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Absorption Mechanism of Sulfur Dioxide into Alcoholic Sodium Hydroxide Solutions

Abdul Khalique*, Adnan Akram, Nusrat Hamid and Izhar H. Khan
Material Science Research Centre, PCSIR Laboratories Complex, Lahore-54600, Pakistan

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Abstract. The chemical absorption of sulfur dioxide into alcoholic solution of sodium hydroxide was studied by simultaneous mass transfer and multiple instantaneous irreversible reaction. The experimental data showed the values of mass transfer enhancement factor to be much higher in the alcoholic sodium hydroxide solution. The results of present studies are compared with reversible and irreversible models over a wide range of sodium hydroxide solution concentrations, reported previously.

Keywords: mass transfer enhancement factor, SO_2 absorption mechanism, SO_2 absorption in alcoholic NaOH, SO_2 absorption in aqueous NaOH, sulfur salts

Introduction

Sulfur-based salts are important for a number of industries, such as dyeing, textile and paper. Presently, these salts are obtained by the absorption of sulfur dioxide gas into aqueous sodium hydroxide solution, which serves as the absorption medium. However, known methods for the production of sulfur salts through this route reported in literature are complicated and found to be cumbersome from the practical point of view. Therefore, there is a need to develop an economical and simple method for the preparation of these salts indigenously, which at present are being imported for various industrial uses.

A number of researchers (Bravo-Rodriguez *et al.,* 2000; Pasiuk-Bronikowska and Rudzinski, 1992; 1991; Chang and Rochelle, 1985; 1982) have studied the absorption of sulfur dioxide into sodium hydroxide solution. Simultaneous absorption of sulfur dioxide and carbon dioxide into sodium hydroxide solution flowing over a single sphere has been suggested (Goettler, 1967). The absorption rates were modeled on the basis of film theory with the assumption that dissolved sulfur dioxide and hydroxide ion participate in a two-step instantaneous and irreversible reaction with the formation of two-reaction planes within the liquid phase. Hikita *et al.* (1972) proposed the solution of penetration theory using the model of two-reaction planes. Hikita *et al.* (1977) also measured the absorption rates of pure sulfur dioxide into aqueous sodium bisulfite, sodium hydroxide, and sodium sulfite solutions in a liquid jet column. They reported these reactions to be irreversible. Onda *et al.* (1971) studied the behaviour of reaction plane movement by absorbing sulfur dioxide into agar gel containing sodium hydroxide or sodium sulfite solution, and the results obtained for the sulfur dioxide-sodium hydroxide system were found to be in close agreement with the penetration theory based on two-reaction plane model. Earlier investigators (Hikita *et al.,* 1977; Onda *et al.,* 1971), however, paid no attention to the reversible hydrolysis of the absorbed sulfur dioxide during their two-reaction plane model studies.

Most previous studies used either pure or concentrated sulfur dioxide in the gas phase under which the sulfur dioxide hydrolysis reaction is highly depressed (Teramoto *et al.,* 1978). However, the sulfur dioxide concentration in stock gas SO_2 scrubbers is normally very low, and under these conditions the sulfur dioxide hydrolysis reaction can have a significant effect on the absorption rate. Chang and Rochelle (1985) thus noted that reversible hydrolysis reaction of sulfur dioxide needs to be considered. They further suggested that hydrogen ions play an important role in the absorption mechanism when the sulfur dioxide partial pressure was less than 0.05 atm.

The present work reports the results of the reaction mechanism in non-aqueous phase on the basis of instantaneous irreversible chemical reactions, which was investigated by absorbing sulfur dioxide at high partial pressure into alcoholic sodium hydroxide system. The observations so obtained showed that the mass transfer was enhanced during sulfur dioxide absorption into alcoholic sodium hydroxide solution. The high values of mass transfer enhancement factor thus obtained by using mass transfer solutions were compared with those reported previously (Kumar *et al.,* 2003; Orthmer, 1964).

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*Author for correspondence

Materials and Methods

Absorption reaction procedure. Fine powder of sulfur was used for the generation of sulfur dioxide using sulfur burner. Distilled and deionised water was used for the preparation of desired concentrations of sodium hydroxide (0.001-2 M). Ethyl alcohol was used as the non-aqueous medium. Nitrogen gas was used for the dilution of sulfur dioxide gas. All reagents used were of analytical grade. A glass separable reaction vessel (500 cm^3) with a lid having four necks was used for the absorption studies (Fig. 1).

Central neck of the reaction vessel was used for the accommodation of condenser (F) and to allow unreacted sulfur dioxide gas to escape through other end of the condenser. The other three necks were used for the introduction of mixture of sulfur dioxide and nitrogen gas (D), for placing the thermometer (C), and for the addition of samples (B). A thermostatically controlled waterbath was used to maintain the reaction temperature at 25 °C (± 0.05 °C). 250 ml of ethyl alcohol was charged in the reaction vessel. 50 ml sodium hydroxide solution of various concentrations (0.001-2 M) was added into the reaction vessel (500 cm^3) and stirred was magnetic stirrer. Sulfur dioxide, diluted with nitrogen gas (8%), was bubbled into the alcohol-sodium hydroxide solution. All experiments were performed at ambient pressure and 25 ± 0.05 °C. The partial pressure of the outlet sulfur dioxide gas stream was measured by a sulfur dioxide analyzer (Thermoelectron model 40). At steady state, samples of outlet liquid were acidified by hydrochloric acid and oxidized by hydrogen peroxide to determine total sulfate concentration by ion chromatography.

Mathematical basis for mass transfer enhancement fector. Mass transfer enhancement factor (ϕ) was calculated by the following equations (Chang and Rochelle, 1985; Orthmer, 1964).

$$[SO_2]_i = (P_{SO_2} - N/K_gA)\,H \qquad (1)$$

$$\phi = \frac{N}{K_l^{\circ}A[(SO_2)_i - (SO_2)_0]} \qquad (2)$$

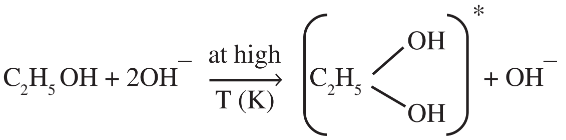
The standard values of K_gA and $K_l^{o}A$ are 1.4 x 10^{-2} g mol/atm per sec and 2.5 x 10^{-4} liter per sec, respectively; N was calculated by material balance, and the value of H was determined as follows:

$$H = \text{Exp}\,(2851.1/T - 9.3795)$$

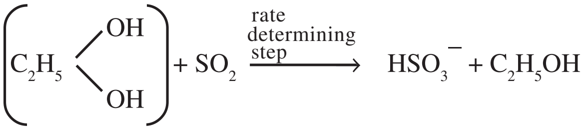
where:

$[SO_2]_i$ = concentration of SO_2 gas at gas-liquid interface
$[SO_2]_o$ = concentration of SO_2 gas in bulk liquid
Pso_2 = SO_2 partial pressure (atm)
N = absorption rate (g mol/sec)
A = mass transfer area (cm^2)
K_gA = gas phase mass transfer coefficient (g mol/atm per sec)
$K_l^{o}A$ = liquid phase mass transfer coefficient (liter/sec)
T = absolute temperature (K) of reaction mixture
Exp = experimental value
ϕ = enhancement factor (ratio of actual diffusion rate to its diffusion rate in the absence of chemical reaction)
H = concentration (g mol/liter per atm)

Reaction mechanism. The following equations were taken into consideration during the present studies when dilute sulfur dioxide was absorbed into alcoholic sodium hydroxide solution producing an intermediate complex as shown below.



$$C_2H_5OH + 2OH^- \xrightarrow[T\,(K)]{\text{at high}} \left(C_2H_5 \begin{matrix} OH \\ OH \end{matrix}\right)^* + OH^- \qquad (3)$$



$$\left(C_2H_5 \begin{matrix} OH \\ OH \end{matrix}\right) + SO_2 \xrightarrow{\text{rate determining step}} HSO_3^- + C_2H_5OH \qquad (4)$$

$$HSO_3^- + 2Na^+ \longrightarrow Na_2SO_3 + H^+ \qquad (5)$$

$$H^+ + OH^- \longrightarrow H_2O \qquad (6)$$

It was observed that reaction (4) was the rate determining step, during which sulfur dioxide reacts with the intermediate complex to produce bisulfite ions and alcohol was regenerated. The reaction proceeded irreversibly at a single-reaction plane, whereas reactions (5) and (6) were important in which bisulfite ions were not present in significant amount in the alcoholic phase. Reactions (4) and (5) took place at the two-reaction plane, which proceeded when hydroxyl ion was the major species in the alcoholic phase.

Results and Discussion

Effect of alcoholic sodium hydroxide concentration on mass transfer enhancement factor (ϕ). The effect of sodium hydroxide concentration on mass transfer enhancement factor was studied by varying its concentration from 0.001-2 M sodium hydroxide solution. Sulfur dioxide gas diluted with nitrogen gas (8%) was passed through the reaction medium containing ethyl alcohol at 25 °C and partial pressure of SO_2 > 0.05 atm to precipitate sodium sulfite. Absorption rate (N) of sulfur dioxide gas and (ϕ) values were calculated by using equations (1) and (2). Results obtained during this study are

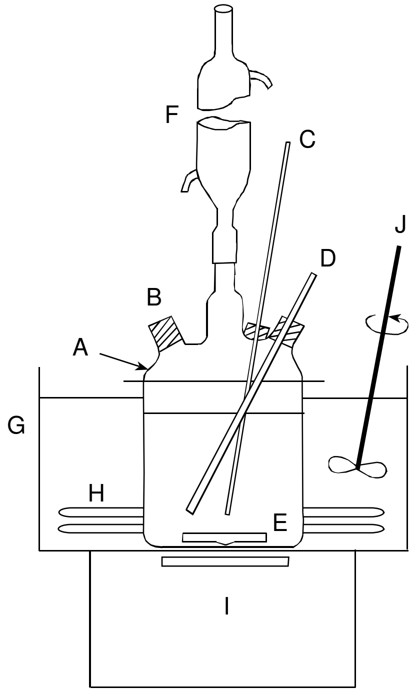


Fig. 1. Absorption reaction assembly: (A) reaction flask (500 cm^3, inner dia 85 mm), (B) sample feed and sampling hole, (C) thermometer, (D) bubbling tube, (E) stirrer, (F) condenser, (G) heater, (H) waterbath, (I) magnetic stirrer, (J) bath agitator.

shown in Table 1. It was observed that absorption of sulfur dioxide in alcoholic sodium hydroxide solution was directly proportional to the concentration of sodium hydroxide solution and to the mass transfer enhancement factor (ϕ), thereby eliminating the reversibility of reactions (4) and (5) at low concentrations of alcoholic sodium hydroxide solutions. Results obtained experimentally for the enhancement factor are shown in Fig. 2 (curve-2). Hikita *et al.* (1977) working with aqueous sodium hydroxide system and at partial pressure of sulfur dioxide much lower than the present studies obtained appreciably less absorption as shown in curve-1 (Fig. 2).

The (ϕ) values obtained in the present studies were much higher than the results obtained by other researchers (Chang and Rochelle, 1985; Hikita *et al.,* 1977) while working with sodium hydroxide in aqueous phase. These high (ϕ) values may be due to the presence of alcohol, which suppresses the reversibility of reaction. Therefore, it may be concluded that mass transfer enhancement factor (ϕ) was high on using non-aqueous phase. Moreover, the degree of conversion rate obtained was greater than the results reported by Chang and Rochelle (1985) and Hikita *et al.* (1977) while studying the absorption mechanism in aqueous phase, as the concentration of sulfur dioxide was approximately zero at the interface of reacting surfaces due to the immediate conversion of sulfur dioxide into sodium sulfite. Sodium sulfite settles down as precipitate and the concentration difference allows further diffusivity of sulfur dioxide into turbulent eddies of the alcoholic sodium hydroxide system (Orthmer, 1964). It may be noted from Fig. 3 that [H$^+$] ions have no influence on the reaction, as their presence is not comparable to the [SO_2] and [HSO_3^-] ions near the gas-liquid interface. Hence, irreversible reactions occurred in the alcoholic NaOH system reported pre-

Table 1. The effect of alcoholic sodium hydroxide concentration on mass transfer enhancement factor (ϕ)

Alcoholic NaOH (g mol/liter)	$[SO_2]_i$ (g mol/liter)	$[SO_2]_i - [SO_2]_0$ (g mol/liter)	N (g mol/sec)	ϕ (experimental)
0.125	0.1134	0.1014	$8.42\text{x}10^{-5}$	3.10
0.250	0.1133	0.1013	$8.87\text{x}10^{-5}$	3.50
0.500	0.1131	0.1011	$1.06\text{x}10^{-4}$	4.20
1.000	0.1125	0.1005	$1.43\text{x}10^{-4}$	5.70
2.000	0.1066	0.0946	$2.15\text{x}10^{-4}$	9.10

T = 298 K; H (concentration: g mol per liter per atm) = 1.2067; P_{SO_2} (partial pressure of SO_2) = 0.10 atm; $[SO_2]_0 = 0.012$; $[SO_2]_i$ = concentration of SO_2 gas at gas-liquid interface; $[SO_2]_0$ = concentration of SO_2 gas in bulk liquid; N = absorption rate of SO_2

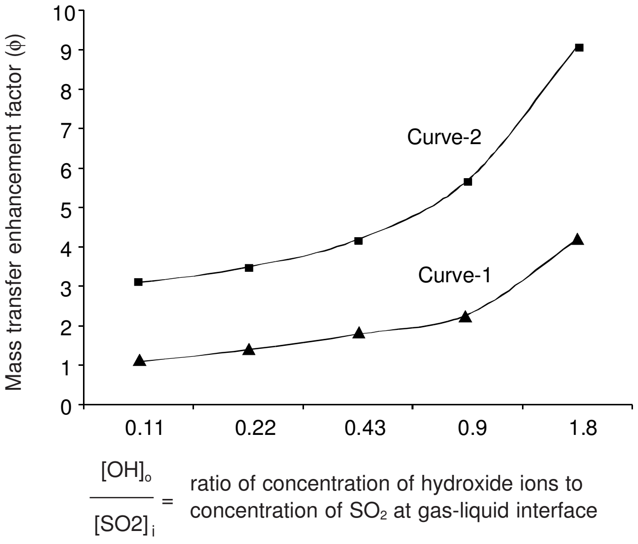


Fig. 2. Comparison of mass transfer enhancement factor (ϕ) values based on present experimental data using alcoholic sodium hydroxide solutions (curve-2) with the values reported by Hikita *et al.* (1977) using aqueous sodium hydroxide (curve-1).

sently. It may also be observed from Fig. 3 that the effect of alcohol as non-aqueous medium was significant as it suppressed [H$^+$] ions, thus resulting in the irreversible reaction. Some researchers (Chang and Rochelle, 1985), however, have suggested that the influence of [H$^+$] ions in the aqueous phase results in reversibility of the absorption reactions.

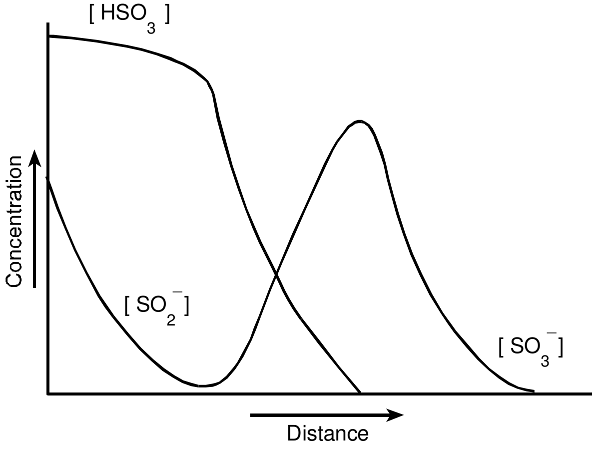


Fig. 3. Concentration profiles for the absorption of sulfur dioxide into alcoholic sodium hydroxide at partial pressure of $SO_2 > 0.05$ atm.

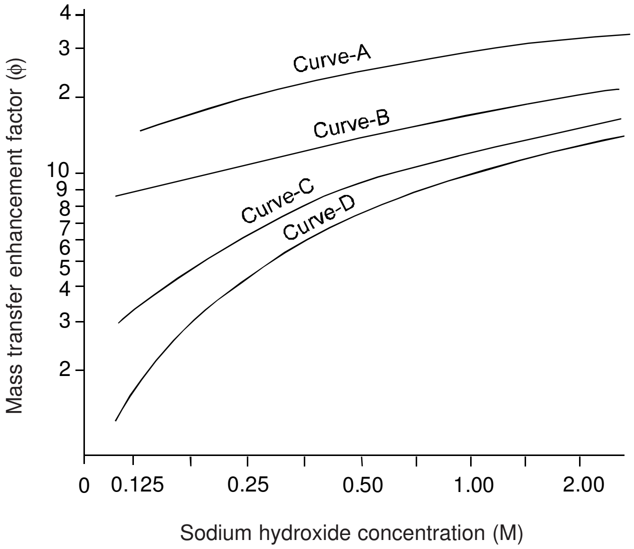


Fig. 4. Comparison of mass transfer enhancement factors predicted from four different models for SO_2/N_2-NaOH system at 0.001 M $[SO_2]_i$: (A) film model with three reversible reactions; (B) surface renewal model with three reversible reactions; (C) present studies for irreversible reactions; (D) penetration model with two irreversible reactions.

Comparison of mass transfer enhancement factors predicted from four different models. A comparison of the present experimental studies for 0.001 M sulfur dioxide in alcoholic sodium hydroxide solution varying from 0.001-2 M, to all previous models is shown in Fig. 4. The results obtained in the present studies, as shown in curve-C, based on surface renewal theory with irreversible reactions involving alcoholic NaOH intermediate complex, fit the data well (Fig. 4).

The results for studies with irreversible reaction in curve-C (Fig. 4) show that alcohol had a profound effect on the absorption of sulfur dioxide resulting in much higher (ϕ) values as compared to penetration model (curve-D). The presence of alcohol was found to suppress the reversible reactions, hydrolysis reaction, and the influence of hydrogen ions on the absorption of SO_2. In addition to these observations, it was also noted during the present investigation of irreversible reactions, that the absorption of sulfur dioxide was much higher and the mass transfer enhancement factor was higher than reported by earlier researchers (Chang and Rochelle, 1985; Hitika *et al.,* 1977), which may be attributed to the presence of alcohol which showed to eliminat reversibility and consequently resulted in higher rates of forward reactions.

References

Bravo-Rodriguez, V., Camacho-Rubio, F., Moya-Vilar, M., Garcia-Lopez, A.I. 2000. Absorption of mixtures of SO_2-N_2 in solutions of NaOH. *Afinidad* **57:** 10-16.

Chang, C.S., Rochelle, G.T. 1985. SO_2 absorption into NaOH and Na_2SO_3 aqueous solutions. *Ind. Engg. Chem. Fundam.* **24:** 7-11.

Chang, C.S., Rochelle, G.T. 1982. Mass transfer enhanced by equilibrium reactions. *Ind. Engg. Chem. Fundam.* **21:** 379-385.

Hikita, H., Asai, S., Tadashi, T. 1977. Absorption of sulfur dioxide into aqueous sodium hydroxide and sodium sulfite solutions. *AIChE Journal* **23:** 538-544.

Hikita, H., Asai, S., Takatsuka, T. 1972. Gas absorption with a two-step instantaneous chemical reaction. *Loughborough Univ. Technol. Chem. Engg. Journal* **4:** 31-40.

Kumar, P.S., Hogendoorn, J.A., Feron, P.H.M., Versteeg, G.F. 2003. Approximate solution to predict the enhancement factor for the reactive absorption of a gas in a liquid flowing through a microporous membrane hollow fiber. *J. Membrane Sci.* **213:** 231-245.

Onda, K., Kobayashi, T., Fujine, M., Takahashi, M. 1971. Behaviour of reaction plane movement by absorbing SO_2 into sodium hydroxide solution. *Chem. Engg. Sci.* **26:** 2009-2012.

Othmer, K. 1964. Molecular diffusion. In: *Encyclopaedia of Chemical Technology,* vol. **13:** p. 109, 2nd edition, Interscience Publishers, John Wiley and Sons Inc., New York, USA.

Pasiuk-Bronikowska, W., Rudzinski, K.J. 1992. Letters to the editor: author's reply to comments by G.T. Rochelle on "absorption of SO_2 into aqueous systems". *Chem. Engg. Sci.* **46:** 3181-2291.

Pasiuk-Bronikowska, W., Rudzinski, K.J. 1991. Absorption of SO_2 into aqueous systems. *Chem. Engg. Sci.* **46:** 2281-2291.

Teramoto, M., Nagamochi, M., Hiramine, S. 1978. Simultaneous absorption of SO_2 and CO_2 in aqueous Na_2SO_3 solutions. *Int. Chem. Engg.* **18:** 250-257.