Absorption of Sulfur Dioxide into Aqueous Sodium Carbonate Solutions and Desorption of Carbon Dioxide

Absorption of Sulfur Dioxide into Aqueous Sodium Carbonate Solutions and Desorption of Carbon Dioxide

Haruo HIKITA* and Yasuhiro KONISHI**

The absorption of sulfur dioxide into aqueous sodium carbonate solutions accompanied by the desorption of carbon dioxide was studied. The experimental data of Sada et al. on the absorption rate of sulfur dioxide and the desorption rate of carbon dioxide were re-analyzed with the chemical absorption theory based on the film model. The measured values of the absorption and desorption rates were in good agreement with the theoretical predictions.

1. Introduction

The removal of sulfur dioxide from gas mixtures by aqueous carbonate solutions is an important industrial absorption process for control of air pollution. Further, this chemical absorption process is of theoretical interest, since it is one in which the absorption is accompanied by a chemical reaction and the subsequent desorption of the volatile reaction product. However, there have been a few studies on the mechanism of chemical absorption of sulfur dioxide into aqueous carbonate solutions.

Ramachandran and Sharma[1] have considered the present problem and proposed the model based on the assumption that only the reaction between the dissolved sulfur dioxide and carbonate ions (reaction (2), below) takes place irreversibly and instantaneously at a single reaction plane, where the reaction product, carbon dioxide, is liberated. The experimental verification of this model, however, has not been attempted. In this model, it was assumed that the reaction between sulfur dioxide and carbonate ions was the only reaction, as described above. However, this assumption seems unreasonable because sulfur dioxide can also react with sulfite ions formed by the above reaction, as found by Hikita et al[2].

Takeuchi et al.[3] have studied the present system experimentally using a baffled agitated vessel. They have presented the model based on the assumption that the dissolved sulfur dioxide reacts irreversibly and instantaneously with carbonate ions and water at a reaction plane, the reaction products being bisulfite and bicarbonate ions, and found that the measured absorption rates of sulfur dioxide agreed with the film theory predictions based on the above model. However, the model proposed by Takeuchi et al. seems unreasonable because the assumed reaction scheme does not take into account the formation of carbon dioxide.

Teramoto et al.[4] have also measured the absorption rates of sulfur dioxide into aqueous sodium carbonate solutions in a baffled agitated vessel. They have proposed the

---

* Department of Chemical Engineering, College of Engineering.
** Graduate Student, Department of Chemical Engineering, College of Engineering.
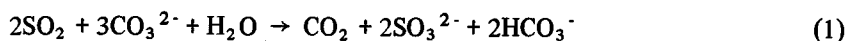
two reaction plane model which is the same as that presented in the present work, and showed that the measured absorption rates were in good agreement with the penetration theory predictions based on the proposed model. However, the experimental confirmation of this model was not attempted for the desorption rates of carbon dioxide.

Sada et al.[5] have carried out the absorption experiments on the present system using a baffled agitated vessel operated continuously, and compared the experimental results with the approximate film theory solutions derived on the basis of the two reaction plane model proposed by Teramoto et al[4]. The measured absorption rates of sulfur dioxide were shown to be in approximate agreement with the theoretical predictions, whereas the measured desorption rates of carbon dioxide were found to deviate upward from the theoretical lines with increasing sodium carbonate concentration.
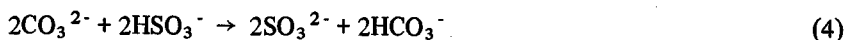
In the present work, the exact film theory solutions for the absorption rate of solute gas and the desorption rate of volatile reaction product were derived on the basis of the two reaction plane model proposed by Teramoto et al.[4], and the experimental data of Sada et al.[5] were compared with the theoretical predictions based on the proposed model.

2. Chemical Absorption Mechanism

When sulfur dioxide in gas phase is absorbed into aqueous sodium carbonate solutions, the following overall reaction between the dissolved sulfur dioxide and carbonate ions may take place in the liquid phase:

$$2SO_2 + 3CO_3^{2-} + H_2O \rightarrow CO_2 + 2SO_3^{2-} + 2HCO_3^- \tag{1}$$

Reaction (1) takes place in three steps :

$$SO_2 + CO_3^{2-} \rightarrow CO_2 + SO_3^{2-} \tag{2}$$

$$SO_2 + SO_3^{2-} + H_2O \rightarrow 2HSO_3^- \tag{3}$$

$$2CO_3^{2-} + 2HSO_3^- \rightarrow 2SO_3^{2-} + 2HCO_3^- \tag{4}$$

The values of the equilibrium constants of reactions (1) to (4), K_1, K_2, K_3 and K_4 respectively, are 2.51×10^{19}, 5.15×10^7, 2.76×10^5 and 1.33×10^3 at 25°C and infinite dilution. These values were estimated from the dissociation constants of carbonic acid[6] and sulfurous acid[7]. In view of these large values of K_1 to K_4, reactions (1) to (4) may be practically irreversible reactions. Further, reactions (2) to (4) may be considered to be very fast as compared to the rates of diffusional processes. Thus, reactions (2) to (4), and then reaction (1), may be regarded as instantaneous irreversible reactions.

The dissolved sulfur dioxide will also react with water according to the hydrolysis reaction:

$$SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+ \tag{5}$$

The value of the equilibrium constant of this reaction, K_5, is equal to 17.2 mol/m^3 at 25°C and infinite dilution[7] and the forward rate constant is 3.4×10^6 s^{-1} at 20 °C[8]. Thus, reaction (5) may be regarded as an instantaneous reversible reaction. However, its equilibrium constant is not very large, so it will not have a significant effect on the

absorption rate of sulfur dioxide or the desorption rate of carbon dioxide. In the present work, therefore, the effect of reaction (5) was neglected for the sake of simplifying the analysis.

Therefore, the absorption of sulfur dioxide into aqueous sodium carbonate solutions would be regarded as a process of absorption accompanied by an instantaneous irreversible three-step reaction represented by reaction (1).

According to the reaction scheme described above, sulfur dioxide cannot coexist with either carbanate ions or sulfite ions, and carbonate ions cannot coexist with bisulfite ions. Therefore, two reaction planes may be formed within the liquid and they will divide the liquid phase into three regions[4,5]. The concentration profile of each species in the liquid phase will be similar to that shown in Figure 1.
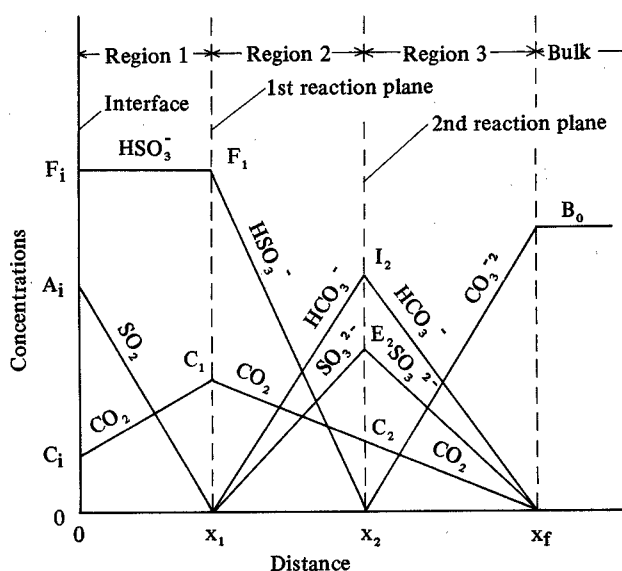

Fig. 1. Schematic diagram of concentration profiles for the absorption of sulfur dioxide into aqueous sodium carbonate solutions.

In this case, reaction (3) and the following reaction (the sum of reaction (2) and reaction (4) in the reverse direction):

$$SO_2 + HCO_3^- \rightarrow CO_2 + HSO_3^- \qquad (6)$$

whose equilibrium constant K_6 (= K_2/K_4) is 3.88×10^4, may take place irreversibly and instantaneously at the first reaction plane located closer to the gas-liquid interface, where carbon dioxide, a product of reaction (6), is liberated. At the second reaction plane, the instantaneous irreversible reaction represented by reaction (4) may occur. Part of carbon dioxide liberated at the first reaction plane diffuses towards the bulk of the liquid and the rest of carbon dioxide diffuses towards the gas-liquid interface and desorbes into the gas phase.

In regions 2 and 3, carbon dioxide and sulfite ions coexist, as seen in Fig. 1. These two species may react according to:

$$CO_2 + SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + HCO_3^- \tag{7}$$
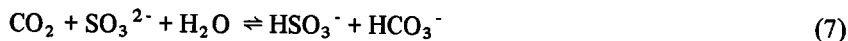
The equilibrium constant of the above reaction, K_7, is 7.12 at 25°C and infinite dilution[6,7], and the forward rate constant is 1.74×10^{-2} m^3/mol s at 25°C and infinite dilution[9]. These values are very low as compared to those of reaction (1). Hence, reaction (7) will make a negligible contribution to the absorption rate of sulfur dioxide or the desorption rate of carbon dioxide.

Further, carbon dioxide and carbonate ions coexist in region 3. These species may react according to:

$$CO_2 + CO_3^{2-} + H_2O \rightarrow 2HCO_3^- \tag{8}$$

the equilibrium constant K_8 being 9.47×10^3 at 25°C and infinite dilution[6]. This reaction is first order with respect to carbon dioxide and its pseudo first-order rate constant is 14 to 37 s^{-1} [10] in the range of the sodium carbonate concentration studied. In the present work, it was assumed that reaction (8) is too slow for an appreciable amount of the dissolved carbon dioxide reacts in region 3.

When the absorption of solute gas A is accompanied by an instantaneous irreversible reaction of the form $2A + 3B \rightarrow C + 2E + 2I$ which is made up of three steps, $A + B \rightarrow C + E$, $A + E \rightarrow 2F$ and $2B + 2F \rightarrow 2E + 2I$, and the desorption of the volatile reaction product C, the absorption rate N_A of solute gas A and the desorption rate N_C of volatile product C are represented by

$$N_A = \beta k_{LA} A_i \tag{9}$$

and

$$N_C = \beta k_{LC}(C_1 - C_i) \tag{10}$$

where β is the reaction factor for the absorption of solute gas A, k_{LA} and k_{LC} are the liquid-phase mass transfer coefficients for solute gas A and volatile product C respectively, A_i is the interfacial concentration of solute gas A, and C_i and C_1 are the concentrations of the volatile product C at the gas-liquid interface and the first reaction plane, respectively.

According to the film model, the reaction factor β is given by:

$$\beta = 1 + \frac{\dfrac{D_F F_i}{D_A A_i} \left(1 + \dfrac{D_F F_i}{D_B B_0}\right)}{\dfrac{D_{E2}}{D_{E3}} + \dfrac{D_F F_i}{D_B B_0}} \tag{11}$$

for the case where the concentrations of the reaction products in the bulk of the liquid are assumed to be zero, that is, $C_0 = E_0 = I_0 = 0$, and the concentration of the volatile product C at the first reaction plane, C_1, is given by:

$$C_1 = \left(1 - \frac{1}{\beta}\right)\left(C_i + 2\frac{D_A}{D_C}A_i - \frac{\dfrac{D_F}{D_C}F_i + \dfrac{D_B}{D_C}B_0}{\beta - 1}\right) \tag{12}$$

where F_i is the interfacial concentration of species F and is given by :

$$F_i = \frac{\dfrac{D_{E2}}{D_{E3}} + \sqrt{(\dfrac{D_{E2}}{D_{E3}})^2 + 8\dfrac{D_{E2}}{D_{E3}}\dfrac{D_{I2}}{D_{I3}}}}{2} \frac{D_B}{D_F} B_0 \qquad (13)$$

When the absorption experiments on the present system are carried out in an agitated vessel operated continuously with respect to the liquid as in the study of Sada et al.[5], the above assumption of $C_0 = E_0 = I_0 = 0$ would be satisfied and hence the absorption rate N_A and the desorption rate N_C in this case can be calculated from Eqs. (9) to (13).

If $D_{E3} = D_{E3}$ and $D_{I2} = D_{I3}$, Eqs. (11) to (13) reduce to :

$$\beta = 1 + 2\frac{D_B}{D_A}\frac{B_0}{A_i} \qquad (14)$$

$$C_1 = C_i + \frac{1}{\beta}(\frac{D_B}{D_C}B_0 - C_i) \qquad (15)$$

$$F_i = 2\frac{D_B}{D_F}B_0 \qquad (16)$$

Equations (14) to (16) are identical to the equations derived by Sada et al[5].

In the previous work, Hikita et al.[11, 12] showed that the mechanism of liquid-phase mass transfer in the baffled agitated vessel can be described by the Lévêque model. The approximate analytical solution based on the Lévêque model for the present problem can be obtained by replacing the diffusivity ratios in the exact analytical solution based on the film model by the two-third roots.

3. Results and Discussion

3.1 Prediction of physical properties

In order to compare the experimental data of Sada et al.[5] with the theoretical equations described above, it is necessary to know the gas-phase and liquid-phase mass transfer coefficients for each of sulfur dioxide and carbon dioxide, and the values of the physical properties of the present system.

When the dissolved sulfur dioxide reacts with sodium carbonate in solution, two reaction planes are formed within the liquid, as shown in Fig. 1, and an aqueous sodium bisulfite (= Na^+ + HSO_3^-) solution of uniform concentration exists in region 1, the region between the gas-liquid interface and the first reaction plane. This uniform concentration of sodium bisulfite, F_i, is given by Eq. (13). Therefore, the values of physical solubility and the liquid-phase diffusivity for each of the two gases in this solution should be used for the analysis of the experimental results.

The gas-phase and liquid-phase mass transfer coefficients, k_G and k_L, for each of the two gases were estimated from the empirical expressions presented in the paper of Sada et al[5].

The liquid-phase diffusivities of sulfur dioxide and carbon dioxide, D_A and D_C, in

aqueous sodium bisulfite solutions were estimated from the following equation proposed by Ratcliff and Holdcroft[13] :

$$D_A/D_{Aw} = D_C/D_{Cw} = 1 - \xi F_i \qquad (17)$$

where D_{Aw} and D_{Cw} are the liquid-phase diffusivities of sulfur dioxide and carbon dioxide in water, respectively, and ξ is the value of the constant for aqueous sodium bisulfite solutions. The value of ξ was estimated from viscosity data for aqueous sodium bisulfite solutions and was taken as 1.29×10^{-4} m^3/mol[13]. The values of D_{Aw} and D_{Cw} at 25 °C were taken to be equal to 1.76×10^{-9} and 1.97×10^{-9} m^2/s, respectively[14].

The ratios of the effective diffusivities of carbonate, sulfite, bisulfite and bicarbonate ions to the liquid-phase diffusivity of sulfur dioxide, that is, D_B/D_A, D_E/D_A, D_F/D_A and D_I/D_A, were assumed to be equal to those at infinite dilution. The effective diffusivities of carbonate, sulfite, bisulfite and bicarbonate ions at infinite dilution were estimated by the method of Vinograd and McBain[15] using the values of the ionic conductance for these species reported in the literature[16].

The interfacial concentrations of sulfur dioxide and carbon dioxide, A_i and C_i, in aqueous sodium bisulfite solution were obtained from the bulk partial pressure and the Henry's law constant for each of the two gases, correcting for gas-phase resistance to mass transfer according to the empirical formula for the gas-phase mass transfer coefficient described above. The gas-phase resistance for sulfur dioxide was 12.9 to 42.4% of the total resistance, but the gas-phase resistance for carbon dioxide was less than 1.8% and hence it was neglected.

The Henry's law constants for sulfur dioxide and carbon dioxide, H_A and H_C, in aqueous sodium bisulfite solutions were estimated from the following equations[17]:

$$\log(H_A/H_{Aw}) = k_{sA}F_i \qquad (18)$$

$$\log(H_C/H_{Cw}) = k_{sC}F_i \qquad (19)$$

where H_{Aw} and H_{Cw} are the Henry's law constants for sulfur dioxide and carbon dioxide in water, respectively, and k_{sA} and k_{sC} are the salting-out parameters for sulfur dioxide and carbon dioxide in aqueous sodium bisulfite solutions, respectively. The salting-out parameter k_s can be expressed as the sum of the contributions due to the positive and negative ions present and the dissolved gas[17] :

$$k_s = i_+ + i_- + i_g \qquad (20)$$

The values of i for sulfur dioxide, carbon dioxide and sodium ions were taken from the data of van Krevelen and Hoftijzer[17], and the value of i for bisulfite ions was estimated from the data of Hikita et al[2]. The estimated values of k_{sA} and k_{sC} at 25 °C were 7.4×10^{-5} and 1.62×10^{-4} m^3/mol, respectively. The Henry's law constants for sulfur dioxide and carbon dioxide, H_{Aw} and H_{Cw}, in water at 25 °C were taken as 84.5 Pa m^3/mol[18] and 2990 Pa m^3/mol[19].

The predicted values of the physical properties for the present system are listed in Table 1.

Table 1.   Physical properties for the sulfur dioxide-sodium carbonate system at 25 °C

B_0 mol/m³	p_A kPa	F_i mol/m³	A_i mol/m³	$D_A \times 10^9$ m²/s	$D_C \times 10^9$ m²/s
113	3.15 – 7.11	198	26.6 – 67.3	1.72	1.92
197	2.93 – 6.31	345	20.2 – 55.1	1.68	1.88
247	3.56 – 6.03	432	22.5 – 48.6	1.66	1.86
293	3.84 – 5.90	512	22.8 – 43.5	1.64	1.84

$D_B/D_A = 0.557$, $D_{E2}/D_A = 0.608$, $D_{E3}/D_A = 0.532$, $D_F/D_A = 0.713$, $D_{I2}/D_A = 0.709$, $D_{I3}/D_A = 0.665$

3.2 Analysis of data of Sada et al.

Some representative data of Sada et al.[5] for the absorption of sulfur dioxide into aqueous sodium carbonate solutions are shown in Fig. 2, where the absorption rate N_A of
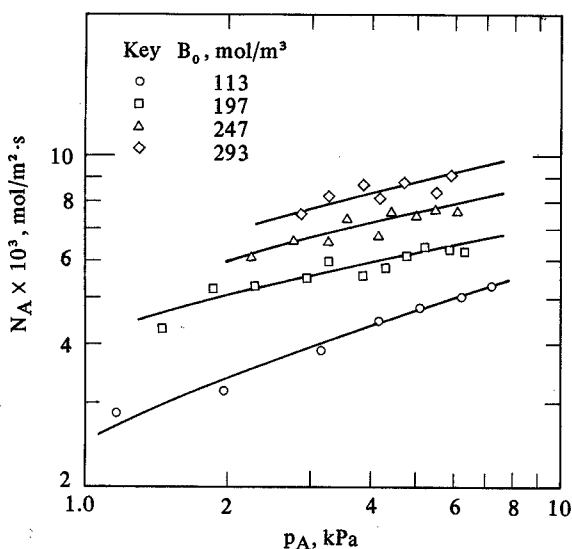

Fig. 2.   Absorption rate of sulfur dioxide into aqueous sodium carbonate solutions at 25 °C.

sulfur dioxide for each solution with a given concentration B_0 of sodium carbonate is plotted on logarithmic coordinates against the gas-phase partial pressure p_A of sulfur dioxide. It can be seen in the figure that the absorption rate N_A decreases rapidly as the bulk concentration B_0 of sodium carbonate decreases. However, for each solution with a given B_0 value, the absorption rate is a weak function of the p_A value and decreases gradually with decreasing p_A.

Figure 3 shows some experimental data of Sada et al.[5] for the desorption of carbon dioxide from aqueous sodium carbonate solutions as a log-log plot of the desorption rate N_C of carbon dioxide for each solution vs. the sulfur dioxide partial pressure p_A. As can

be seen in this figure, the effect of the B_0 value on the desorption rate N_C is similar to that for the absorption rate shown in Fig. 2. However, the effect of the p_A value is somewhat different from that for the absorption rate, and the desorption rate N_C remains almost constant at higher p_A values, while it decreases rapidly with decreasing p_A at lower p_A values.

The theoretical absorption rate N_A of sulfur dioxide and the theoretical desorption rate N_C of carbon dioxide can be represented as

$$N_A = k_{LA} \left[\frac{\eta(\eta + 1)}{\eta + \dfrac{D_{E2}}{D_{E3}}} \frac{D_B}{D_A} B_0 + A_i \right] \tag{21}$$

and

$$N_C = k_{LC} \left[\frac{(\eta + 1)(\eta - \dfrac{D_{E2}}{D_{E3}})}{\eta + \dfrac{D_{E2}}{D_{E3}}} \frac{D_B}{D_A} B_0 - C_i \right] \tag{22}$$

with

$$\eta = \frac{1}{2} \frac{D_{E2}}{D_{E3}} \left[1 + (1 + 8 \frac{D_{E3}}{D_{E2}} \frac{D_{I2}}{D_{I3}})^{1/2} \right] \tag{23}$$
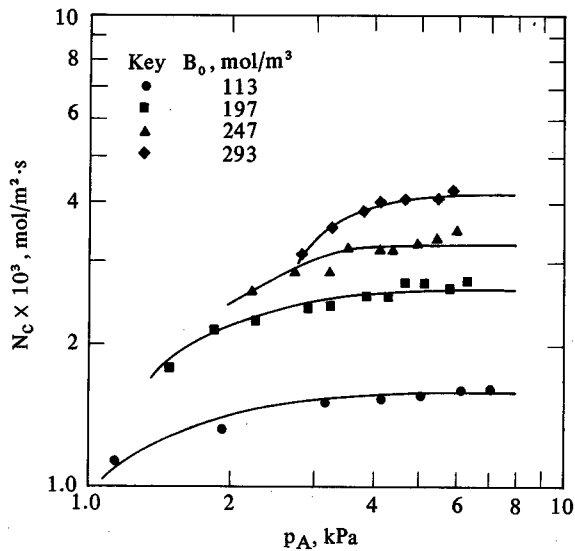

Fig. 3. Desorption rate of carbon dioxide from aqueous sodium carbonate solutions at 25 °C.

which are obtained by substituting Eqs. (11) to (13) into Eqs. (9) and (10). Under the experimental conditions studied, the first term of Eq. (21) is greater by only one order of magnitude than the second term, while the first term of Eq. (22) is greater by three orders of magnitude than the second term. This indicates that the absorption rate N_A depends on

not only B_0 but also A_i, i.e. p_A, but the desorption rate N_C is a function of B_0 alone and remains constant irrespective of p_A. As shown in Fig. 3, the measured desorption rates at lower p_A values have a tendency to decrease with decreasing p_A. This tendency differs from that be expected from theory. In the present work, therefore, the data of Sada et al.[5] obtained at the lower p_A values were not used.

3.3 Comparison of experimental data with theory

Figure 4 shows the comparison of the experimental data of Sada et al.[5] obtained for 197 mol/m³ aqueous sodium carbonate solution with the theoretical predictions based on the film and Lévêque models. In this figure, the absorption rate N_A of sulfur dioxide and the desorption rate N_C of carbon dioxide are plotted against the partial pressure p_A of sulfur dioxide on logarithmic coordinates. The solid lines represent the theoretical lines based on the film model, calculated from Eqs. (9) to (13) using the values of liquid-phase mass transfer coefficient and various physical properties predicted by the abovementioned methods. The dashed lines are the theoretical lines based on the Lévêque model, calculated from Eqs. (9) to (13), replacing the various diffusivity ratios by the two-third roots. As can be seen in Fig. 4, the measured values of N_A and N_C fall appreciably below the theoretical lines based on the Lévêque model and agree well with the theoretical lines based on the film model, as already found by Sada et al[5].

This fact differs from the finding of Hikita et al. They found that the mechanism of liquid-phase mass transfer in the baffled agitated vessel can be described by the Lévêque
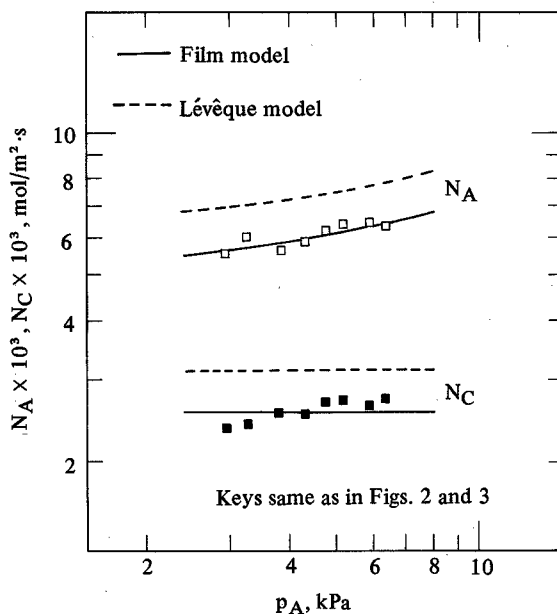

Fig. 4.   Comparison of measured absorption and desorption rates with theoretical predictions based on film and Lévêque models.

model[11, 12] and showed that the experimental data on the absorption rate obtained with the chlorine-ferrous chloride, hydrogen sulfide-sodium hydroxide and carbon dioxide-sodium carbonate/bicarbonate systems were in good agreement with the theoretical predictions based on the Lévêque model[12, 20, 21]. This disagreement between Sada et al. and Hikita et al. as to the choice of mass transfer model may be attributed to the difference in the hydrodynamic conditions of the liquid near the gas-liquid interface, presumably caused by the difference in the size and geometry of the agitated vessel. In the present work, therefore, the film model was used to analyze the experimental data of Sada et al.

In Fig. 5 the experimental data of Sada et al.[5] are presented as a log-log plot of the reaction factor β vs. the concentration ratio B_0/A_i and compared with the various theoretical predictions based on the film model. The experimental β values were calculated from the measured values of absorption rates N_A and desorption rates N_C, using the values of A_i, C_i, k_{LA} and k_{LC} predicted by the abovementioned methods and the values of C_1 calculated from Eq. (12). In calculating β from the N_C value, C_i was always negligible as compared to C_1.

The solid line in Fig. 5 represents the two reaction plane model proposed in the present work, calculated from Eqs. (11) and (13), while the dashed line shows the simplified two reaction plane model proposed by Sada et al.[5], calculated from Eq. (14). Further, the dash-dot line represents the one reaction plane model proposed by Ramachandran
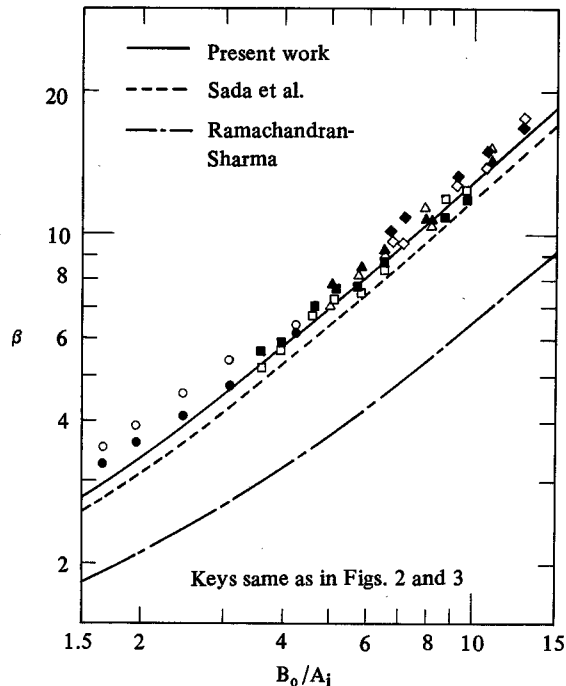

Fig. 5.   Comparison of measured reaction factors with theoretical predictions.

and Sharma[1] on the assumption that only the reaction between the dissolved sulfur dioxide and carbonate ions, i.e. reaction (2), takes place instantaneously and irreversibly at a single reaction plane, and was calculated from the following well-known equation :

$$\beta = 1 + \frac{D_B}{D_A} \frac{B_0}{A_i} \qquad (24)$$

It can be seen in Fig. 5 that the measured values of β are in good agreement with the theoretical line based on the model of the present authors, with the average deviation of 6.1%, and do not support the absorption mechanism based on the model of Sada et al. or the model of Ramachandran and Sharma.

As mentioned earlier, Sada et al.[5] showed that the measured absorption rates of sulfur dioxide were in good agreement with the theoretical predictions based on the model they proposed. In calculating the theoretical absorption rates, Sada et al. used the total solubility of sulfur dioxide in water as A_i. The use of the total solubility for A_i, however, is considered unreasonable in the present problem, because the total solubility is about 60 to 160% greater than the A_i value used in the present work. Thus, the good agreement observed by Sada et al.[5] between the experimental data and their theoretical predictions might be a coincidence due to overestimated values of the interfacial concentration of sulfur dioxide.

Notation

A : concentration of sulfur dioxide in solution, mol/m^3
B : concentration of carbonate ions in solution, mol/m^3
C : concentration of carbon dioxide in solution, mol/m^3
D : liquid-phase diffusivity, m^2/s
E : concentration of sulfite ions in solution, mol/m^3
F : concentration of bisulfite ions in solution, mol/m^3
H : Henry's law constant, $Pa\ m^3/mol$
I : concentration of bicarbonate ions in solution, mol/m^3
i_+, i_-, i_g : contributions of positive ions, negative ions and solute gas to salting-out parameter, m^3/mol
K : equilibrium constant
k_L : liquid-phase mass transfer coefficient, m/s
k_s : salting-out parameter, m^3/mol
N_A : absorption rate of sulfur dioxide, $mol/m^2\ s$
N_C : desorption rate of carbon dioxide, $mol/m^2\ s$
p_A : partial pressure of sulfur dioxide, Pa
x : distance from gas-liquid interface, m

Greek letters

β : reaction factor for the absorption of sulfur dioxide
η : parameter defined by Eq. (23)

ξ : constant in Eq. (17), m^3/mol

Subscripts

    A : sulfur dioxide

    B : carbonate ions

    C : carbon dioxide

    E : sulfite ions

    F : bisulfite ions

    I : bicarbonate ions

    i : gas-liquid interface

    w : water

    0   : bulk of liquid

    1   : first reaction plane

    2   : second reaction plane

References

1) P. A. Ramachandran and M. M. Sharma, Trans. Instn. Chem. Engrs., 49, 253 (1971).

2) H. Hikita, S. Asai and T. Tsuji, AIChE J., 23, 538 (1977).

3) H. Takeuchi, Y. Maeda and K. Ito, Kagaku Kogaku Ronbunshu, 1, 257 (1975).

4) M. Teramoto, M. Nagamochi, T. Tanaka, T. Hara and H. Teranishi, Preprint of the 9th Autumn Meeting of The Soc. of Chem. Engrs., Japan, Fukuoka, p.499 (1975).

5) E. Sada, H. Kumazawa and T. Hoshino, Chem. Eng. J., 18, 125 (1979).

6) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 3rd ed., p.691, Reinhold, New York (1958).

7) H. V. Tartar and H. H. Garretson, J. Am. Chem. Soc., 63, 808 (1941).

8) M. Eigen, K. Kustin and G. Maass, Z. phys. chem. Frankfurt, 30, 130 (1961).

9) H. Hikita, S. Asai and A. Yano, Preprint of the 6th Autumn Meeting of The Soc. of Chem. Engrs., Japan, Tokyo, p.381 (1972).

10) D. Roberts and P. V. Danckwerts, Chem. Eng. Sci., 17, 961 (1962).

11) H. Hikita and H. Ishikawa, Bull. Univ. Osaka Pref., A18, 427 (1969).

12) H. Hikita, S. Asai, H. Ishikawa and Y. Saito, Chem. Eng. Sci., 30, 607 (1975).

13) G. A. Ratcliff and J. G. Holdcroft, Trans. Instn. Chem. Engrs., 41, 315 (1963).

14) D. W. Peaceman, Sc. D. thesis, M. I. T. (1951).

15) J. R. Vinograd and J. W. McBain, J. Am. Chem. Soc., 63, 2008 (1941).

16) "Landolt-Börnstein Physikalisch-Chemische Tabellen", Bd. II-7, p.259, Springer-Verlag, Berlin (1960).

17) D. W. van Krevelen and P. J. Hoftijzer, Chim. Ind. XXIme Congress, Instn. Chim. Ind. p.168 (1948).

18) A. E. Rabe and J. F. Harris, J. Chem. Eng. Data, 8, 333 (1963).

19) W. F. Linke and A. Seidell, "Solubilities of Inorganic and Metal-Organic Compounds", 4th ed., Vol. I, p.459, van Nostrand, New York (1958).

20) H. Hikita, H. Ishikawa and Y. Murakami, Bull. Univ. Osaka Pref., A19, 349 (1970).

21) H. Hikita and H. Ishikawa, Kagaku Kogaku Ronbunshu, 1, 45 (1975).