

## Simultaneous absorption of carbon dioxide, sulfur dioxide, and nitrogen dioxide into aqueous 1, 8-diamino-p-menthane

Kwang-Joong Oh\*, Byoung-Moo Min\*\*, Seong-Soo Kim\*\*\*, and Sang-Wook Park\*\*\*\*†

\*School of Civil and Environmental Engineering, Pusan National University, Busan 609-735, Korea

\*\*Greenhouse Gas Research Center, Korea Institute of Energy Research, Daejeon 305-343, Korea

\*\*\*Department of Environmental Administration, Catholic University of Pusan, Busan 609-757, Korea

\*\*\*\*School of Chemical and Biomolecular Engineering, Pusan National University, Busan 609-735, Korea

(Received 5 January 2011 • accepted 30 January 2011)

**Abstract**—3 Gaseous mixtures of CO<sub>2</sub>, SO<sub>2</sub>, and NO<sub>2</sub> were simultaneously absorbed into 1, 8-diamino-p-menthane (DAM) in a stirred, semi-batch tank with a planar, gas-liquid interface within a range of 0-2.0 kmol/m<sup>3</sup> of DAM, 0.05-0.3 atm of CO<sub>2</sub>, 0.0025-0.04 atm of SO<sub>2</sub>, and 298.15-323.15 K at a fixed NO<sub>2</sub> of 0.001 atm to measure their total molar fluxes. Diffusivity and Henry constants of CO<sub>2</sub>, SO<sub>2</sub>, and NO<sub>2</sub> were obtained using the reference data, measured by N<sub>2</sub>O analogy. The mass transfer coefficient of each gas, needed to obtain the absorption rate without a chemical reaction, was modified with viscosity of aqueous DAM solution. In CO<sub>2</sub>-SO<sub>2</sub>-NO<sub>2</sub>-DAM system accompanied by first-order reaction with respect to CO<sub>2</sub> and instantaneous reactions with respect to SO<sub>2</sub> and NO<sub>2</sub>, the enhancement factors of CO<sub>2</sub> and SO<sub>2</sub> were obtained by using an approximate solution of mass balances consisting of reaction regimes of two gases, one of which reacts instantaneously, and then, the enhancement factor of NO<sub>2</sub> by comparing the instantaneous rates of SO<sub>2</sub> and NO<sub>2</sub>. The observed values of the molar flux approached to the calculated values very well.

Key words: Simultaneous Absorption, Carbon Dioxide, Sulfur Dioxide, Nitrogen Dioxide, 1,8-Diamino-p-menthane

### INTRODUCTION

Carbon dioxide (CO<sub>2</sub>; 15-20%), sulfur dioxide (SO<sub>2</sub>; 0.1-0.4%), and nitrogen dioxide (NO<sub>2</sub>; 0.001%) 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 [1]. Simultaneous absorption of these gaseous mixtures into one solvent may become the preferred treatment over that of conventional individual separation using different solvents in the viewpoint of energy-efficient separation.

Many studies have been done on the mechanisms and kinetics of the reaction of CO<sub>2</sub> with various alkanolamines, employing simple mass balance analysis and resulting in the zwitterion mechanism proposed by Caplow [2] and Danckwerts [3]. Obtaining the order of the overall reactions and the rate constants, some discrepancies [4] remain according to the reaction mechanism through the types of amines, gas/liquid contactor, and analysis method of the experimental absorption data. Recently, a group of sterically hindered amines were developed [5], providing a high capacity of 1.0 mol of CO<sub>2</sub>/mol of amine and a relatively high absorption rate, even at high CO<sub>2</sub> loading. The absorption of SO<sub>2</sub> [6,7] into aqueous slurries of sodium, calcium and magnesium compounds, serving as the absorbent, and alkaline solutions, has been studied for decades. The medium used in the alkaline solutions was typically alkaline salts [8], inorganic acids [9], organic acids [10], and amines for reversible reaction [11, 12]. Danckwerts [13] showed that SO<sub>2</sub> in an alkaline solution was absorbed by an instantaneous reaction. The reaction mechanism

between NO<sub>2</sub> and alkaline solvent has been reported as an instantaneous reaction [14-18] in the absorption of NO<sub>2</sub> into aqueous alkaline solution.

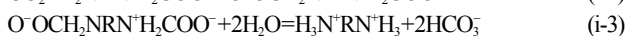
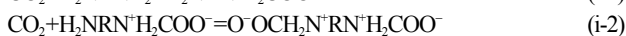
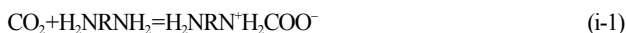
Most of the work mentioned above has been done towards determining the absorption mechanism and reaction kinetics in the individual absorption of one kind of gas [1]. Gas mixtures containing two gases such as NO and SO<sub>2</sub> [19] or NO<sub>2</sub> and SO<sub>2</sub> [20] emitted from stationary combustion facilities, and H<sub>2</sub>S and SO<sub>2</sub> [21] from natural, coal, and refinery gases, have been separated by simultaneous absorption into aqueous slurries or alkaline solutions. CO<sub>2</sub> and SO<sub>2</sub> were simultaneously separated using 2-amino-methyl-1-propanol (AMP) [22] and 1,8-diamino-p-menthane (DAM) [23] containing two amino functional groups as an absorbent of acid gas with a larger capacity than AMP, and CO<sub>2</sub> and NO<sub>2</sub> [24] using AMP. Absorption kinetics in these articles have been found to be a first-order reaction with respect to CO<sub>2</sub> in alkaline system and an instantaneous reaction with respect to both SO<sub>2</sub> and NO<sub>2</sub>. Goetter and Pigford [25] and Hikita et al. [26] presented theoretically the simultaneous absorption kinetics of two gases in an alkaline system. On the other hand, gas mixtures containing three gases of CO<sub>2</sub>, SO<sub>2</sub>, and NO<sub>2</sub> were separated using AMP [27] and AMP blended with ammonia [28]. To our knowledge, no literature report about absorption containing three gases of CO<sub>2</sub>, SO<sub>2</sub>, and NO<sub>2</sub> has yet been published except the articles mentioned above.

In this work, DAM was used as an absorbent to absorb and predict the simultaneous absorption rates of CO<sub>2</sub>, SO<sub>2</sub>, and NO<sub>2</sub>, which was one of a series of studies containing the previous works [22-24,27]. This study will make a new attempt for removal of the gases emitted from power plant flues for the effective capture and utilization of carbon dioxide.

†To whom correspondence should be addressed.  
E-mail: swpark@pusan.ac.kr

## THEORY

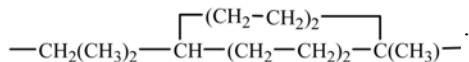
The zwitterion mechanism originally proposed by Caplow (2) and later reintroduced by Danckwerts (3) is generally accepted as the reaction mechanism in the absorption of  $\text{CO}_2$  into aqueous alkaline, such as DAM, as follows:



with the overall reaction being:



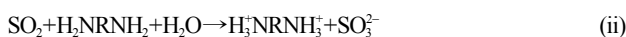
where R presents



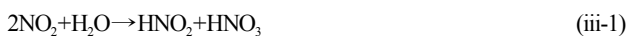
The reactions [25] of  $\text{SO}_2$  in aqueous alkaline are as follows:



with the overall reaction being:



Reactions [15-19] of  $\text{NO}_2$  in aqueous alkaline are as follows:



with the overall reaction being:



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



where  $j$  presents  $\text{CO}_2$ ,  $\text{SO}_2$ , and  $\text{NO}_2$ , and are simplified as  $A_1$ ,  $A_2$ , and  $A_3$ , respectively. C is DAM and  $\eta_j$  a stoichiometric coefficients of species  $j$ ;  $\nu_{A1}$  is 0.5,  $\nu_{A2}$ , 1,  $\nu_{A3}$ , 1, respectively [27].

The following assumptions [27] are made to set up the mass balance of species  $j$ :

1) Henry's law holds, 2) the isothermal condition prevails, 3) species C is a nonvolatile solute, 4) the presence of one gas does not affect the rate of absorption of another gas because the gases do not compete for the common liquid-phase reactant C, and 5) reaction (iv) is a first-order with respect to  $j$  and a first order with respect to C, of which the reaction rate ( $r_j$ ) of species,  $j$  is expressed by:

$$r_j = k_j C_j C_C \quad (\text{v})$$

For simultaneous absorption of the gases,  $j$  into reactive C solution, the mass balances using the film theory accompanied by the chemical reaction and the boundary conditions are given as follows:

$$D_j \frac{d^2 C_j}{dz^2} = k_j C_j C_C \quad (\text{1})$$

$$D_C \frac{d^2 C_C}{dz^2} = \sum_{j=A_1}^{A_3} \nu_j k_j C_j C_C \quad (\text{2})$$

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

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

The enhancement factor ( $\beta_j$ ) of species,  $j$ , defined as the ratio of molar flux with the chemical reaction to that obtained without the chemical reaction, is as follows:

$$\beta_j = - \left. \frac{d(C_j/C_{ji})}{d(z/\delta)} \right|_{z=0} \quad (\text{5})$$

$\beta_j$  can be obtained from the simultaneous solution of the differential equations of Eq. (1) and (2) through Eq. (5).

The individual and total absorption rates ( $N_j$  and  $N_S$ ) of species,  $j$  are obtained as follows, respectively:

$$N_j = \beta_j k_{Lj} C_{ji} \quad (\text{6})$$

$$N_S = \sum_{j=A_1}^{A_3} \beta_j k_{Lj} C_{ji} \quad (\text{7})$$

The regime of  $\text{CO}_2$  in alkaline system has been classified into a first-order fast reaction with respect to  $\text{CO}_2$ , and  $\text{SO}_2$  and  $\text{NO}_2$  into instantaneous reactions [22-24,27]. Because the reaction rate constant of  $\text{CO}_2$  has a finite value, but those values of  $\text{SO}_2$  and  $\text{NO}_2$  cannot be measurable, the governing equations of Eq. (1) and (2) cannot be used to obtain the enhancement factors of these gases. Therefore, the enhancement factors of  $\text{CO}_2$  and  $\text{SO}_2$  were obtained by using an approximate solution of mass balances consisting of reaction regimes of two gases, one of which reacts instantaneously, and then, the enhancement factor of  $\text{NO}_2$  by comparing the instantaneous rates of  $\text{SO}_2$  and  $\text{NO}_2$  as follows [27];

$$\beta_{A1} = \frac{[(1+r_B q_B + r_C q_C) - (1+r_B q_B) \beta_{A1}] \gamma \eta}{(1+r_C q_C - \beta_{A1}) \tanh(\gamma \eta)} \quad (\text{8})$$

$$\text{where, } \eta = \frac{1+r_C q_C - \beta_{A1}}{1+r_B q_B + r_C q_C - \beta_{A1}} \sqrt{\frac{1+r_B q_B + r_C q_C - (1+r_B q_B) \beta_{A1}}{3 r_C q_C \beta_{A1}}}$$

$$\beta_{A2} = \frac{1+r_B q_B + r_C q_C - \beta_{A1}}{r_B q_B} \quad (\text{9})$$

where,  $r_B = D_{A2}/D_{A1}$ ,  $r_C = D_C/D_{A1}$ ,  $q_B = \nu_{A2} C_{A2}/\nu_{A1} C_{A1}$ ,  $q_C = C_C/\nu_{A1} C_{A1}$ ,  $\gamma = \sqrt{k_{A1} C_{Co} D_{A1}/k_L}$ , and species  $A_1$  ( $\text{CO}_2$ ) is a gas with a fast reaction and  $A_2$  ( $\text{SO}_2$ ) with instantaneous reaction.  $\beta_{A1}$  and  $\beta_{A2}$  are calculated by a trial and error procedure of Eqs. (8) and (9) with given dimensionless parameters, such as  $r_B$ ,  $r_C$ ,  $q_B$ ,  $q_C$ , and  $\gamma$ .

On the other hand, the each enhancement factor ( $\beta_{A2}$  and  $\beta_{A3}$ ) of  $A_2$  and  $A_3$  ( $\text{NO}_2$ ) in the regime of instantaneous reaction is given as follows, respectively [28]:

$$\beta_{A2} = 1 + \frac{C_{Co}}{C_{A2i}} \frac{D_C}{\nu_{A2} D_{A2}} \equiv \frac{C_{Co}}{C_{A2i}} \frac{D_C}{\nu_{A2} D_{A2}} \quad (\text{10})$$

$$\beta_{A3} = 1 + \frac{C_{Co}}{C_{A3i}} \frac{D_C}{\nu_{A3} D_{A3}} \equiv \frac{C_{Co}}{C_{A3i}} \frac{D_C}{\nu_{A3} D_{A3}} \quad (\text{11})$$

Comparing the instantaneous rates of  $\text{SO}_2$  and  $\text{NO}_2$  with Eq. (10) and (11),  $\beta_{A3}$  is given as follows:

$$\beta_{A3} = \beta_{A2} \frac{C_{A2i} \nu_{A2} D_{A2}}{C_{A3i} \nu_{A3} D_{A3}} \quad (\text{12})$$

$\beta_{A1}$  and  $\beta_{A2}$  are obtained by using Eqs. (8) and (9) with a regime of fast and instantaneous reaction, and then,  $\beta_{A3}$  is obtained by using Eq. (12).

## EXPERIMENTAL

### 1. Chemicals

All chemicals were of reagent grade, and used without further purification. Distilled water was used and DAM was of reagent grade (Aldrich Chem. Co., more than 99%). Purity of  $N_2$ ,  $CO_2$ , and  $SO_2$  was more than 99.9%. A stock gaseous mixture (Rigas Standard Gas Co.) containing  $N_2$  was used as a source of  $NO_2$  with a 0.1%.

### 2. Simultaneous Absorption Rate of $CO_2$ , $SO_2$ , and $NO_2$

Absorption experiments were performed in an agitated vessel [27, 30]. The glass absorption vessel had 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 phases 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  $cm^2$ . To obtain the interfacial area of the liquid, a flat surface was used, and then, the agitation speed was fixed at 50 rpm. The value of the cumulative volume of the soap bubble was measured by a soap bubbler for the change of absorption time to obtain the absorption rate of  $CO_2$ ,  $SO_2$ , and  $NO_2$ . Each experiment was duplicated at least once under identical conditions. It was assumed that the volumetric rising rate of the soap bubble in the soap bubbler attached to the absorption vessel was equal to the value of the absorption rate of gases. The gaseous compositions of  $CO_2$ ,  $SO_2$  and  $NO_2$  at the inlet of the absorber were measured with a gas chromatograph (column A for  $CO_2$  and  $SO_2$ : PTFE, 6 feet x 1/8 inch OD, Chromosorb 107, 80/100; column B for  $NO_2$ : SS, 30 ft x 1/8 in OD, Gas Chrom MP-1, 100/120; Detector: TCD at 100 °C; He: 18  $cm^3/min$ ; retention time of  $CO_2$ : 6.13 min,  $NO_2$ : 7.73 min,  $SO_2$ ,

9.56 min). The absorption experiments were carried out in a range of 0–2.0  $kmol/m^3$  of DAM, 0.05–0.3 atm of  $CO_2$ , 0.005–0.04 atm of  $SO_2$ , and a fixed  $NO_2$  of 0.001 atm at 298–323 K and 1 atm to measure the simultaneous molar flux of  $CO_2$ ,  $SO_2$  and  $NO_2$ .

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

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

$$k_{fjw} = \frac{P_T - P_w^0}{SC_{ji}RT t_1} V \quad (13)$$

where  $P_T$  is the atmospheric pressure,  $P_w^0$  the vapor pressure of water, S the surface area of liquid phase,  $C_{ji}$  the solubility of j gas in water, and V( $t_1$ ) the cumulative volume of gas during the absorption time,  $t_1$ .

### 3. Physicochemical Properties

Both the solubility and diffusivity of the solute gases in the liquid medium, which affect the derived reaction rate parameters, as seen in Eq. (8), (9), and (12), are obtained by using an approximate method of the nitrous oxide analogy as follows.

The Henry constants of  $N_2O$  and  $CO_2$  in water are obtained from the following empirical equations [31]:

$$H_{N_2O}^0 = 8.547 \times 10^6 \exp\left(-\frac{2284}{T}\right) \quad (14)$$

$$H_{A1}^0 = 2.8249 \times 10^6 \exp\left(-\frac{2044}{T}\right) \quad (15)$$

The Henry constant of  $N_2O$  in aqueous DAM solution was estimated accordingly [32]:

$$H_{N_2O} = (5.52 + 0.7C_{Co}) \times 10^6 \exp\left(-\frac{2166}{T}\right) \quad (16)$$

The Henry constant of  $SO_2$  in water was estimated by the empirical formula [33]:

$$H_{A2}^0 = 101.3 / \exp\left(\frac{510}{T_0} - 26970T_1 + 155T_2 - 0.0175T_0T_3/R\right) \quad (17)$$

where,  $T_0 = 298.15$ ,  $T_1 = 1/T_0 - 1/T$ ,  $T_3 = T_0/T - 1 + \ln(T/T_0)$ ,  $T_2 = T/T_0 - T_0/T - 2\ln(T/T_0)$

The Henry constants of  $CO_2$  and  $SO_2$  in aqueous DAM solution

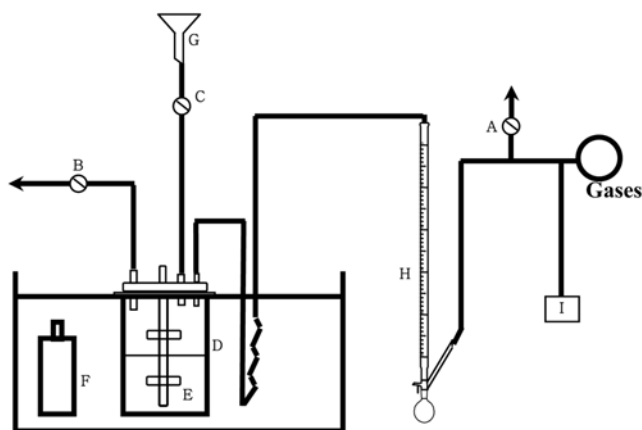


Fig. 1. Schematic diagram of the agitated vessel.

- |                  |                       |
|------------------|-----------------------|
| A, B, C. Valve   | G. Funnel             |
| D. Absorber      | H. Soap film meter    |
| E. Impeller      | I. Gas chromatography |
| F. Sample bottle |                       |

were estimated by the N<sub>2</sub>O analogy as follows:

$$H_j = H_j^0 \frac{H_{N_2O}}{H_{N_2O}^0} \quad (18)$$

The Henry constant ( $H_{A3}$ ) of NO<sub>2</sub> in water was estimated by inter- and extrapolation using 1.044 atm·m<sup>3</sup>/kmol at 25 °C and 2.844 atm·m<sup>3</sup>/kmol at 40 °C [16].

The solubility ( $C_{ji}$ ) of species,  $j$  at a partial pressure ( $P_j$ ) was estimated as follows:

$$P_j = H_j C_{ji} \quad (19)$$

where  $j$  presents CO<sub>2</sub>, SO<sub>2</sub>, and NO<sub>2</sub>, respectively.

The diffusivities of N<sub>2</sub>O and CO<sub>2</sub> in water were obtained from the following empirical equations [31]:

$$D_{N_2O}^0 = 5.07 \times 10^{-6} \exp\left(-\frac{2371}{T}\right) \quad (20)$$

$$D_{A1}^0 = 2.35 \times 10^{-6} \exp\left(-\frac{2119}{T}\right) \quad (21)$$

Saha et al. [32] have reported that experimental diffusivity data of N<sub>2</sub>O in aqueous DAM solution did not follow the Stokes-Einstein relation ( $D\mu/T = \text{constant}$ ) along with an empirical formula as follows:

$$\frac{D_{N_2O} \mu^{0.82}}{T} = 2.12 \times 10^{-14} \quad (22)$$

The diffusivity of SO<sub>2</sub> in water was estimated by the empirical formula [33]:

$$D_{A2}^0 = 5.08982 \times 10^{-12} T \exp\left(5.15581 - \frac{1243.06}{T - 53.19}\right) \quad (23)$$

The diffusivities of CO<sub>2</sub> and SO<sub>2</sub> in aqueous DAM solution were estimated using the N<sub>2</sub>O analogy:

$$D_j = D_j^0 \frac{D_{N_2O}}{D_{N_2O}^0} \quad (24)$$

The diffusivity ( $D_{A3}^0$ ) of NO<sub>2</sub> in water at 25 °C was taken as  $1.40 \times 10^{-9}$  m<sup>2</sup>/s [34]. Diffusivity ( $D_{A3}$ ) of NO<sub>2</sub> in aqueous DAM solution was estimated from the following equation corrected [35] with viscosity of the aqueous DAM solution:

$$D_{A3} = D_{A3}^0 \left(\frac{\mu_w}{\mu}\right)^{2/3} \quad (25)$$

The diffusivity ( $D_c$ ) of AMP in DAM solution was estimated by the method of Wilke [13].

Viscosity of the aqueous DAM solution was measured with a Brookfield viscometer (Brookfield Eng. Lab. Inc, USA).

The mass transfer coefficients ( $k_{Lj}$ ) of species,  $j$  in DAM solution were calculated from the relationship between the mass transfer coefficient in water and diffusivity ratio in reference as follows [36]:

$$k_{Lj} = k_{Ljw} (D_j/D_{jw})^{2/3} \quad (26)$$

The mass transfer coefficient ( $k_{Ljw}$ ) of species,  $j$  in water was measured by using the absorption rates of pure CO<sub>2</sub>, SO<sub>2</sub> and NO<sub>2</sub> at vari-

ous temperatures and 50 rpm, respectively.

The reaction rate constant ( $k_{A1}$ ) between CO<sub>2</sub> and DAM was obtained from the following equation [22]:

$$k_{A1} = 1.72 \times 10^{12} \exp(-5747/T) \quad (27)$$

## RESULTS AND DISCUSSION

If  $\beta_j$  is dependent on the various variables of physicochemical properties such  $k_{A1}$ ,  $C_{jB}$ ,  $D_j$ , and  $k_{Lj}$  as shown in Eq. (8) and (9), it may be reasonable and convenient to use dimensionless parameters such as  $r_{A1}$ ,  $r_{B1}$ ,  $q_{A1}$ ,  $q_{B1}$  and  $\gamma$  to observe the effect of the variables on  $\beta_j$  [13].

SO<sub>2</sub> was selected as a gas of an instantaneous reaction between SO<sub>2</sub> and NO<sub>2</sub> to be applied to Eq. (8) and (9) based on absorption of two gases, because one of them can be obtained from Eq. (12).  $\beta_{A1}$  and  $\beta_{A2}$  are estimated using Eq. (8) and (9) at a given value of  $\gamma$  with the parameters of  $r_{B1}q_{B1}$  and  $r_{C1}q_{C1}$  and plotted in Fig. 2.

As shown in Fig. 2,  $\beta_{A1}$  increases and  $\beta_{A2}$  decreases with increasing  $\gamma$  at a given  $r_{B1}q_{B1}$  and  $r_{C1}q_{C1}$ .  $\beta_{A1}$  increases with increasing  $k_{A1}$ ,  $C_{CO_2}$  or decreasing  $k_L$ . Because  $\beta_{A1}$  and  $\beta_{A2}$  inversely change each other at given  $r_{B1}q_{B1}$  and  $r_{C1}q_{C1}$  in Eq. (9),  $\beta_{A2}$  decreased with increasing  $\beta_{A1}$ . At a given  $r_{C1}q_{C1}$  of 20 and  $\gamma$ ,  $\beta_{A1}$  and  $\beta_{A2}$  decrease with increasing  $r_{B1}q_{B1}$  from 1 to 2. Decrease of  $\beta_{A1}$  means that  $\beta_{A1}$  is smaller when more SO<sub>2</sub> is present, because more DAM is then available for reaction with SO<sub>2</sub> due to the instantaneous reaction of SO<sub>2</sub> with DAM.  $\beta_{A2}$  should increase with decreasing  $\beta_{A1}$ . This result may be due to the fact that the value of  $r_{B1}q_{B1}$  increases on a large scale than increase of  $\beta_{A1}$  in Eq. (9).

At a given  $r_{B1}q_{B1}$  of 2 and  $\gamma$ ,  $\beta_{A1}$  and  $\beta_{A2}$  increase with increasing  $r_{C1}q_{C1}$  from 20 to 40.  $\beta_{A2}$  should decrease with increasing  $\beta_{A1}$ . This result may be because the value of  $r_{C1}q_{C1}$  increases on a larger scale than the increase of  $\beta_{A1}$  in Eq. (9).  $\beta_{A3}$  has a similar behavior to  $\beta_{A2}$  from the relationship between  $\beta_{A2}$  and  $\beta_{A3}$  in Eq. (12).

Simultaneous molar fluxes ( $N_{S,exp}$ ) of three gaseous mixtures were

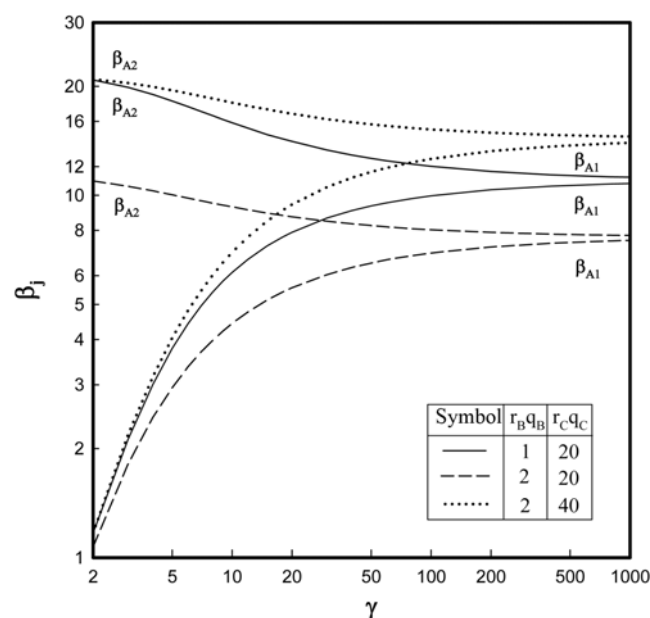


Fig. 2. Effect of  $\gamma$  on  $\beta_{A1}$  and  $\beta_{A2}$  with parameters of  $r_{B1}q_{B1}$  and  $r_{C1}q_{C1}$ .

measured within a range of 0-2.0 kmol/m<sup>3</sup> of DAM, 0.05-0.3 atm of CO<sub>2</sub>, 0.0025-0.04 atm of SO<sub>2</sub>, and 298.15-323.15 K at a fixed NO<sub>2</sub> of 0.001 atm to observe the effects on the experimental variables such as  $P_{A1}$ ,  $P_{A2}$ ,  $C_{Co}$ , and temperature.

To observe the effect of  $P_{A1}$  on  $N_s$ ,  $\beta_{A1}$  and  $\beta_{A2}$  were estimated by using Eq. (8) and (9), and  $\beta_{A3}$  by Eq. (12) at a given value of the physicochemical properties based on the typical experimental conditions of  $C_{Co}=2$  kmol/m<sup>3</sup>,  $P_{A2}=0.01$  atm,  $P_{A3}=0.001$  atm, and  $T=313.15$  K. The obtained  $\beta_j$  was plotted vs.  $P_{A1}$  within a range of 0.05-0.3 atm of CO<sub>2</sub> in Fig. 3.

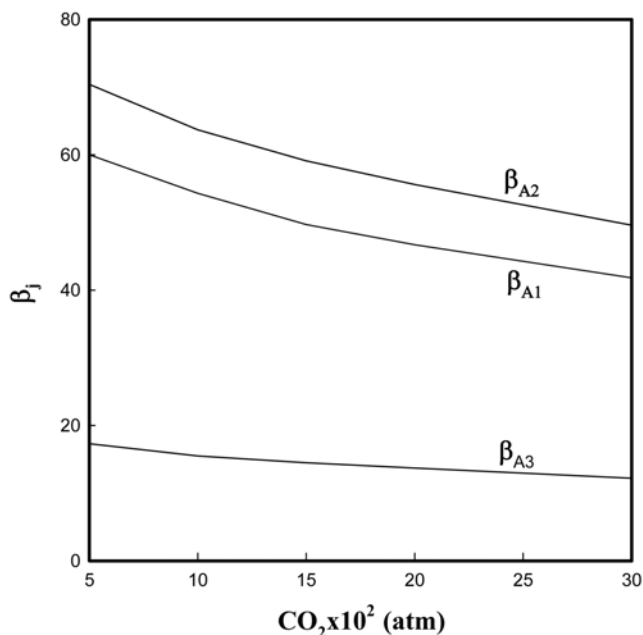


Fig. 3.  $\beta_j$  vs.  $y_{A1}$  at  $C_{Co}=2.0$  kmol/m<sup>3</sup>,  $P_{A2}=0.01$  atm,  $P_{A3}=0.001$  atm, and  $T=313.15$  K.

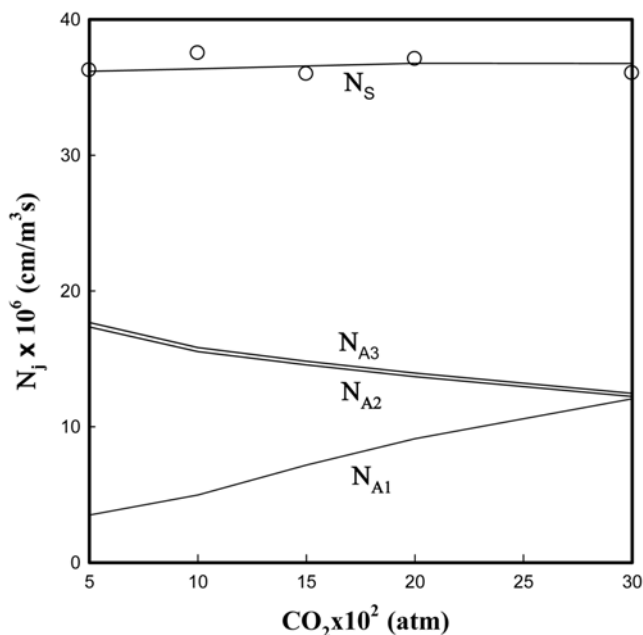


Fig. 4.  $N_j$  vs.  $y_{A1}$  at  $C_{Co}=2.0$  kmol/m<sup>3</sup>,  $P_{A2}=0.01$  atm,  $P_{A3}=0.001$  atm, and  $T=313.15$  K.

As shown in Fig. 3,  $\beta_j$  decreases with increasing  $y_{A1}$ . Because  $r_B q_B$  and  $r_C q_C$  decrease simultaneously with increasing  $C_{A1}$  by increase of  $P_{A1}$ , as shown in Fig. 2,  $\beta_{A1}$  decreases with increasing  $P_{A1}$ . Decrease of  $\beta_{A2}$  may be because  $r_B q_B$  and  $r_C q_C$  increase on a larger scale than the decrease of  $\beta_{A1}$  in Eq. (9).

$N_{s,exp}$  were plotted vs.  $P_{A1}$  as a symbol of circle in Fig. 4.  $N_{j,cal}$  were calculated by Eq. (6) using  $C_{jB}$ ,  $k_{Lj}$ , and  $\beta_j$  in Fig. 3 to present in Fig. 4 as solid lines.

As shown in Fig. 4,  $N_{A1}$  increases and  $N_{A2}$  and  $N_{A3}$  decrease with increasing  $P_{A1}$ . Increase of  $N_{A1}$  is due to increasing the solubility of CO<sub>2</sub>. Decrease of  $N_{A2}$  is due to decrease of DAM, which can react with SO<sub>2</sub>.

$N_{s,exp}$  were plotted vs.  $y_{A2}$  within a range of 0.025-0.04 atm of SO<sub>2</sub> as a symbol of circle in Fig. 5 under the typical conditions of  $C_{Co}=2.0$  kmol/m<sup>3</sup>,  $P_{A1}=0.15$  atm,  $P_{A3}=0.001$  atm, and  $T=313.15$  K.  $N_{j,cal}$  were presented in Fig. 5 as solid lines.

As shown in Fig. 5,  $N_{A1}$  decreases and  $N_{A2}$  and  $N_{A3}$  increase with increasing  $P_{A2}$ . Increase of  $N_{A2}$  is due to increase of solubility of SO<sub>2</sub> and that the reaction rate of SO<sub>2</sub> is faster than that of CO<sub>2</sub>.

From the results of Fig. 3, 4, and 5, the molar flux of each species is mainly dependent on its solubility, as shown in Eq. (8), (9), and (12).

To observe the effect of  $C_{Co}$  on  $N_s$ ,  $N_{s,exp}$  were plotted vs.  $C_{Co}$  within a range of 0-2.0 kmol/m<sup>3</sup> of DAM as a symbol of circle in Fig. 6 under the typical conditions of  $P_{A1}=0.3$  atm,  $P_{A2}=0.01$  atm,  $P_{A3}=0.001$  atm, and  $T=313.15$  K.

As shown in Fig. 6,  $N_j$  increase with increasing  $C_{Co}$ . Increase of  $N_j$  is due to increasing the reactant of DAM.

To observe the effect of temperature on  $N_s$ ,  $N_{s,exp}$  were plotted vs. temperature within a range of 298.15-323.15 K as a circle symbol in Fig. 7 under the typical conditions of  $C_{Co}=2.0$  kmol/m<sup>3</sup>,  $P_{A1}=0.15$  atm,  $P_{A2}=0.04$  atm, and  $P_{A3}=0.001$  atm.

As shown in Fig. 7,  $N_{A1}$  increases, while  $N_{A2}$  and  $N_{A3}$  decrease with increasing  $T$ . As shown in Eq. (6),  $N_j$  is affected by  $\beta_j$ ,  $k_{Lj}$  and

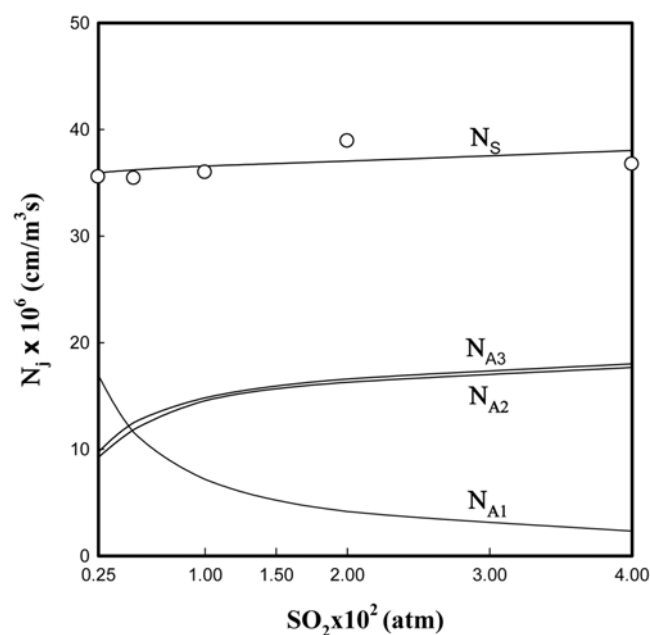


Fig. 5.  $N_j$  vs.  $y_{A2}$  at  $C_{Co}=2.0$  kmol/m<sup>3</sup>,  $P_{A1}=0.15$  atm,  $P_{A3}=0.001$  atm, and  $T=313.15$  K.

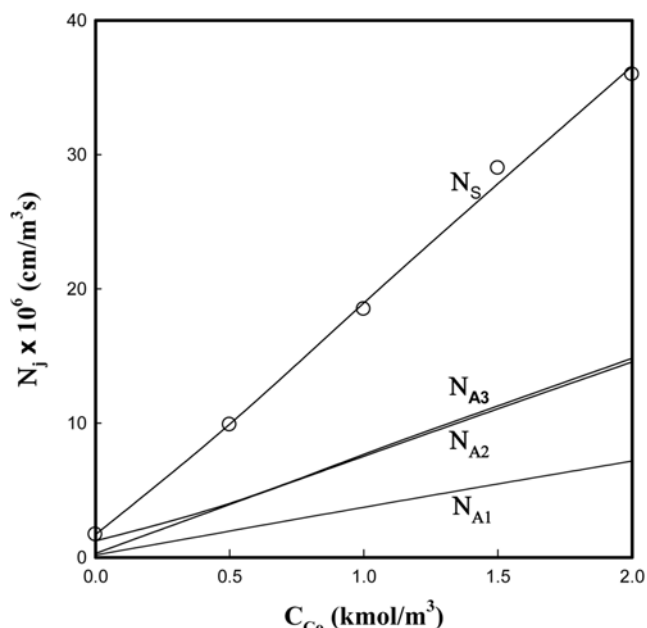


Fig. 6.  $N_j$  vs.  $C_{Co}$  at  $P_{A2}=0.3$  atm,  $P_{A2}=0.01$  atm,  $P_{A3}=0.001$  atm, and  $T=313.15$  K.

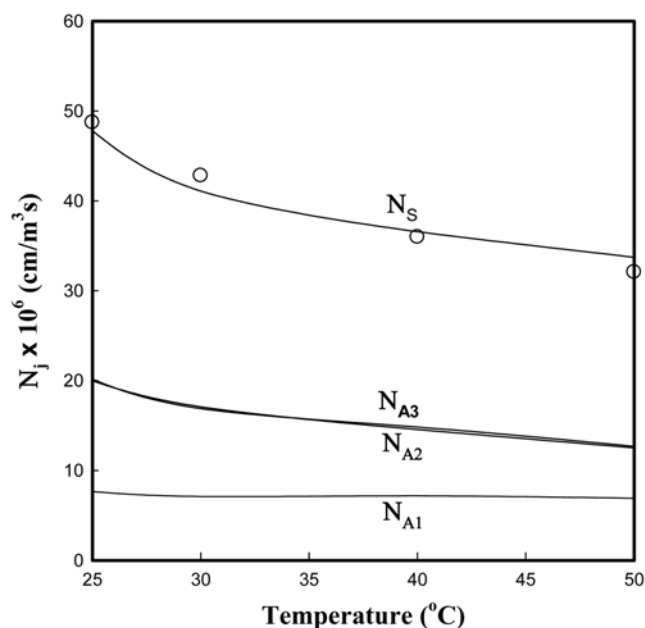


Fig. 7.  $N_j$  vs. temperature at  $C_{Co}=2.0$  kmol/m<sup>3</sup>,  $P_{A2}=0.15$  atm,  $P_{A2}=0.04$  atm,  $P_{A3}=0.001$  atm.

$C_{ji}$ . The values of  $k_{ij}$  are almost constant [27], but,  $\beta_j$  and  $C_{ji}$  increase and decrease with increasing temperature, respectively. From these results, the molar flux of each component for the change of temperature may be given according to the relative size of its solubility and the enhancement factor.

$N_{s,cal}$  were plotted vs.  $N_{s,exp}$  in Fig. 8 under all experimental conditions of 60 within a range of 0-2.0 kmol/m<sup>3</sup> of DAM, 0.05-0.3 atm of CO<sub>2</sub>, 0.0025-0.04 atm of SO<sub>2</sub>, and 298.15-323.15 K at a fixed NO<sub>2</sub> of 0.001 atm.

As shown in Fig. 8, the observed values of the molar flux agree

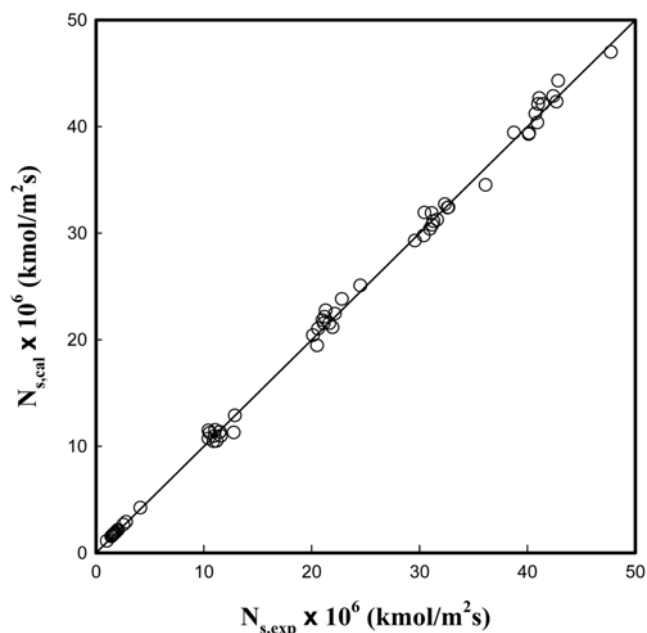


Fig. 8. Comparison of the calculated and measured molar flux of mixed gases within a range of 0-2.0 kmol/m<sup>3</sup> of DAM, 0.05-0.3 atm of CO<sub>2</sub>, 0.0025-0.04 atm of SO<sub>2</sub>, and 298.15-323.15 K at a fixed NO<sub>2</sub> of 0.001 atm.

with the calculated values with correlation coefficient=0.9978.

## CONCLUSIONS

Simultaneous absorption rate of CO<sub>2</sub>, SO<sub>2</sub>, and NO<sub>2</sub> was measured into aqueous DAM in a stirred, semi-batch tank with a planar, gas-liquid interface under the experimental conditions such as  $C_{Co}=0-2.0$  kmol/m<sup>3</sup>,  $P_{A1}=0.05-0.3$  atm,  $P_{A2}=0.0025-0.4$  atm, and  $T=298.15-323.15$  K at a fixed  $P_{A3}=0.001$  atm. Physicochemical properties were obtained from the reference data measured by N<sub>2</sub>O analogy.

Mass balances consisting of reaction regimes of two gases, one gas of which reacted instantaneously in a heterogeneous reaction was extended to the complicated chemical reactions of three gases to predict the simultaneous absorption rates. The enhancement factors of CO<sub>2</sub> and SO<sub>2</sub> were obtained by an approximate solution of the mass balances accompanied by a first-order reaction with respect to both CO<sub>2</sub> and DAM, and an instantaneous reaction with respect to both SO<sub>2</sub> and DAM in CO<sub>2</sub>-SO<sub>2</sub>-DAM system, and then, the enhancement factors of NO<sub>2</sub> were obtained by comparing the instantaneous reaction rate of SO<sub>2</sub> and NO<sub>2</sub> with DAM. The observed values of the molar flux approached to the calculated values very well. The molar flux of each component was affected according to the relative size of its solubility and the enhancement factor.

## NOMENCLATURE

- $C_j$  : concentration of species, j [kmol/m<sup>3</sup>]
- $C_{ji}$  : solubility of species, j [kmol/m<sup>3</sup>]
- $D_j$  : diffusivity of species, j [m<sup>2</sup>/s]
- $H_j$  : henry constant of species, j [atm·m<sup>3</sup>/kmol]
- $k_j$  : reaction rate constant of species, j [m<sup>3</sup>/kmol·s]

$k_{Lj}$  : liquid-side mass transfer coefficient of species, j [m/s]  
 MD : mean deviation  
 $N_j$  : molar flux of species, j [kg mol/m<sup>2</sup>·s]  
 $N_s$  : total molar flux [kmol/m<sup>2</sup>·s]  
 $P_j$  : partial pressure of species, j [atm]  
 $r^2$  : correlation coefficient  
 SD : standard deviation  
 T : temperature [°K]  
 Z : diffusion coordinate of gas [m]  
 $z_L$  : film thickness [m]

### Greek Letters

$\beta_j$  : enhancement factor of species, j  
 $\mu$  : viscosity of liquid [N·s/m<sup>2</sup>]  
 $\nu_j$  : a stoichiometric coefficients of species, j

### Subscripts

$A_1$  : CO<sub>2</sub>  
 $A_2$  : SO<sub>2</sub>  
 $A_3$  : NO<sub>2</sub>  
 C : AMP  
 J : species  
 O : feed  
 W : water

### ACKNOWLEDGEMENTS

This work was supported by the Energy Efficiency & Resources of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy (No. 2006CCD11P011A-21-3-010).

### REFERENCES

1. M. Aresta, *Carbon dioxide recovery and utilization*, Kluwer Academic Pub., Boston (2003).
2. M. Caplow, *J. Am. Chem. Soc.*, **90**, 6795 (1968).
3. P. V. Danckwerts, *Chem. Eng. Sci.*, **34**, 443 (1979).
4. E. F. da Silva and H. F. Sindsen, *Ind. Eng. Chem. Res.*, **43**, 3413 (2004).
5. T. Mimura, T. Suda, A. Honda and H. Kumazawa, *Chem. Eng. Commun.*, **170**, 245 (1998).
6. J. Stein, M. Kind and E. Schlunder, *Chem. Eng. J.*, **86**, 17 (2002).
7. S. H. Jung, G. T. Jeong, G. Y. Lee, J. M. Cha and D. H. Park, *Korean J. Chem. Eng.*, **24**, 1064 (2007).
8. S. Ebrahimi, C. Picioreanu, R. Kleerebezem, J. J. Heijnen and M. C. M. van Loosdrecht, *Chem. Eng. Sci.*, **58**, 3589 (2003).
9. S. Colle, J. Vanerschuren and D. Thomas, *Chem. Eng. Process*, **43**, 1397 (2004).
10. J. Xia, B. Rumpf and G. Maurer, *Ind. Eng. Chem. Res.*, **38**, 1149 (1999).
11. M. H. H. an Dam, A. S. Lamine, D. Roizard, P. Lochon and P. Roizard, *Ind. Eng. Chem. Res.*, **36**, 4628 (1997).
12. D. Nagel, R. de Kermadec, H. G. Lintz, C. Roizard and F. Lapique, *Chem. Eng. Sci.*, **57**, 4883 (2002).
13. P. V. Danckwerts, *Gas-liquid reactions*, McGraw-Hill, New York (1970).
14. K. G. Denbigh and A. J. Prince, *J. Am. Chem. Soc.*, **69**, 790 (1947).
15. P. Gray and A. D. Yoffe, *Chem. Rev.*, **55**, 1069 (1955).
16. J. J. Carberry, *Chem. Eng. Sci.*, **9**, 189 (1959).
17. P. G. Caudle and K. G. Denbigh, *Trans. Faraday Soc.*, **49**, 39 (1959).
18. M. M. Wendel and R. L. Pigford, *J. Am. Chem. Soc.*, **4**, 249 (1958).
19. M. P. Ho and G. E. Klinzing, *Can J. Chem. Eng.*, **64**, 243 (1986).
20. E. Sada, H. Kumazawa and Y. Yoshikawa, *J. Am. Chem. Soc.*, **34**, 1215 (1988).
21. E. Y. Kenig, R. Schneider and A. Gorak, *Chem. Eng. Sci.*, **54**, 5195 (1999).
22. S. W. Park, D. W. Park, K. J. Oh and S. S. Kim, *Sep. Sci. Technol.*, **44**, 543 (2009).
23. K. S. Hwang, D. W. Kim, S. W. Park, D. W. Park, K. J. Oh and S. S. Kim, *Sep. Sci. Technol.*, **44**, 3888 (2009).
24. K. J. Oh, S. S. Kim and S. W. Park, *Sep. Sci. Technol.*, To be accepted (2010).
25. L. A. Goetter and R. L. Pigford, *J. Am. Chem. Soc.*, **17**, 793 (1971).
26. H. Hikita, S. Asai and H. Ishikawa, *Chem. Eng. J.*, **18**, 169 (1979).
27. K. J. Oh, Y. S. Choi, S. S. Kim and S. W. Park, *Korean J. Chem. Eng.*, To be accepted (2010).
28. J. B. Seo, S. B. Jeon, W. J. Choi, J. W. Kim, G. H. Lee and K. J. Oh, *Korean J. Chem. Eng.*, **28**, 170 (2011).
29. L. K. Daraiswany and M. M. Sharma, *Heterogeneous reaction: Analysis, example and reactor design*, Wiley, New York (1984).
30. W. Yu, G. Astarita and D. W. Savage, *Chem. Eng. Sci.*, **40**, 1585 (1985).
31. G. F. Versteeg and W. P. M. van Swaaij, *J. Chem. Eng. Data*, **33**, 29 (1988).
32. A. K. Saha, S. S. Bandyopadhyay and A. K. Biswas, *J. Chem. Eng. Data*, **38**, 78 (1993).
33. W. Pasiuk-Bronikowska and K. J. Rudzinski, *Chem. Eng. Sci.*, **46**, 2281 (1991).
34. F. T. Shadid and D. Handley, *Chem. Eng. Res. Dev.*, **67**, 185 (1989).
35. E. L. Cussler, *Diffusion*, Cambridge University Press, New York (1984).
36. G. Carta and R. L. Pigford, *Ind. Eng. Chem. Fundam.*, **22**, 329 (1983).