be formulated as follows:

$$j + \nu_j C \rightarrow products \tag{vii}$$

where j is A or B, and ν_j is a stoichiometric coefficients of species j.

The following assumptions are made to set up the mass balance of species j:

1. Henry's law holds,
2. isothermal condition prevails, and
3. species C is a nonvolatile solute, and
4. reaction (viii) is mth order with respect to j and nth order with respect to C, of which the reaction rate (r_j) of species j is expressed by:

$$r_j = k_j C_j^m C_C^n \tag{viii}$$

For simultaneous absorption of both gases A and B into reactive C solution, such as absorption of CO_2 (A) and SO_2 (B) into aqueous AMP (C), the following assumptions are made to set up the mass balance of species j and C:

1. The presence of one gas does not affect the rate of absorption of the other gas because the gases do not compete for the common liquid-phase reactant C,
2. the reaction orders with respect to A and B are 1 and 1, respectively.

The mass balances of species j and C using the film theory accompanied by chemical reaction and the boundary conditions are given as follows:

$$D_j \frac{d^2 C_j}{dz^2} = k_j C_j C_C \tag{1}$$

$$D_C \frac{d^2 C_C}{dz^2} = \sum_{j=A}^{B} \nu_j k_j C_j C_C \tag{2}$$

$$z = 0; \quad C_j = C_{ji}; \quad \frac{dC_C}{dz} = 0 \tag{3}$$

$$z = \delta; \quad C_j = 0, \quad C_C = C_{Co} \tag{4}$$

The flux of species j at the interface of the gas-liquid phase is defined by

$$N_j = -D_j \left(\frac{dC_j}{dz} \right)_{z=0} \tag{5}$$

The enhancement factor (β) here is defined as the ratio of molar flux of Eq. (5) with the chemical reaction to that obtained without chemical reaction:

$$\beta_j = -\frac{N_j}{k_{Lj}} C_{ji} \bigg|_{Z=0} \tag{6}$$

The solution of Eq. (1) and (2) is used to obtain the value of β_j through Eq. (6).

The total absorption rate (N_S) for the simultaneous absorption of CO_2 and SO_2 is obtained using β_j and physical absorption rate of species

j (N_{jo}) as follows:

$$N_S = \sum_{j=A}^{B} \beta_j N_{jo} \tag{7}$$

If the reaction between CO_2 and AMP of Eq. (iii) is assumed to be a second-order reaction of finite rate and the reaction between SO_2 and AMP of Eq. (vi) to be an instantaneous reaction, the reaction of SO_2 and AMP occurs at a reaction plane (λ), where the concentration of both SO_2 and AMP are zero. CO_2 diffuses beyond the reaction plane and reacts with C in the region between the reaction plane and the bulk liquid.

The mass balance describing the diffusion of A, B, and C in the liquid film, based on film theory, is as follows:

$$0 < z < \lambda,$$

$$D_A \frac{d^2 C_A}{dz^2} = 0 \tag{8}$$

$$D_B \frac{d^2 C_B}{dz^2} = 0 \tag{9}$$

$$\lambda < z < \delta,$$

$$D_A \frac{d^2 C_A}{dz^2} = k_A C_A C_C \tag{10}$$

$$D_C \frac{d^2 C_C}{dz^2} = \nu_A k_A C_A C_C \tag{11}$$

The boundary conditions are:

$$z = 0 : C_A = C_{Ai}, \quad C_B = C_{Bi} \tag{12}$$

$$z = \lambda : C_A = C_A{}^*, \quad C_B = 0, \qquad C_c = 0 \tag{13}$$

$$-\nu_B D_B (dC_B/dz) = D_C (dC_C/dz) \tag{14}$$

$$z = \delta : C_A = 0, \quad C_c = C_{Co} \tag{15}$$

Eq. (10) and (11) are nonlinear and cannot be solved analytically.

However, Hikita et al. (36) have presented an approximate analytical solution with the enhancement factors (β_A and β_B) of species A and B absorbing two gases, one of which reacts instantaneously in the liquid phase, as follows:

$$\beta_A = \frac{[1 + r_B q_B + r_C q_C) - (1 + r_B q_B)\beta_A]\gamma\eta}{(1 + r_C q_C - \beta_A)\tanh(\gamma\eta)} \tag{16}$$

where,

$$\eta = \frac{1 + r_C q_C - \beta_A}{1 + r_B q_B + r_C q_C - \beta_A}\sqrt{\frac{1 + r_B q_B + r_C q_C - (1 + r_B q_B)\beta_A}{3 r_C q_C \beta_A}}$$

$$\beta_B = \frac{1 + r_B q_B + r_C q_C - \beta_A}{r_B q_B} \tag{17}$$

where,

$$r_B = \frac{D_B}{D_A}, r_C = \frac{D_C}{D_A}, q_B = \frac{\nu_B C_{Bi}}{\nu_A C_{Ai}}, q_C = \frac{C_{Co}}{\nu_A C_{Ai}}, \gamma = \frac{\sqrt{k_A C_{Co} D_A}}{k_L}$$

β_A and β_B are calculated from Eq. (16) and (17) by a trial and error procedure with given, dimensionless parameters such as r_B, r_C, q_B, q_C, and γ.

To verify the reaction between CO_2 and AMP to be first order with respect to both CO_2 and AMP, and the reaction between SO_2 and AMP to be instantaneous in CO_2-SO_2-AMP system, absorption mechanisms of each gas in CO_2-AMP and SO_2-AMP system are presented as follows:

Absorption of CO_2 Accompanied by Reaction with mth and nth Order in CO_2-AMP System

The mass balances of species A and C in CO_2-AMP system using the film theory accompanied by reaction (viii) and the boundary conditions are given as follows:

$$D_A \frac{d^2 C_A}{dz^2} = k_A C_A^m C_C^n \tag{18}$$

$$D_C \frac{d^2 C_C}{dz^2} = \nu_A k_A C_A^m C_C^n \tag{19}$$

$$z = 0; \quad C_A = C_{Ai}, \quad \frac{dC_C}{dz} = 0 \tag{20}$$

$$z = \delta; \quad C_A = 0, \quad C_C = C_{Co} \tag{21}$$

Depending on the relative rates of diffusion and reaction by using the dimensionless groups listed below, for convenience, the systems may be classified into four regimes: very slow reaction, slow reaction, fast reaction, and instantaneous reaction. The condition for validity of a fast pseudo-mth -order reaction with respect to species *j*, where the interfacial concentration of species C is the same as that in the bulk liquid phase, is given by the following expression (37):

$$3 < Ha << Ei \tag{22}$$

where

$$Ha = \frac{\sqrt{\frac{2}{m+1} D_j k_j C_{ji}^{m-1} C_{Co}^n}}{k_{LA}} \text{ and } Ei = 1 + \frac{C_{Co}}{\nu_j C_{ji}} \frac{D_C}{D_j} \tag{23}$$

Using the condition of Eq. (22), Eq. (18) can be written as:

$$D_A \frac{d^2 C_A}{dz^2} = k_A C_A^m C_{Co}^n = k_m C_A^m \tag{24}$$

where

$$k_m = k_A C_{Co}^n \tag{25}$$

Using the analytical solution of Eq. (24) with the boundary conditions of Eq. (20) and (21), N_A at the interface is:

$$N_A = C_{Ai} \sqrt{\frac{2}{m+1} D_A k_A C_{Ai}^{m-1} C_{Co}^n} \tag{26}$$

Where the resistance in the gas phase was not negligible and the expression for N_A for the pseudo-mth order reaction regime was derived as follows:

$$\frac{P_A}{N_A} = \frac{1}{k_G} + \frac{H_A}{\sqrt{\frac{2}{m+1} D_A k_A C_{Ai}^{m-1} C_{Co}^{n}}} \tag{27}$$

According to Eq. (27), Plots of P_A/N_A vs. $H_A/(D_A k_A C_{Co})^{0.5}$ at m = n = 1 should be a straight line with slope of 1.

Absorption of SO_2 Accompanied by Instantaneous Reaction in SO_2-AMP System

SO_2 absorption in an alkaline solution immediately precedes instantaneous hydration of SO_2 (14,29). The necessary conditions for particular reaction regime in SO_2-AMP system are as follows (37):

$$Ha \geq Ei \tag{28}$$

where the rate of diffusion of the dissolved species *j* through the region between the interface and the reaction plane (i.e., $0 < z < \lambda_B$) will be equal to the rate of diffusion of the reactive species C through the region between the reaction plane and the bulk liquid phase boundary (i.e., $\lambda_B < z < \delta_B$). A stoichiometric balance of fluxes at the reaction plane of λ_B gives the following equation:

$$\frac{D_B C_{Bi}}{\lambda_B} = \frac{D_C C_{Co}}{\nu_B(\delta_B - \lambda_B)} \tag{29}$$

The molar flux of species B (N_B) of Eq. (5) is

$$N_B = \frac{D_B C_{Bi}}{\lambda_B} = \frac{D_C C_{Co}}{\nu_B(\delta_B - \lambda_B)} \tag{30}$$

Eliminating λ_B from Eq. (29) and (30), N_B was derived as follows:

$$N_B = k_{LB} C_{Bi} \ (1 + \frac{C_{Co}}{\nu_B C_{Bi}} \frac{D_C}{D_B}) \tag{31}$$

Using *Ei* of Eq. (23), N_B of Eq. (31) was arranged as follows:

$$N_B = k_{LB} C_{Bi} Ei \tag{32}$$

where the resistance in the gas phase is not negligible and the expression for N_B for the instantaneous reaction regime was derived as follows:

$$\frac{P_B}{N_B} = \frac{1}{k_G} + \frac{H_B}{k_{LB}Ei} \tag{33}$$

Plots of P_B/N_B vs. $H_B/(k_{LB}Ei)$ should, according to Eq. (33), be a straight line with slope of 1.

EXPERIMENTAL

Chemicals

All chemicals were of regent grade, and used without further purification, Purity of CO_2, N_2, SO_2 were more than 99.9%.

Absorption Rate of CO_2 and SO_2

Absorption experiments were carried out in an agitated vessel (38,39). The absorption vessel was constructed of glass with an inside diameter of 0.073 m and a height of 0.151 m. Four, equally spaced vertical baffles, each one-tenth of the vessel diameter in width, were attached to the internal wall of the vessel. The gas and liquid phase were agitated with an agitator driven by a 1/4 Hp variable speed motor. A straight impeller 0.034 m in length and 0.05 m in width was used as the liquid phase agitator and located at the middle position of the liquid phase. The surface area was calculated as a ratio of the volume of added water to the measured height of water in the absorber, and its value was 40.947 cm^2. The gas and liquid in the vessel were agitated at a speed of 50 rpm. The value of the cumulative volume of the soup bubble was measured by a soup bubbler for the change of absorption time to obtain the absorption rate of CO_2 and SO_2. Each experiment was duplicated at least once under identical conditions. It was assumed that the volumetric rising rate of the soup bubble in the soup bubbler attached to the absorption vessel was equal to the value of absorption rate of gases. The gaseous compositions of CO_2 and SO_2 at inlet of the absorber were using gas chromatography (column: PTFE, 6 feet × 1/8 inch OD, Chromosorb 107, 80/100; Detector: TCD). The absorption experiments were carried out in a range of 0–4.0 $kmol/m^3$ of AMP, 0.03–0.3 mole fraction of CO_2, 0.005–0.2 of SO_2, and 298–318 K at atmospheric pressure, as previously reported.

A sketch of the experimental set up is presented in Fig. 1. A typical experimental run was carried out as follows:

The vent valve A is initially closed and the purge value B is open, gas is flowed continuously through the absorber D, so as to make sure that the latter is filled with gas at the start of the experiment. During this initial period, the water bath temperature is brought up to the desired value, and the liquid batch is kept in bottle F inside the water bath. At the start of the experiment, the liquid batch is poured into funnel G and the agitator E in D is started. The liquid feed valve C is closed, the purge value B is closed, and the vent valve A is opened, as simultaneously as possible. Measurements are started at the soap film meter H taking care that there are always two soap films in the meter so that a continuous reading of the cumulative volume of gas which has flowed through the soap film meter (V) can be recorded as a function of time. The gas absorption rate was obtained as a slope of the plots of V vs. time at an initial time. The mass transfer coefficient (k_L) was calculated by the following equation with the initial volumetric absorption rates of CO_2, $V(t_1)/t_1$, obtained from the cumulative volume of gas which has flowed through the soap film meter.

$$k_L = \frac{P_T - P_B^o}{SC_{Ai}RT}\frac{V(t_1)}{t_1} \tag{34}$$

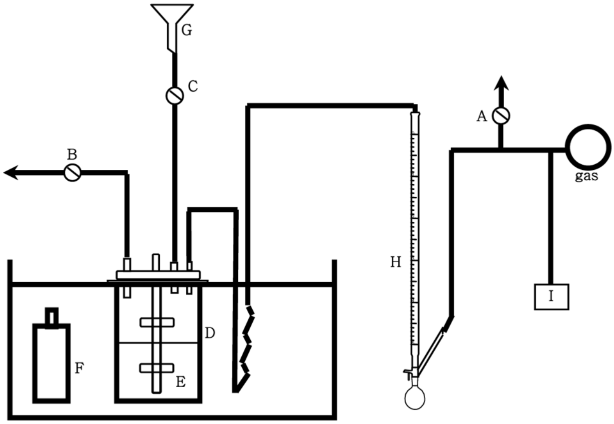

Figure 1. Schematic diagram of the agitated vessel.

where P_T is the atmospheric pressure, P_B^o, the vapor pressure of water, S, the surface area of liquid phase, C_{Ai}, the solubility of gas in benzene solution, $V(t_1)$, the cumulative volume of gas during the absorption time, t_1.

Physicochemical Properties

Both the solubility and diffusivity of solute gases in the liquid medium, which affect the derived reaction rate parameters, as seen in Eq. (1), (2), (16), and (17), are obtained using an approximate method of the nitrous oxide analogy (39–41) as follows:

The Henry constants of N_2O and CO_2 in water are obtained from the empirical equations (40):

$$H^o_{N_2O} = 8.547 \times 10^6 \exp\left(-\frac{2284}{T}\right) \tag{35}$$

$$H^o_A = 2.8249 \times 10^6 \exp\left(-\frac{2044}{T}\right) \tag{36}$$

The Henry constant of N_2O in aqueous AMP solution was estimated (41):

$$H_{N_2O} = (5.52 + 0.7C_{Co}) \times 10^6 \exp\left(-\frac{2166}{T}\right) \tag{37}$$

The Henry constant of CO_2 in aqueous AMP solution was estimated by the N_2O analogy as follows:

$$H_A = H^o_A \frac{H_{N_2O}}{H^O_{N_2O}} \tag{38}$$

The solubility (C_{Ai}) of CO_2 of a given partial pressure of CO_2 in aqueous solution of a given concentration of AMP was estimated as follows:

$$P_A = H_A C_{Ai} \tag{39}$$

The diffusivities of N_2O and CO_2 in water are obtained from the empirical equations (40):

$$D^o_{N_2O} = 5.07 \times 10^{-6} \exp\left(-\frac{2371}{T}\right) \tag{40}$$

$$D_A^o = 2.35 \times 10^{-6} \exp\left(-\frac{2119}{T}\right) \tag{41}$$

Saha et al. (41) have reported that experimental diffusivity data of N_2O in aqueous AMP solution did not follow Stokes-Einstein relation ($D\mu/T = \text{constant}$) along with an empirical formula as follows:

$$\frac{D_{N_2O}\mu^{0.82}}{T} = 2.12 \times 10^{-14} \tag{42}$$

The diffusivity of CO_2 in aqueous AMP solution was estimated by the N_2O analogy:

$$D_A = D_A^o \frac{D_{N_2O}}{N_{N_2O}^o} \tag{43}$$

The Henry constant of SO_2 in water was estimated by the empirical formula (42):

$$H_B^o = 101.3/\exp\left(\frac{510}{T_o} - 26970T_1 + 155T_2 - 0.0175T_oT_3/R\right) \tag{44}$$

where, $T_o = 298.15$, $T_1 = 1/T_o - 1/T$. $T_3 = T_o/T - 1 + \ln(T/T_o)$, $T_3 = T/T_o - T_o/T - 2\ln(T/T_o)$

The diffusivity of SO_2 in water was estimated by the empirical formula (42):

$$D_B^o = 5.08982 \times 10^{-12} T \exp\left(5.15581 - \frac{1243.06}{T - 53.19}\right) \tag{45}$$

If it is assumed that the behavior of SO_2 is applied to the N_2O analogy, the Henry constant and diffusivity of SO_2 in aqueous AMP solution are estimated as follows:

$$H_B = H_B^o \frac{H_{N_2O}}{H_{N_2O}^o} \tag{46}$$

$$D_B = D_B^o \frac{D_{N_2O}}{N_{N_2O}^o} \tag{47}$$

D_C was estimated by the method of Wilke (29).

Viscosity of aqueous AMP solution was measured using Brookfield viscometer (Brookfield Eng. Lab. Inc, USA).

The liquid-side mass transfer coefficient (k_{LA} and k_{LB}) of CO_2 and SO_2 in water are obtained using the absorption rate of pure CO_2 and SO_2 at 25°C and 50 rpm, respectively.

RESULTS AND DISCUSSION

Absorption of CO_2 in CO_2-AMP System

To determine the reaction order with respect to CO_2 and AMP in CO_2-AMP system, the absorption rates ($N_{A,\text{exp}}$) of CO_2 were measured with a range of 0–4.0 kmol/m^3 of AMP, 0.03–0.12 mole fraction of CO_2, and 298–318 K.

To determine the reaction order with respect to CO_2, logarithmic plots of $N_{A,\text{exp}}$ vs. C_{Ai} at a typical C_{Co} of 1 kmol/m^3 are shown in Fig. 2.

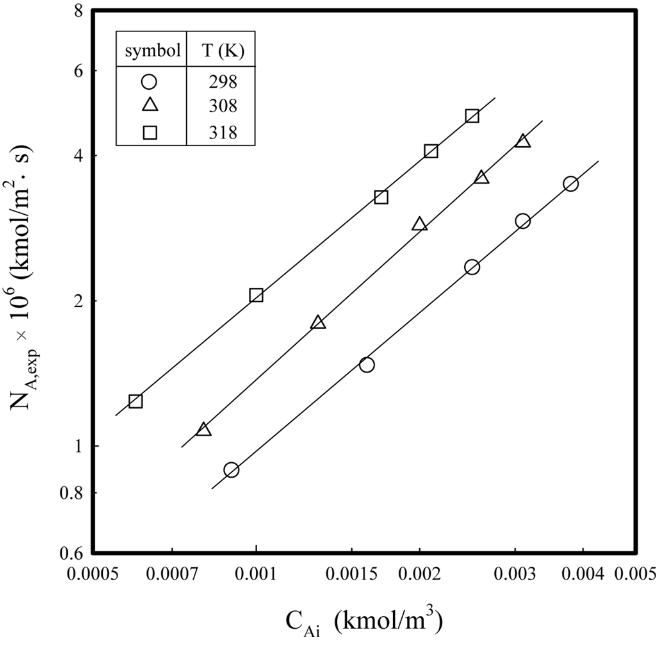

Figure 2. Effect of C_{Ai} on N_A into aqueous AMP at $C_{Co} = 1.0$ kmol/m^3 and different temperatures.

The plots present straight lines (correlation coefficient >0.999) with a slope of unity in each temperature. This, according to Eq. (26), indicates that the reaction order with respect to CO_2 is 1.

To determine the reaction order with respect to the concentration of AMP, logarithmic plots of $(N_{A,\text{exp}}/C_{Ai}D_A{}^{0.5})$ vs. C_{Co} at a typical y_A of 0.3 are shown in Fig. 3.

Each of these plots as shown in Fig. 3 is a straight line (correlation coefficient >0.999) with a slope of 1. This, according to Eq. (26), indicates that the reaction order with respect to AMP is 1.

The values of the reaction rate constant were calculated from the intercept of the plots of data in Fig. 2. The second order rate constant has been found to be 451.66, 782.33, 1323.07 m^3/kmolôñs at 298, 308, 318 K, respectively. Figure 4 shows the Arrhenius plots of the values of the reaction rate constant of CO_2-AMP at different temperatures using data mentioned above.

Linear regression analysis of the Arrhenius plots gives the following expression for k_A (correlation coefficient = 0.998).

$$k_A = 1.2 \times 10^{10}\text{Exp}(-5096.4/T) \tag{48}$$

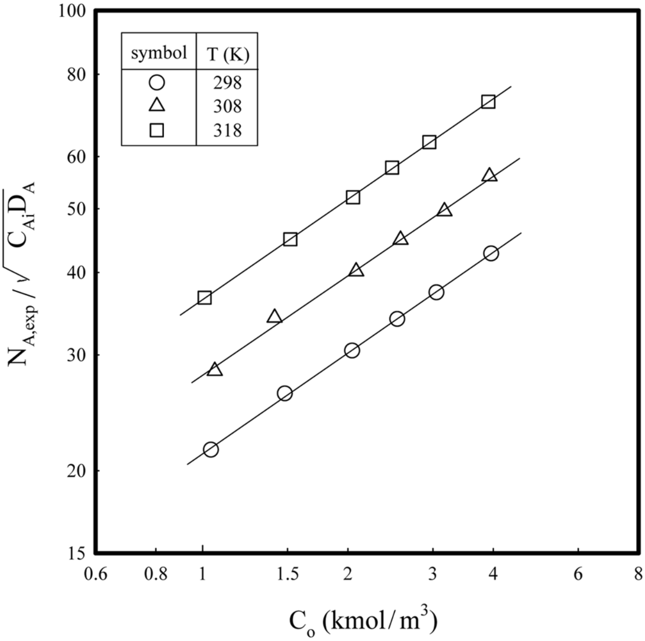

Figure 3. Determination of reaction rate constant (k_A) and order with respect to AMP at $y_A = 0.3$ and different temperatures.

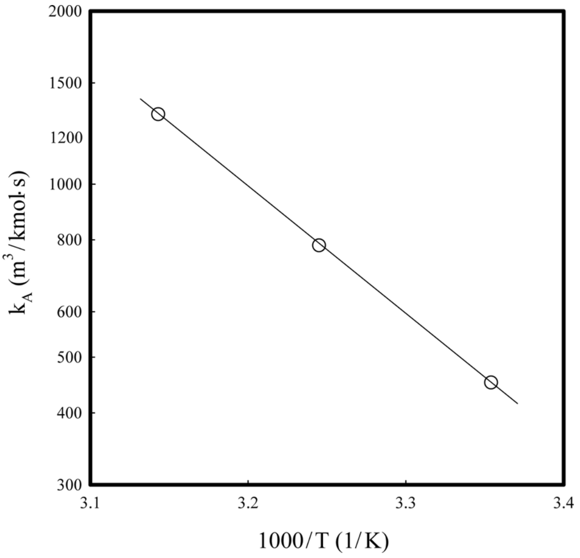

Figure 4. Arrhenius plot of the CO_2-AMP system.

The corresponding value of the activation energy has been calculated to be 42.4 kJ/mol.

The reaction rate constants determined previously are listed in Table 1, indicating the reaction rate constants in this study to be in the same range.

To validate the condition of a fast pseudo-first-order reaction with respect to CO_2, the values of Ha and Ei were calculated and listed in Table 2. Because the values of Ha and Ei in Table 2 satisfy Eq. (22), the absorption of CO_2 into AMP solution in this study belongs to a fast reaction regime.

To ensure that the gas phase resistance is really negligible in all run, plots of $P_A/N_{A,\text{exp}}$ vs. $H_A/(k_A D_A C_{Co})^{0.5}$ at different temperatures have been made following Eq. (27) for m = 1, n = 1. The corresponding values of H_A and D_A have been estimated using Eq. (38) and (43). These plots are presented in Fig. 5.

It can be seen from Fig. 5 that all plots of $P_A/N_{A,\text{exp}}$ vs. $H_A/(k_A D_A C_{Co})^{0.5}$ are straight lines with slope of 1, passing through the origin. This, according to Eq. (27), signifies negligible gas phase resistance.

The specific rate ($N_{A,\text{fem}}$) of CO_2 absorption was estimated by Eq. (5) using the concentration profile of A, which was obtained from the solution of Eq. (18) and (19) with the boundary conditions of Eq. (20) and

Table 1. Second-order reaction rate constants for CO_2 in aqueous AMP

Investigators	Contactor	C_{Co} (kmol/m^3)	k_A (m^3/kmol · s)
This Study	Agitated vessel	1.0–4.0	452 (25°C), 782 (35°C), 1323 (45°C)
Saha et al. (41)	Westted-wall column	0.5–2.0	437 (21°C), 681 (28.5°C), 1183 (38.5°C), 1631 (45°C)
Yih and Shem (43)	Wetted-wall column	0.258–3.0	1270 (40°C)
Messaoudi and Sada (44)	Liquid-jet	0.5–2.0	190 (20°C), 369 (30°C), 740 (40°C)
Xiao et al. (45)	Wetted-wall column	1.5–1.7	1259 (30°C), 1430 (35°C), 1629 (40°C)
Mandal et al. (46)	Wetted-wall column	2.8–3.3	1400 40°C)

(21), using the numerical method of FEMLAB program. The comparison of observed and estimated molar flux of CO_2 in AMP concentration range of 1.0–4.0 kmol/m^3, 0.03–3.0 mole fraction of CO_2, and 298–313 K is shown in Fig. 6.

As shown in Fig. 6, the observed values of the molar flux agree with the estimated values (correlation coefficient = 0.9948), suggesting that the governing equation of Eq. (18) and (19), as well as the estimated physical properties such as C_{Ai}, D_A, and D_C, may be plausible.

Absorption of SO_2 in SO_2-AMP System

To confirm the instantaneous reaction regime of SO_2 absorption in SO_2-AMP system, the absorption rates ($N_{B,\mathrm{exp}}$) of SO_2 are measured in the range of 0–3.0 kmol/m^3 of AMP, 0.005–0.2 mole fraction of SO_2, and 298–318 K.

The molar flux ($N_{B,\mathrm{cal}}$) of SO_2 under the instantaneous reaction regime was calculated using Eq. (32) and plotted in Fig. 7 with the measured values of $N_{B,\mathrm{exp}}$. As shown in Fig. 7, the observed values of the molar flux agree with the estimated values (correlation coefficient = 0.981).

From the results in Fig. 7, the SO_2-AMP reaction was instantaneous.

Table 2. The values of Ha and Ei in CO_2/AMP system

T(K)	C_{Co} (kmol/m^3)	y_A	Ha	E_i	T(K)	C_{Co} (kmol/m^3)	y_A	Ha	E_i	T(K)	C_{Co} (kmol/m^3)	y_A	Ha	E_i
298	1.0	0.03	100	407	298	2.0	0.03	98	891	298	3.0	0.03	113	1471
		0.05	91	244			0.05	92	535			0.05	110	883
		0.08	63	153			0.08	88	335			0.08	109	552
		0.10	62	123			0.10	87	268			0.10	107	442
		0.12	61	102			0.12	85	224			0.12	104	369
308	1.0	0.03	64	495	308	2.0	0.03	89	1098	308	3.0	0.03	129	1814
		0.05	58	297			0.05	83	659			0.05	116	1089
		0.08	55	186			0.08	77	412			0.08	96	681
		0.10	52	149			0.10	73	330			0.10	90	545
		0.12	50	124			0.12	70	275			0.12	86	454
318	1.0	0.03	52	603	318	2.0	0.03	69	1337	318	3.0	0.03	157	2201
		0.05	49	362			0.05	64	803			0.05	119	1321
		0.08	47	227			0.08	59	502			0.08	100	826
		0.10	40	182			0.10	55	402			0.10	66	661
		0.12	39	152			0.12	53	335			0.12	63	551
298	1.0	0.3	61	62	308	1.0	0.3	49	53	318	0.3	1.0	38	61
	1.5		72	63		1.5		57	73			1.5	47	97
	2.0		85	92		2.0		69	116			2.0	55	138
	2.5		95	119		2.5		77	149			2.5	61	173
	3.0		104	150		3.0		86	195			3.0	66	216
	4.0		119	211		4.0		95	257			4.0	77	311

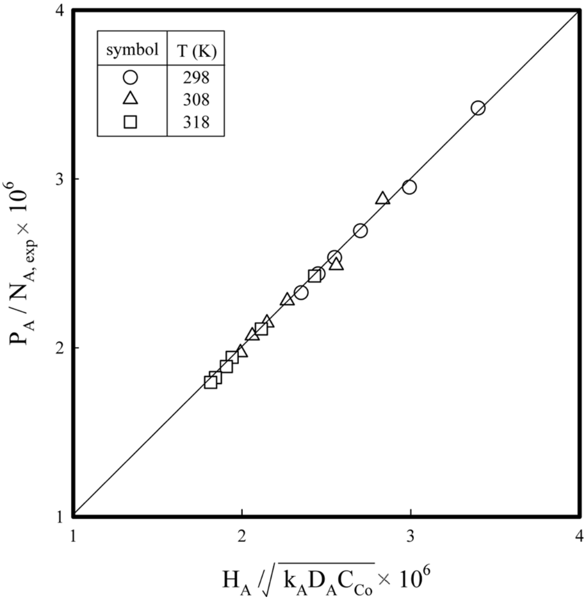

Figure 5. Verification of no gas phase resistance for absorption of CO_2 into aqueous AMP at $y_A = 0.3$ and different C_{CO} and temperatures.

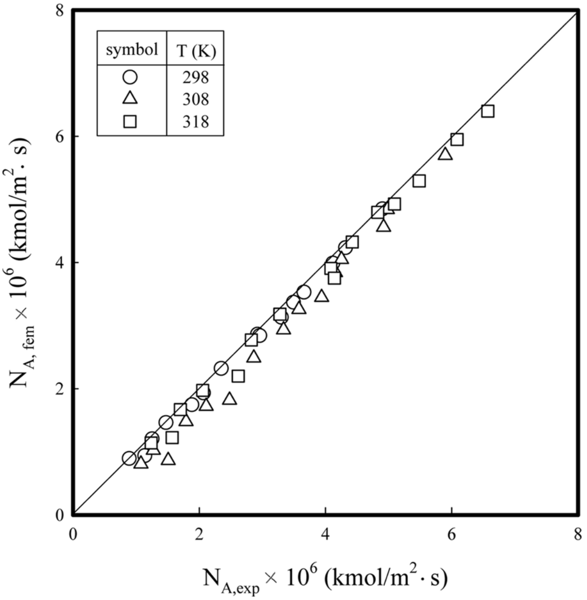

Figure 6. Comparison of estimated and measured values of absorption rate of CO_2.

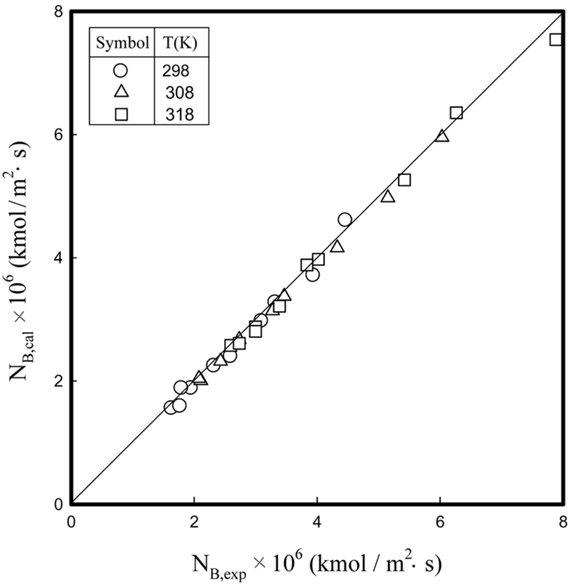

Figure 7. Comparison of estimated and measured values of absorption rate of SO_2.

To ensure that the gas phase resistance was really negligible in all run, plots of $P_B/N_{B,\text{exp}}$ vs. $H_B/(k_{LB}Ei)$ at different temperatures have been made following Eq. (33). The corresponding values of H_B and D_B have been estimated using Eq. (46) and (47), and the mass transfer coefficients in AMP solution were calculated from relationship between the mass transfer coefficient in water and diffusivity ratio in reference as following [47]:

$$k_L = k_{Lw}(D_j/D_{jw})^{2/3} \tag{49}$$

It can be seen from Fig. 8 that all plots of $P_B/N_{B,\text{exp}}$ vs. $H_B/(k_{LB}\ Ei)$ are straight lines with slope of 1 and passing through the origin. This, according to Eq. (33), signifies negligible gas phase resistance in the instantaneous reaction regime.

Simultaneous Absorption of CO_2 and SO_2 in CO_2-SO_2-AMP System

Mixtures gases of CO_2 and SO_2 are simultaneously absorbed into aqueous AMP solution within a range of 1.0–3.0 kmol/m^3 of AMP,

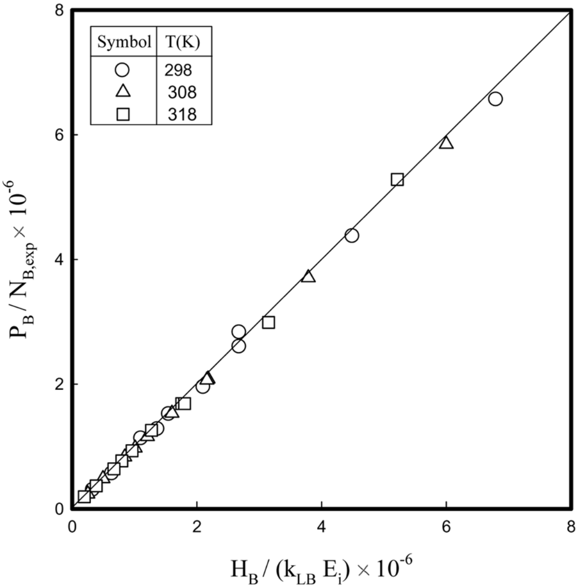

Figure 8. Verification of no gas phase resistance for absorption of SO_2 into aqueous AMP at $y_B = 0.05$ and different C_{CO} and temperatures.

0.1–0.3 mole fraction of CO_2, 0.01–0.2 mole fraction of SO_2, and 298–318 K to obtain the simultaneous absorption rate (N_S).

To observe the effect of y_A on N_S, the experimental absorption rate ($N_{S,\mathrm{exp}}$) was plotted against y_A at a typical y_B of 0.01 in Fig. 9.

As shown in Fig. 9, $N_{S,\mathrm{exp}}$ increases with increasing y_A and C_{Co}, due to increase in concentrations of the reactant, CO_2 and AMP. The solid lines present the calculated N_S, estimated by Eq. (7) through β_A and β_B of Eq. (16) and (17), where k_A was used as in CO_2-AMP system.

To observe the effect of y_B on N_S, $N_{S,\mathrm{exp}}$ was plotted against y_B at a typical y_A of 0.1 in Fig. 10.

As shown in Fig. 10, $N_{S,\mathrm{exp}}$ increases with increasing C_{Co}, with a minimum range of $y_B = 0.05$ and higher. At fixed values of y_A and C_{Co} using the corresponding values of the physical properties, the calculated values of β_A and β_B decrease and C_{Bi} increase with increasing y_B. Because the molar flux of species j (N_j) is β_j C_{ji} k_{Lj} and increase in y_B increases C_{Bi} more effectively than a decrease in β_B, the molar flux of SO_2 (N_B) increases under conditions shown in Fig. 11. This increase of N_B and decrease of N_A give a minimum value of $N_{S,\mathrm{exp}}$.

To observe the effect of C_{Co} on N_S, $N_{S2,exp}$ was plotted against C_{Co} at typical y_A of 0.1 and y_B of 0.01 in Fig. 11.

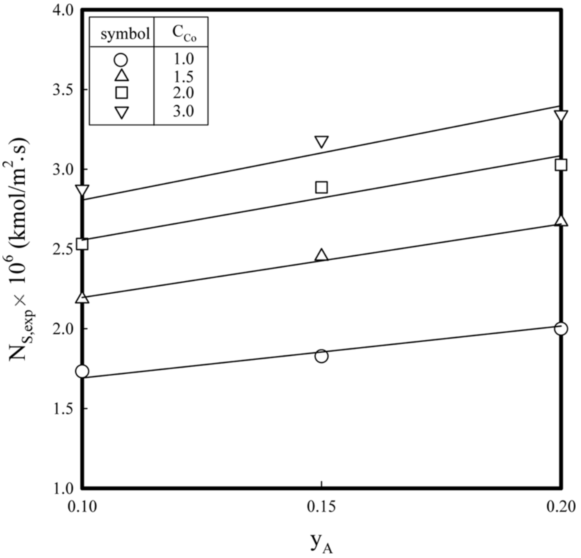

Figure 9. Effect of y_A on N_S into aqueous AMP at $y_B = 0.01$ and different C_{Co} and 298 K.

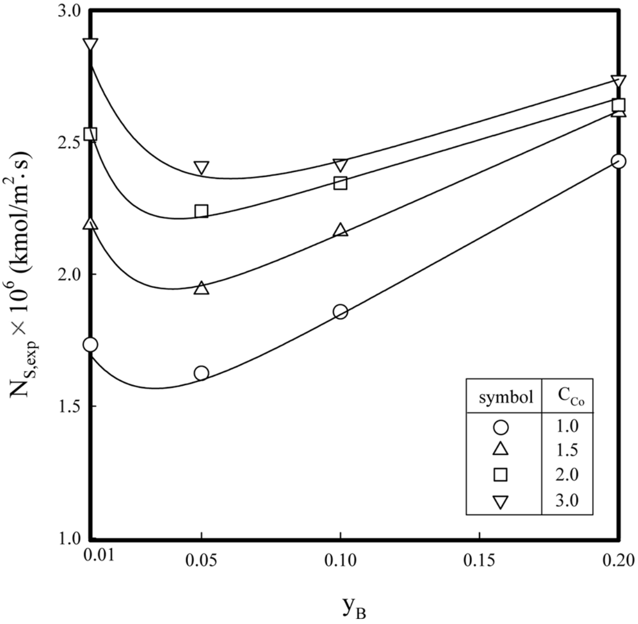

Figure 10. Effect of y_B on N_S into aqueous AMP at $y_A = 0.1$ and different C_{Co} and 298 K.

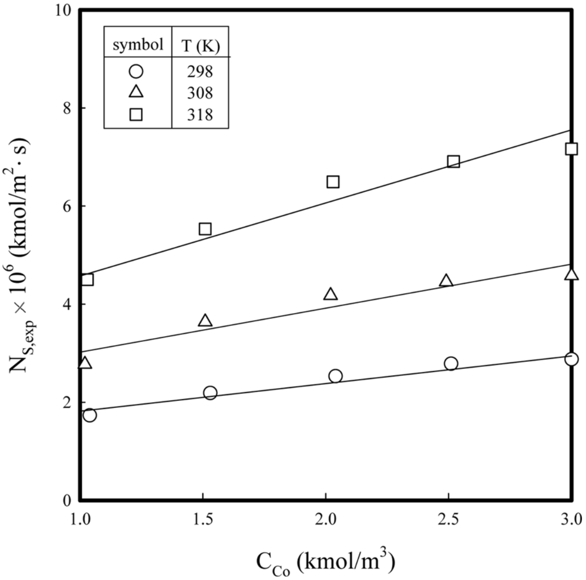

Figure 11. Effect of C_{Co} on N_S into aqueous AMP at $y_A = 0.1$ and $y_B = 0.01$ at different temperatures.

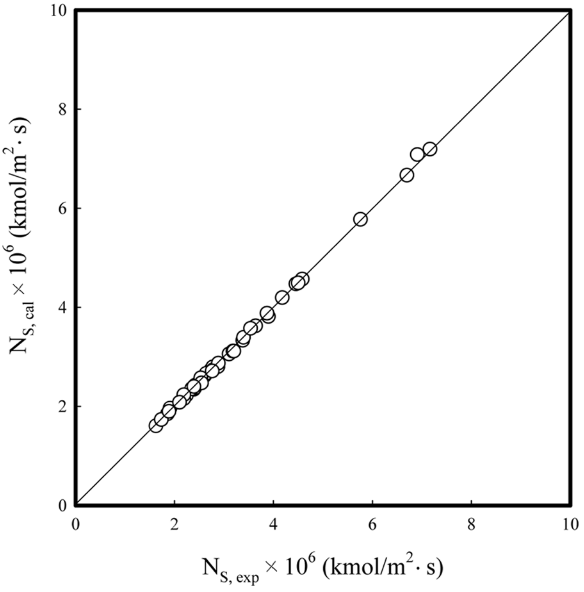

Figure 12. Comparison of calculated and measured values of simultaneous absorption rate of CO_2 and SO_2.

As shown in Fig. 11, N_S increases with increasing C_{Co} and temperature.

The simultaneous molar flux ($N_{S,\mathrm{cal}}$) of CO_2 and SO_2 was obtained using Eq. (7) with β_A and β_B by Eq. (16) and (17), As shown in Fig. 12, the observed values of the molar flux agree with the calculated values (correlation coefficient = 0.989).

CONCLUSIONS

Mixture of CO_2 and SO_2 are simultaneously absorbed into AMP in a stirred, semi-batch tank with a planar, gas-liquid interface within a range of 0–4.0 kmol/m^3 of AMP, 0.03–0.3 mole fraction of CO_2, 0.005–0.2 mole fraction of SO_2, and 298–318 K. Diffusivity and Henry constants of CO_2 and SO_2 were obtained from the reference data measured by N_2O analogy.

Absorption data of each gas in CO_2-AMP and SO_2-AMP systems are used to verify that the reaction between CO_2 and AMP is first order with respect to both CO_2 and AMP, and the reaction between SO_2 and AMP is instantaneous. The measured rates of simultaneous absorption of CO_2 and SO_2 were compared with those calculated by approximate solutions of mass balances with reaction regimes of both gases through verification of the reaction regime in CO_2-SO_2-AMP system.

ACKNOWLEDGMENTS

This work was supported by Brain Korea 21 Project and a grant (2006-C-CD-11-P-03-0-000-2007) from the Energy Technology R&D of Korea Energy Management Corporation. Dae-Won Park is also thankful for KOSEF (R01-2007-000-10183-0).

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