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Absorption of Sulfur Dioxide into Aqueous Ammonia and Ammonium Sulfite Solutions

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The rates of absorption of pure sulfur dioxide into aqueous ammonia solutions and aqueous ammonium sulfite solutions containing ammonium bisulfite were measured at 25°C using a liquid jet column. The absorption rates obtained for the present systems were in good agreement with the theoretical predictions based on the penetration theory.

1. Introduction

The removal of sulfur dioxide from gas mixtures by contacting the gases with an aqueous alkaline solution is an important industrial absorption process for control of air pollution. In the previous paper[1)], we reported results of the study of the absorption of sulfur dioxide in aqueous sodium hydroxide and sodium sulfite solutions. In the present work, the kinetics of absorption of sulfur dioxide into aqueous ammonia and ammonium sulfite solutions is studied.

2. Chemical Absorption Mechanism

When sulfur dioxide is absorbed into aqueous ammonia solutions, the following two reactions may take place in the liquid phase:

$$SO_2 + NH_3 + H_2O \rightleftharpoons NH_4^+ + HSO_3^- \tag{1}$$

$$HSO_3^- + NH_3 \rightleftharpoons NH_4^+ + SO_3^{2-} \ . \tag{2}$$

The values of the equilibrium constants for reactions (1) and (2), K_1 and K_2, are given respectively, as

$$K_1 = \frac{[NH_4^+]\ [HSO_3^-]}{[SO_2]\ [NH_3]} = 3.1 \times 10^7$$

$$K_2 = \frac{[NH_4^+]\ [SO_3^{2-}]}{[HSO_3^-]\ [NH_3]} = 1.1 \times 10^2$$

at 25°C and at infinite dilution. These values were estimated from the dissociation con-

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stants of sulfurous acid and ammonium hydroxide[2]. Reaction (1) may be considered to be very fast. Reaction (2) has a very much higher rate constant than reaction (1), since it is a proton transfer reaction. Thus, both reactions (1) and (2) may be regarded as instantaneous reactions.

In aqueous ammonia solutions, reaction (1) is followed by reaction (2). Then, the overall reaction is

$$SO_2 + 2NH_3 + H_2O \longrightarrow 2NH_4^+ + SO_3^{2-} . \tag{3}$$

In aqueous ammonium sulfite solutions, ammonia is formed according to the instantaneous reversible reaction

$$NH_4^+ + SO_3^{2-} \rightleftharpoons NH_3 + HSO_3^- , \tag{4}$$

which is the reverse reaction of (2). Thus, the overall reaction in this case is

$$SO_2 + SO_3^{2-} + H_2O \longrightarrow 2HSO_3^- . \tag{5}$$

Therefore, the reactions which affect the rate of absorption of sulfur dioxide into aqueous solutions of ammonia and ammonium sulfite are reaction (2) and the forward part of reaction (1).

As described above, the values of the equilibrium constants of reactions (1) and (2), K_1 and K_2, and the equilibrium constant ratio K_1/K_2 (which is equal to 2.8×10^5) are very large. Therefore, the chemical absorption theory proposed by Hikita et al.[3] for absorption accompanied by a two-step instantaneous reaction may be applicable to the present system. According to this theory, the concentration profiles of each species for the SO_2-NH_3 and SO_2-SO_3^{2-} systems will be similar to those shown in Figs. 1(a) and 1(b).

In the case of the SO_2-NH_3 system, the two reaction plane model is applicable and

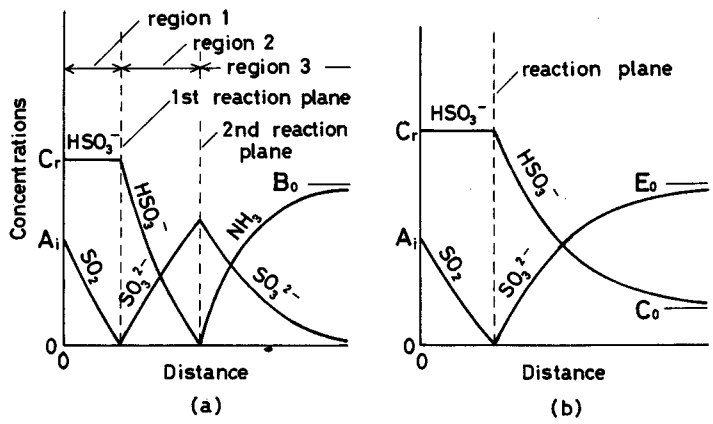

Fig. 1. Schematic diagram of concentration profiles for the absorption of sulfur dioxide into aqueous solutions of ammonia and ammonium sulfite;
(a) SO_2-NH_3 system, (b) SO_2-$(NH_4)_2SO_3$ system.

the irreversible reactions (5) and (2) may take place at the first and second reaction planes, respectively. The average rate of absorption N_A of sulfur dioxide for this case can be represented by

$$N_A = \beta(2A_i\sqrt{D_A/\pi t}) \ . \tag{6}$$

The reaction factor β can be obtained from the following equations[4]:

$$\beta = 1/\mathrm{erf}(\sigma_1) \tag{7}$$

$$2\mathrm{erfc}(\frac{\sigma_2}{\sqrt{r_B}})\exp[(\frac{1}{r_C}-1)\sigma_1^2+(\frac{1}{r_B}-\frac{1}{r_C})\sigma_2^2] = \sqrt{r_B}\,q_B\,\mathrm{erf}(\sigma_1) \tag{8}$$

$$\begin{aligned}&\mathrm{erfc}(\frac{\sigma_2}{\sqrt{r_{E3}}})\exp[(\frac{1}{r_{E2}}-1)\sigma_1^2+(\frac{1}{r_{E3}}-\frac{1}{r_{E2}})\sigma_2^2]\\&-2\mathrm{erfc}(\frac{\sigma_2}{\sqrt{r_{E3}}})\exp[(\frac{1}{r_C}-1)\sigma_1^2+(\frac{1}{r_{E3}}-\frac{1}{r_C})\sigma_2^2]\\&+\sqrt{\frac{r_{E3}}{r_{E2}}}[\mathrm{erf}(\frac{\sigma_2}{\sqrt{r_{E2}}})-\mathrm{erf}(\frac{\sigma_1}{\sqrt{r_{E2}}})]\exp[(\frac{1}{r_{E2}}-1)\sigma_1^2]\\&=\sqrt{r_{E3}}\,q_E\,\mathrm{erf}(\sigma_1).\end{aligned} \tag{9}$$

Here, σ_1 and σ_2 are the constants representing the dimensionless positions of the first and second reaction planes, and q_B, q_E, r_B, r_C, r_{E2} and r_{E3} are the dimensionless parameters defined by

$$q_B = B_0/A_i \qquad q_E = E_0/A_i \tag{10}$$

$$r_B = D_B/D_A \qquad r_C = D_C/D_A \tag{11a}$$

$$r_{E2} = D_{E2}/D_A \qquad r_{E3} = D_{E3}/D_A \ , \tag{11b}$$

where the subscripts 2 and 3 for D_E denote the values in region 2 and region 3, respectively (see Fig. 1(a)).

In the case of the SO_2-SO_3^{2-} system, only the irreversible reaction (5) may occur at the single reaction plane. In this case, Eqs. (8) and (9) reduce to

$$\mathrm{erfc}(\frac{\sigma_1}{\sqrt{r_{E2}}})\exp[(\frac{1}{r_{E2}}-1)\sigma_1^2] = \sqrt{r_{E2}}\,q_E\,\mathrm{erf}(\sigma_1), \tag{12}$$

from which the constant σ_1 can be determined.

3. Experimental

3.1 Apparatus and procedure

Absorption experiments were carried out with a liquid jet column which was the same as that used by Hikita et al[1]. The exposure time of the liquid to the gas was varied from 0.0008 to 0.017 sec. Absorption rate was determined by means of a soap-film meter. All the experiments were conducted at atmospheric pressure and at 25°C. The gas phase was pure sulfur dioxide saturated with water vapor, and the absorbents used were aqueous ammonia solutions and aqueous ammonium sulfite solutions containing ammonium bisulfite. Some experimental runs were carried out using the absorbents with 0.05 vol% of a surface active agent, Emulgen 147 or Scourol 450 (Kao-Atlas Co.), to check for the existence of interfacial turbulence in the present systems. The compositions of the solutions are given in Tables 1 and 2.

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

B_0 [g-mol/ℓ]	C_r [g-mol/ℓ]	A_i [g-mol/ℓ]	$D_A \times 10^5$ [cm²/sec]
0.125	0.131	1.15	1.74
0.25	0.262	1.15	1.72
0.5	0.530	1.14	1.69
1.0	1.07	1.13	1.61
2.0	2.13	1.10	1.46
$r_B = 1.32$,	$r_C = 0.705$,	$r_{E2} = 0.614$,	$r_{E3} = 0.824$

Table 2. Physical properties for the sulfur dioxide-ammonium sulfite system at 25°C

E_0 [g-mol/ℓ]	C_0 [g-mol/ℓ]	C_r [g-mol/ℓ]	A_i [g-mol/ℓ]	$D_A \times 10^5$ [cm²/sec]	r_C [——]	r_{E2} [——]
0.125	0.262	0.508	1.14	1.69	0.653	0.568
0.201	0.565	0.959	1.13	1.63	0.653	0.564
0.410	0.864	1.66	1.11	1.53	0.659	0.568
1.12	0.888	3.05	1.07	1.33	0.671	0.585
2.09	2.32	6.32	0.985	0.875	0.665	0.580

3.2 Results

Figures 2 and 3 show the results for the absorption of sulfur dioxide into aqueous solutions of ammonia and ammonium sulfite at 25°C, respectively, as log-log plots of the average absorption rate N_A of sulfur dioxide vs. the exposure time t. The effect of the addition of surface active agents was studied only for the cases of 2.0 g-mol/ℓ ammonia solution and of 2.09 g-mol/ℓ ammonium sulfite solution containing 2.32

g-mol/ℓ ammonium bisulfite, and it was found that the rates of absorption into the solutions with and without surface active agents were the same for each case. This means that interfacial turbulence is absent in these systems. Figures 2 and 3 show that data points for each solution fall on a straight line with a slope of – 1/2. This implies that the absorption of sulfur dioxide into aqueous solutions of ammonia or ammonium sulfite is accompanied by an instantaneous reaction between the dissolved sulfur dioxide and ammonia or ammonium sulfite in the solution.

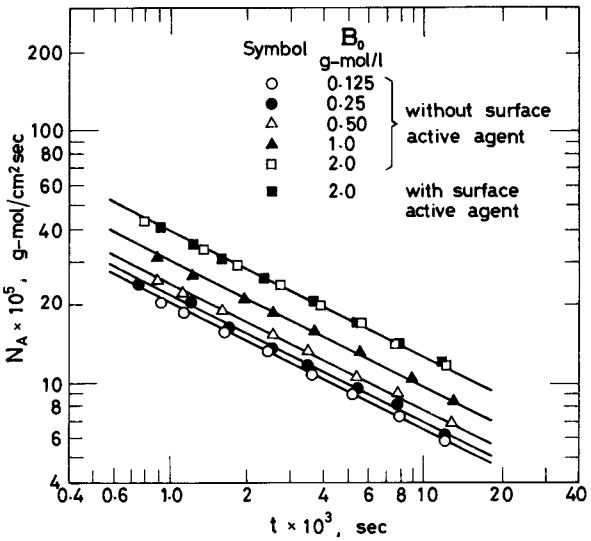

Fig. 2. Absorption rate of sulfur dioxide into aqueous ammonia solutions at 25°C.

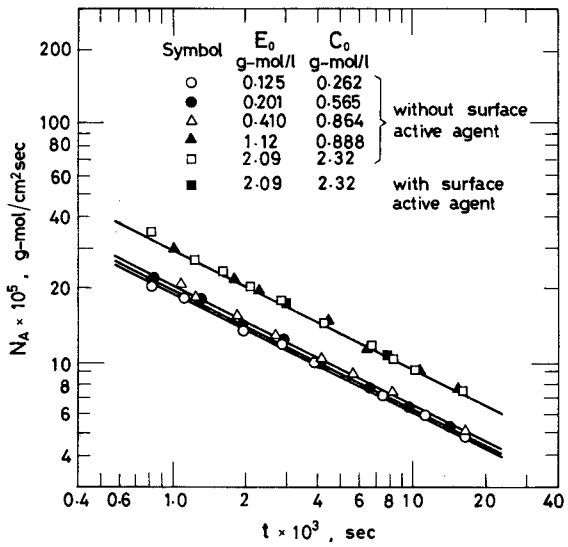

Fig. 3. Absorption rate of sulfur dioxide into aqueous ammonium sulfite solutions containing ammonium bisulfite at 25°C.

4. Analysis and Discussion

4.1 Prediction of physical properties

In order to analyze the experimental results, it is necessary to know the values of the physical properties of the present systems, such as A_i, D_A, D_B, D_C, D_E etc.

Sulfur dioxide – ammonia system When the two-step reaction between the dissolved sulfur dioxide and ammonia in the solution proceeds instantaneously, two reaction planes are formed within the liquid, as shown in Fig. 1(a), and an aqueous ammonium bisulfite ($NH_4^+ + HSO_3^-$) solution of uniform concentration exists in region 1. This uniform concentration C_r of ammonium bisulfite is given by the equation[3]:

$$C_r = B_0\sqrt{\frac{r_B}{r_C}}\exp\left[\left(\frac{1}{r_C}-\frac{1}{r_B}\right)\sigma_2^2\right]\frac{\mathrm{erf}(\sigma_2/\sqrt{r_C})-\mathrm{erf}(\sigma_1/\sqrt{r_C})}{\mathrm{erfc}(\sigma_2/\sqrt{r_B})} \quad . \tag{13}$$

Therefore, the physical solubility and the liquid-phase diffusivity of sulfur dioxide in this solution should be taken as the values of A_i and D_A, respectively.

The physical solubility A_i of sulfur dioxide in aqueous ammonia bisulfite solutions was estimated from the following expression[5]:

$$\log(A_i/A_{iw}) = -k_s I \ , \tag{14}$$

where

$$k_s = i_+ + i_- + i_g \ . \tag{15}$$

The values of i for sulfur dioxide and NH_4^+ ions were taken from the data of van Krevelen and Hoftijzer[5] and the value of i for HSO_3^- ions was estimated from the data of Hikita et al[1]. The estimated value of k_s at 25°C is 0.011 ℓ/g-ion. The value of A_{iw} was obtained from the Henry's law constant for the sulfur dioxide-water system[6], and was taken as 1.16 g-mol/ℓ at 25°C.

The liquid-phase diffusivity D_A of sulfur dioxide in aqueous ammonium bisulfite solutions was estimated from[7]

$$D_A/D_{AW} = 1 - \xi C_e \ . \tag{16}$$

The value of ξ was estimated from viscosity data for aqueous ammonium bisulfite solutions and the empirical equation proposed by Ratcliff and Holdcroft[7] and was taken as 0.0795 ℓ/g-mol. The value of D_{AW} at 25°C was taken to be equal to 1.76×10^{-5} cm^2/sec; this was predicted from the value of 2.00×10^{-5} cm^2/sec[8], estimated at 30°C for molecular sulfur dioxide in water by correcting for the temperature and viscosity of water according to the well-known Stokes-Einstein relation.

The ratios of the liquid-phase diffusivity of ammonia and of the effective diffusivities of HSO_3^- and SO_3^{2-} ions to the liquid-phase diffusivity of sulfur dioxide, that is, r_B, r_C and r_E, were assumed to be equal to those at infinite dilution or in water. The

liquid-phase diffusivity D_B of ammonia in water was taken as 2.33×10^{-5} cm^2/sec[9] at 25°C. The effective diffusivities D_C and D_E of HSO_3^- and SO_3^{2-} ions at infinite dilution were estimated by the method of Vinograd and McBain[10] using the values of the ionic conductance for these species reported in the literature[11]. The calculated values of the effective diffusivity of SO_3^{2-} ions in regions 2 and 3, D_{E2} and D_{E3}, were considerably different from each other, D_{E3} being 34% greater than D_{E2}.

The predicted values of the physical properties for the sulfur dioxide - ammonia system are listed in Table 1.

Sulfur dioxide - ammonium sulfite system When the instantaneous irreversible reaction between the dissolved sulfur dioxide and ammonium sulfite in solution takes place, the concentration profiles may be shown in Fig. 1(b), and the uniform concentration of ammonium bisulfite near the gas-liquid interface can be calculated from the equation[12,13]:

$$C_r = 2E_0 \sqrt{\frac{r_{E2}}{r_C}} \exp\left[\left(\frac{1}{r_C} - \frac{1}{r_{E2}}\right)\sigma_1^2\right] \frac{\mathrm{erfc}(\sigma_1/\sqrt{r_C})}{\mathrm{erfc}(\sigma_1/\sqrt{r_{E2}})} \quad . \tag{17}$$

The physical solubility A_i of sulfur dioxide in aqueous ammonium bisulfite solutions was estimated from Eq. (14) with $A_{iw} = 1.16$ g-mol/ℓ and $k_s = 0.011$ ℓ/g-ion.

The diffusivity ratios r_B, r_C and r_E for the present system were estimated by means of the same procedure as employed for the sulfur dioxide-ammonia system.

Table 2 shows the predicted values of the physical properties for the sulfur dioxide-ammonium sulfite system.

4.2 Comparison of experimental results with theory

The experimental results for the sulfur dioxide-ammonia system are shown in Fig. 4 as a log-log plot of the reaction factor β against the concentration ratio q_B. The solid line represents the theoretical line based on the two reaction plane model, calculated from Eqs. (7) to (9). It can be seen that the measured values of β are in good agree-

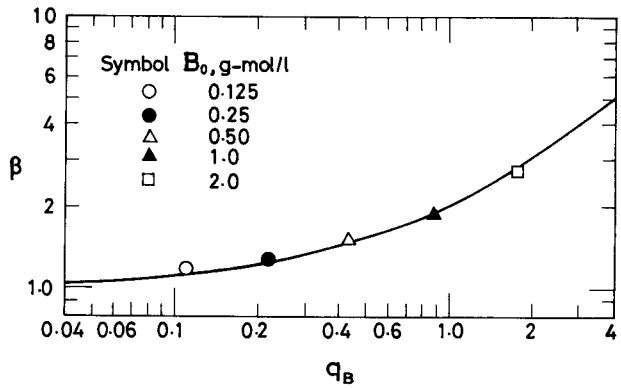

Fig. 4. Reaction factor for the absorption of sulfur dioxide into aqueous ammonia solutions.

ment with the theoretical line, the average deviation being 4.0%.

Figure 5 represents the experimental results for the sulfur dioxide-ammonium sulfite system as a log-log plot of the measured values of β against the theoretical values

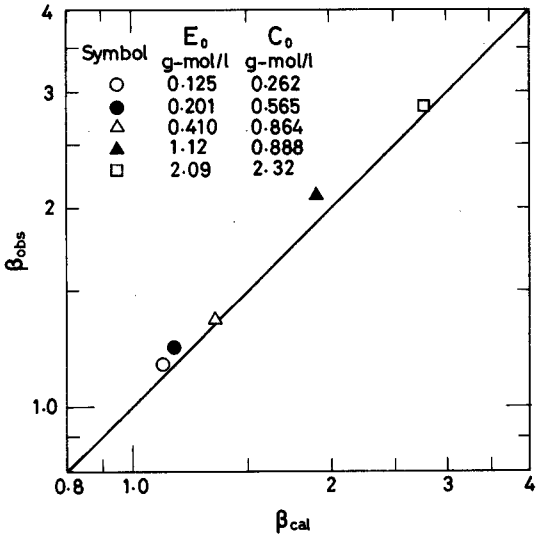

Fig. 5. Reaction factor for the absorption of sulfur dioxide into aqueous ammonium sulfite solutions containing ammonium bisulfite.

of β calculated from Eqs. (7) and (12), which are the theoretical equations for absorption accompanied by the instantaneous irreversible reaction given by reaction (5). As can be seen in this figure, the observed values of β, β_{obs}, agree well with the theoretical predictions, β_{cal}, with an average deviation of 4.9%.

5. Conclusion

The absorption of sulfur dioxide into aqueous ammonia solutions is accompanied by a two-step instantaneous reaction between the dissolved sulfur dioxide and ammonia in the solution, and the absorption rate data agree well with the theoretical predictions based on the two reaction plane model proposed by Hikita et al[3].

The absorption of sulfur dioxide into aqueous ammonium sulfite solutions is accompanied by an instantaneous irreversible single reaction between the sulfur dioxide and SO_3^{2-} ions in the solution, and the absorption rate results are in good agreement with the theoretical predictions.

Notation

A_i : interfacial concentration or physical solubility of sulfur dioxide in solution, g-mol/ℓ

A_{iw} : physical solubility of sulfur dioxide in water, g-mol/ℓ

B_0	:	concentration of ammonia in bulk of solution, g-mol/ℓ
C_e	:	concentration of HSO_3^- ions in solution, g-mol/ℓ
C_r	:	uniform concentration of HSO_3^- ions near gas-liquid interface, g-mol/ℓ
C_0	:	concentration of HSO_3^- ions in bulk of solution, g-mol/ℓ
D_A	:	liquid-phase diffusivity of sulfur dioxide in solution, cm^2/sec
D_{AW}	:	liquid-phase diffusivity of sulfur dioxide in water, cm^2/sec
D_B	:	liquid-phase diffusivity of ammonia in solution, cm^2/sec
D_C, D_E	:	effective diffusivities of HSO_3^-, SO_3^{2-} ions in solution, cm^2/sec
D_{E2}, D_{E3}	:	effective diffusivities of SO_3^{2-} ions in regions 2 and 3 of solution, cm^2/sec
E_0	:	concentration of SO_3^{2-} ions in bulk of solution, g-mol/ℓ
I	:	ionic strength of aqueous ammonium bisulfite solution, g-mol/ℓ
i_+, i_-, i_g	:	contributions of positive ions, negative ions, solute gas to salting-out parameter, ℓ/g-ion
K_1	:	equilibrium constant of reaction (1), —
K_2	:	equilibrium constant of reaction (2), —
k_s	:	salting-out parameter, ℓ/g-ion
N_A	:	average absorption rate of sulfur dioxide, g-mol/cm^2 sec
q_B, q_E	:	concentration ratios defined as B_0/A_i, E_0/A_i, —
r_B, r_C, r_{E2}, r_{E3}	:	diffusivity ratios defined as D_B/D_A, D_C/D_A, D_{E2}/D_A, D_{E3}/D_A, —
t	:	exposure time of liquid to gas, sec

Greek letters

β	:	reaction factor, —
ξ	:	coefficient in Eq. (16), ℓ/g-mol
σ_1, σ_2	:	dimensionless parameters to be determined from Eqs. (8) and (9), —

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