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EFFECT OF ADDITION OF LIGNINS ON LIQUID PHASE OXIDATION OF SULFIDES WITH OXYGEN

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Abstract

Absorption of oxygen into alkaline solutions of Na_2S and Na_2S_4 and into black liquor diluted with water was studied in the presence of lignin compounds in a stirred vessel with a plane liquid interface. The absorption rates were discussed on the basis of the theory of gas absorption with a chemical reaction. The sulfide oxidation was found to be first-order with respect to reduced sulfur species; while the order in oxygen changed from 0 to 1 at an oxygen concentration in equilibrium with a partial pressure between 0.7 and 0.8 *atm*. Also the apparent rate constants for the oxidation in the presence of lignins were determined as an index of the catalytic activity; it was found that a certain lignin has a significant effect on sulfide oxidation.

1. Introduction

Sulfide often occurs naturally in water, and also occurs in industrial waste water such as waste water from oil refineries, fossile fuel, gas purification plants, pulp mills and so on, which cause significant environmental pollutant. At present, many processes have been proposed for treating wastewater containing sulfide (*11*); however, oxidation of sulfide ions is required for its complete removal.

According to Chen and Morris (*3*), oxidation of aqueous sulfide by O_2 is not a simple reaction, *i. e.* the oxygenation is characterized by an induction period as well as the complex dependence of reaction rates with regard to oxygen and sulfide, the sensitivity of the reaction to impurities, and the number of intermediates and their products. Further, the reaction rate is slow; they gave a rate constant $k=22.2\,(mol/l)^{-0.9}hr^{-1}$ at $pH=11.10$ and 25℃; Chandrasekaeran and

Sharma (*2*) found a second-order reaction rate constant to be 6.170 *l/mol·s* at 75℃.

The present study was made to investigate the effect of the addition of lignin compounds on the rate of sulfide oxidation in aqueous alkaline solutions, *i. e.* the kinetics of the overall absorption of oxygen in the sulfide solutions. It was thought that the above absorption system might prove useful in developing processes for the treatment of wastewater containing sulfide as well as oxidizing black liquors.

2. Experimental

A schematic drawing of the experimental setup is shown in Figure 1. The agitated vessel consisted of a glass tube of 10.6 *cm* i. d. and 15 *cm* length fitted with four baffles and a water jacket. The stirrer for the liquid phase comprised an impeller with six flat blades set as half the liquid depth, mounted on a shaft driven by an electric motor. The vessel was provided with two inlets and two outlets for the gas and liquid phases.

The agitated vessel was first flushed with nitrogen gas and then a 880 *ml* of sodium sulfide solution was introduced in the vessel. The vessel was again flushed with the gas of a given composition for five minutes, which had been saturated with water vapor at 25 ℃. The experimental run was then started by adjusting a stirring speed. After several minutes, the gas flow was stopped and the volumetric uptake of oxygen was measured by a soap-film meter; then the gas was again passed through the vessel and the measurements were repeated at 5-10 *min* intervals for about 80 minutes. The absorption rate of oxygen was determined from only the volumetric rates, using a gas-liquid contact area of 87 cm^2.

The liquids used were aqueous solutions of sodium sulfide (99.9 %, *Wako Chemical Co. Ltd.*) and sodium tetrasulfide (96 %, *Alfa Products Co. Ltd.*). The stock solution of sulfide was prepared by dissolving prewashed crystal of $Na_2S\cdot$

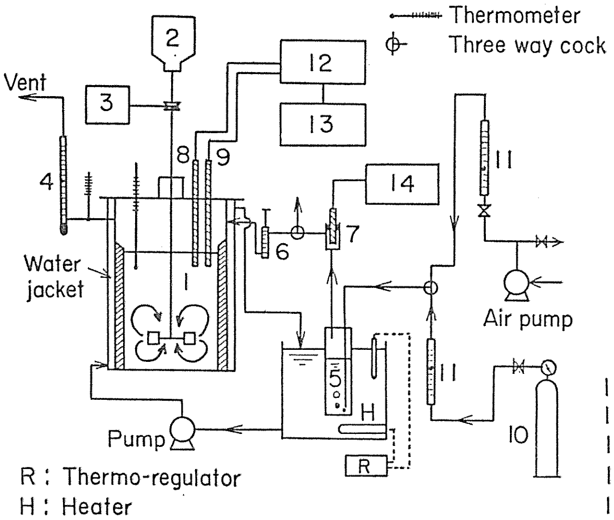

Fig. 1. Schematic diagram of the experimental apparatus.

$9H_2O$ in deaerated distilled water; the concentration was determined by titrating with a standard $AgNO_3$ solution using an Ag^+-S^{2-} ion electrode. While, an aqueous tetrasulfide solution was prepared by dissolving the powder of Na_2S_4 in a deaerated aqueous NaOH solution just before the absorption run.

Additives used were black liquor, five kinds of lignins and Sulfur Black B dye (*SBB*). The black liquor (denote with *BL*) was from *Nagoya Pulp Co. Ltd.*, and the original liquor contained the residue of 62 *wt%* after drying at 90℃. In addition, an oxidized *BL* was prepared by aerating the diluted solution of 8 *wt% BL* for 50 hours at 25℃, and the resulting solution was further diluted with water.

The lignins were as follows: two kinds of the commercial dealkaline lignin of brown powder of 95% grade (denote with *Lignin A*) and of blackish brown powder of 80% grade (denote with *Lignin B*); a kraft lignin (brown powder, Tokai pulp Co. Ltd.); the other lignins were of a sulfite pulp waste from chesnut and a milled wood lignin (*MWL*) from red pine. The latter two lignins were prepared and offered by Prof. Terashima (Nagoya University. Dept. of Agricultural). The sulfite pulp waste was a black solid produced by a $(Ca(OH)_2+SO_2)$ cooking, followed β-naphtylamine treatment; while the *MWL* of a light brown powder was obtained by extraction with a dioxane-water mixture following an alcohol-benzene treatment. All of the lignins used are insoluble in water, but soluble in aqueous NaOH solution.

3. Results and Discussion

3. 1. Determination of liquid phase mass transfer coefficient k_L

Absorption experiments of pure CO_2 and O_2 into water were carried out in a flow and/or batch manner as 25℃. The absorption rates of CO_2 and O_2 in the flow manner were examined in terms of the volumetric uptake of the gas and the change in concentration of the gas absorbed in the liquid stream. The results showed that the liquid film coefficients k_LA for O_2 absorption were expressed by Eq. (1) in the range of the stirring speed n of 1.3 to 3.7 *rps*.

$$k_LA=0.0663n^{0.71} \tag{1}$$

On the other hand, typical data from the volumetric rate of O_2 absorption in the batch manner are shown in Figure 2 as a plot of $\log N_AA$ vs. t. In such a physical absorption, the theoretical rate is expressed by Eq. (2), assuming that the concentration profile in the liquid film is in a quasi-steady state (*10*).

$$N_AA=k_LA(C_i-C_o)\exp(-k_LAt/V_L) \tag{2}$$

where C_O is the initial concentration of solute gas in the liquid phase and V_L is the liquid volume. Using k_LA value from Eq. (1), one obtains a straight line shown in Fig. 2; then the data points are in good agreement with the theoretical line. Thus, in the following experiments, only the volumetric uptake of oxygen by the sulfide solutions with and without additives was measured, the results being discussed on the basis of gas absorption with a chemical reaction.

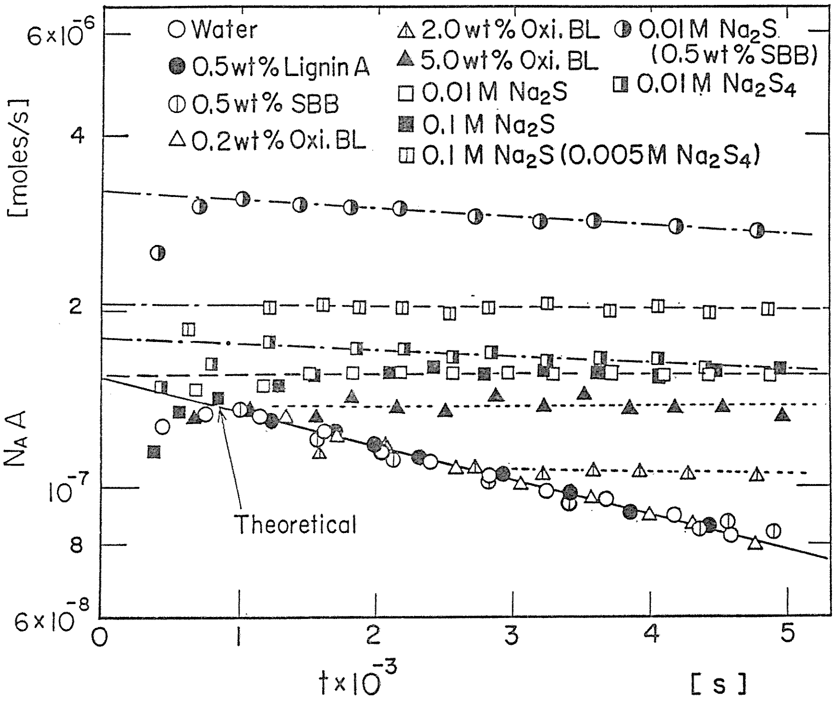

Fig. 2. Effects of contact time and additives on the rate of O_2 absorption into alkaline solutions ($pH=11\sim12.8$, $p_{O_2}=0.975\,atm$, $n=150\,rpm$, 25°C). The solid line represents the theoretical value for water ($C_O=0$) from Eq. (2).

3. 2. *Absorption of* O_2 *into* Na_2S *solutions with and without additive*

Results for both solutions of $0.01\,M$ and $0.1\,M$ Na_2S are also shown in Fig. 2, wherein no effect of sulfide concentration and of contact time t on the absorption rate is found from a dashed line. Such a behavior indicates that a reaction in the liquid bulk is rate determing in the gas absorption process, *i. e.* the oxidation rate is very slow. In addition, the absorption rate N_AA is independent of the contact time in the range measured in the present study. This can be also estimated from a theory based on the gas absorption accompanied by a pseudo-first-order chemical reaction *(10)*.

On the other hand, the result for the $0.01\,M$ Na_2S_4 as polysulfides suggests that a reaction with O_2 takes place within the liquid film and also the concentration of S_4^{2-} in the liquid bulk gradually decreases with t, as shown with a dash-dot line in Fig. 2. Time dependence of N_AA becomes greater as the reactant concentration is lower or the oxidation rate is higher. Thus in the following discussion, we used the extrapolated value of N_AA to $t=0$.

Results for the alkaline solution containing only additive are also shown in Fig. 2. As the figure shows. *Lignin A* as well as *SBB* has no effect on the O_2 absorption, whereas the oxi. *BL* contains a certain component that reacts with oxygen in the liquid bulk, and hence enhances the rate of O_2 absorption. This suggests that reaction equilibria among S_o, S_x^{2-} and OH^- exist in alkaline oxidized black liquors (*6*). According to Sakai et al. (*12*), sulfur black B dyes catalyze the oxidation of Na_2S. The present result also shows such a remarkable effect, as can be seen in Fig. 2. However, taking the molecular structure of *SBB*, $C_{24}H_{17}O_4N_5S_n$ ($n=6\sim8$), into consideration, it is probable that in Na_2S solution the $-S_n-$ bond is cut into S_x^{2-} and the resultant products contribute to the enhancement of absorption rate of O_2.

3. 3. *Absorption of* O_2 *in diluted black liquor*

Original *BL* used in the present work contained total Na^+ of *ca.* 100 *g/l*, and total sulfide of *ca.* 15 *g/l*. Thus the aqueous solution of 2 *wt% BL* corresponds to a solution of $[Na^+]=0.087$ *mol/l* and $[S_x^{2-}]=0.01$ *mol/l*; the viscosity and density are 0.941 *cP* and 1000 kg/m^3 at 25℃, respectively. For the 5 *wt% BL* the viscosity was 1.008 *cP* and therefore the diffusivity of O_2 in the solution would decrease about 11% than that in water (2.15×10^{-5} cm^2/s), according to an equation by Onda et al. (*9*).

For the solubility of O_2 the salting-out effect can not be evaluated in the presence of organic substances as well as some ionic species. Here, assuming the concentration of Na_2SO_4 solution corresponding to the amount of Na^+, we estimated the solubility of O_2 in the *BL* solution as well as Na_2S and Na_2S_4 solutions from an equation of Onda et al. (*8*). As a result, the Henry's law constant for the 5 *wt% BL* was obtained to be $H/H_w=0.912$, where H_w for pure water is 1.239×10^{-6} $mol/cm^3\cdot atm$ at 25℃.

Figure 3 shows the typical results for the *BL* solution, in which log N_AA are plotted against t. Comparing the result for the 2 *wt% BL* with that for 0.01 *M* Na_2S solution shown in Fig. 2, one can also find that black liquors contains a substance which catalyzed the oxidation of sulfides, as was suggested by Ziegelme-

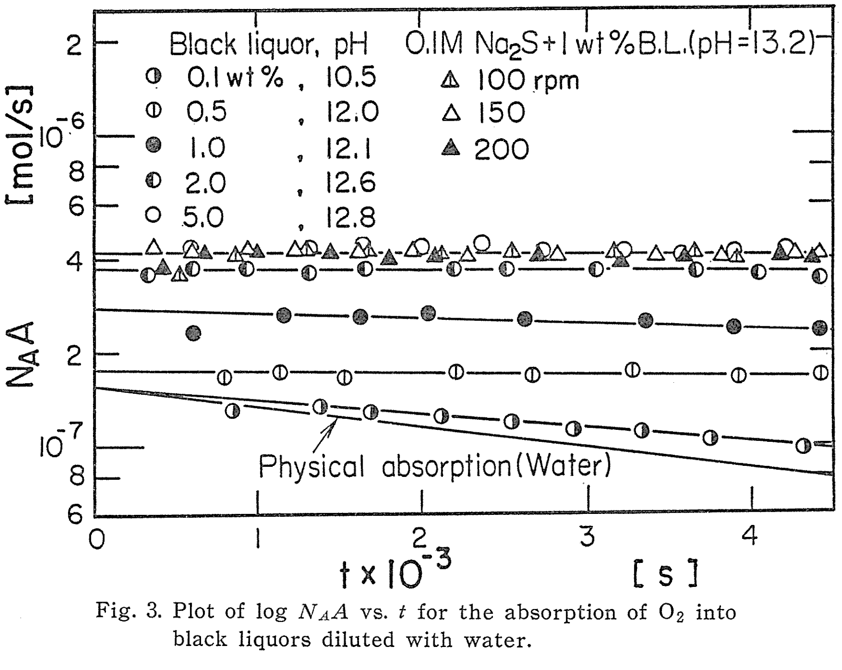

Fig. 3. Plot of log N_AA vs. t for the absorption of O_2 into black liquors diluted with water.

yer and Feischl (*15*), As for the 5*wt% BL* solution, the viscosity is about 1.13 times larger than that of water; hence a lowering in k_L should be brought about. Neverthless, the absorption rates of O_2 in 0.1*M* Na_2S solution containing 1*wt%* of the *BL* were not influenced by the liquid phase stirring speed, as shown with a top line in Fig. 3. From such a discussion, it can be concluded that the kinetics of O_2 absorption into Na_2S solution containing *BL* involved a pseudo-*m*th-order reaction with respect to O_2.

3. 4. *Effect of addition of lignins on the liquid phase oxidation of* Na_2S

Results for the O_2 absorption in 0.1*M* Na_2S solution containing the various lignins are shown in Fig. 4. As the figure shows, the increase in the absorption rates is due to both of the content and sort of the lignin; then *Lignin A* has a catalytic activity similar to that of the kraft lignin on the sulfide oxidation. In addition, there are some similarities in the outside appearance between the two lignins. The red pine *MWL* has less effect on the oxidation, for it is a residue obtained by extraction with a mixture of ethanol and benzene from the milled wood without cooking; hence the molecular weight could be largest among the lignins used in the present work.

Lignins are, in general, complex, aromatic compounds having many functional groups of =O, −OH, −O− and −OMe (*13*). Large molecule of lignins is cut into many segments with lower molecular weight by cooking a raw wood and the

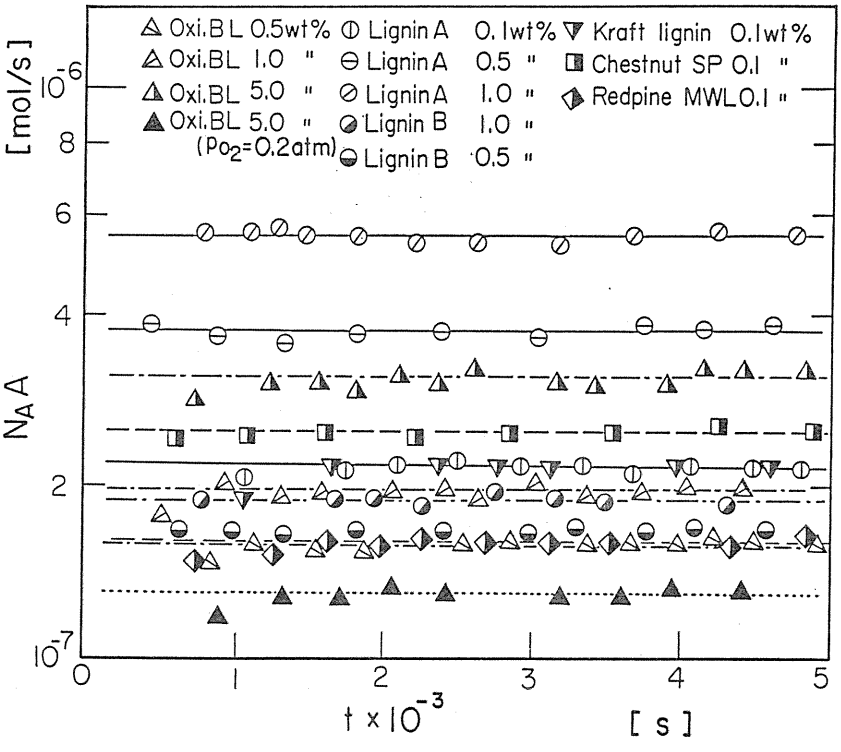

Fig. 4. Effect of the addition of lignin compounds on the rate of O_2 absorption into 0.1*M* Na_2S (*pH*=13.1, p_{O_2}=0.975 *atm*, *n*=150 *rpm*).

resultant lignin becomes soluble in alkaline solutions. Thus, lignins differ in each other in the molecular structure and physical properties, which are attributed to the isolation method as well as raw woods. Having quinone- and hydroquinon-groups in greater or lesser degree, however, lignins might act as a catalyst of the sulfide oxidation: a redox catalyst (*14*). Such an example is found in several desulfurization processes based on liquid phase oxidation of hydrogen sulfide, *i. e.* quinone-type compounds have been used as the catalyst or carrier in the Perox, Stretford and Takahax processes (*5*). The present data also suggest that a certain lignin is useful to enhancing the rate of oxidation of hydrogen sulfide.

3. 5. *Absorption of* O_2 *into polysulfide solution*

Since sodium tetrasulfide is insoluble to water, it was also dissolved in aqueous NaOH solution. Results for the O_2 absorption in the Na_2S_4 solution are shown in Fig. 5 as a plot of log $N_A A$ vs t. As the figure shows, tetrasulfide ion is much liable to be oxidized by O_2 than monosulfide in the presence of lignins. Such a behavior might be responsible for a catalytic activity of poly-sulfide ions on the sulfide oxidation, as was suggested by Bower et al. (*1*). Further, the absorption rate of O_2 depends on the solution pH, increasing with the alkalinity, but showing a maximum at about $pH=13$ in the covered range.

Oxidation of sulfides in alkaline solution is, in general, complex competitive and parallel reaction (*3, 6*), but the main chemistry may be regarded with Eqs. (3), (4) and (5).

$$S^{2-}+\frac{3}{2}O_2 \longrightarrow SO_3^{2-} \tag{3}$$

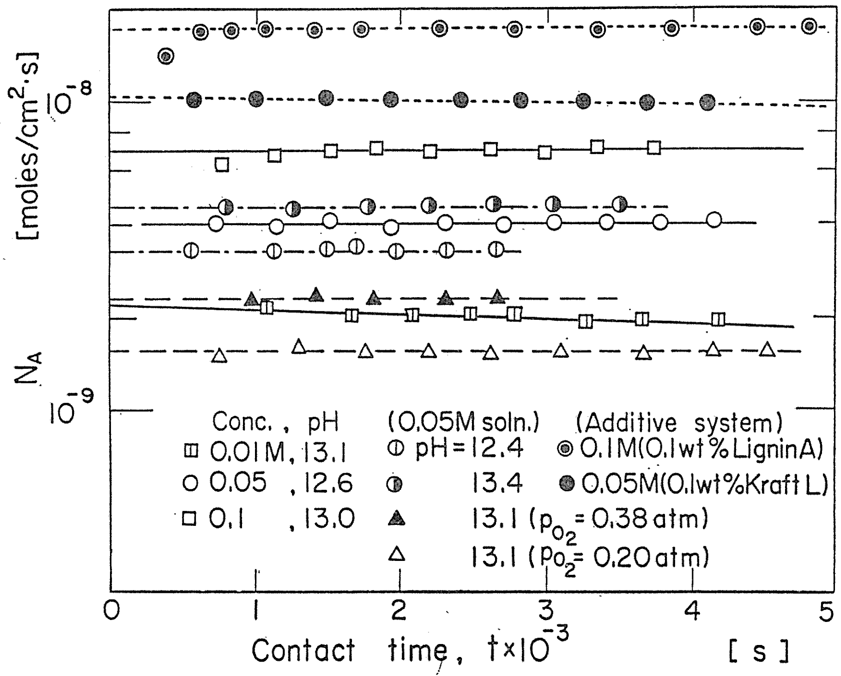

Fig. 5. Plot of log N_A vs. t for the absorption of O_2 into aqueous Na_2S_4 solutions of NaOH in the pH range of 12.6~13.1.

$$S^{2-}+\frac{3}{2}O_2 \longrightarrow \frac{1}{2}S_2O_3^{2-} \tag{4}$$

$$S_x^{2-}+\frac{1}{2}O_2 \longrightarrow xS^\circ \tag{5}$$

Subsequently, these sulfite and thiosulfate are oxidized to sulfate; further a portion of the product S° turns into S^{2-} as follows:

$$4S^\circ+3OH^- \longrightarrow 2S^{2-}+S_2O_3^{2-}+3H^+ \tag{6}$$

$$4S^\circ+4OH^- \longrightarrow 3S^{2-}+SO_4^{2-}+4H^+ \tag{7}$$

O'Brien and Birkner *(7)* and Chen and Morris *(3)* have reported that a high ratio of $[S_x^{2-}]/[O_2]$ leads to the formation of sulfur. Also in the present system, the considerable amount of sulfur particles was observed not only on the liquid surface but also in the liquid bulk during the absorption; the absorption rate of O_2 increased with an increase in the pH value, as mentioned above. The increase in N_A may be attributed to Eqs. (6) and (7); then one could conclude that the absorption process follows a pseudo-mth-order reaction regime. In the following discussion, therefore, we assumed that the absorption rate is not affected by the formation of sulfur, provided that the change in the solution pH is negligible.

4. Kinetics of Sulfide Oxidation by O_2

For gas absorption with an irreversible chemical reaction, it is well known that the film and penetration models predict the same absorption rate when there is no gasphase mass transfer resistance, and give the following equations *(4)*.

$$N_A=\phi k_L C_{Ai} \tag{8}$$

$$\phi=\sqrt{M}\eta/\tanh\sqrt{M}\eta \tag{9}$$

where

$$\sqrt{M}=\sqrt{\left(\frac{2}{m+1}\right)k_{mn}D_A C_{Ai}^{m-1}C_{BO}^{n}}\;/k_L \tag{10}$$

$$\eta=\left(\frac{C_{Bi}}{C_{BO}}\right)^n=\left(\frac{\phi_a-\phi}{\phi_a-1}\right)^n \tag{11}$$

$$\phi_a=\sqrt{\frac{D_A}{D_B}}+\frac{C_{BO}}{\nu C_{Ai}}\sqrt{\frac{D_B}{D_A}} \tag{12}$$

For gas absorption accompanied by a pseudo-mth-order chemical reaction, the absorption rate in the region of $\sqrt{M}>3$ is given by the expression:

$$N_A=\sqrt{\left(\frac{2}{m+1}\right)k_{mn}D_A C_{Ai}^{m+1}C_{BO}^{n}} \tag{13}$$

where k_{mn} is the rate constant for (m, n)th-order reaction, being determined from the observation of N_A with the values of C_{Ai}, D_A, m and n.

4. 1. *Order with respect to oxygen*

In order to determine the value of m, a log-log plot of N_A vs. p_{O_2} was prepared, whose slope is $(m+1)/2$, provided that $\phi(\equiv N_{A obs}/N_A^* = \sqrt{M}) > 3$ and the Henry's law holds. Figure 6 is such plot for alkaline solutions of Na_2S and Na_2S_4 with/without lignins. From the figure, it is evident that there is a sharp bend in these lines at an oxygen partial pressure between 0.7 and 0.8 *atm*, except for the *2wt % BL* solution. The slope of the lines at higher p_{O_2} is 1.0, which accords with gas absorption accompanied by a reaction of first-order in O_2. On the other hand, the slope at lower p_{O_2} is 0.5 in Fig. 6, implying that the absorption is with a zero-order chemical reaction in O_2.

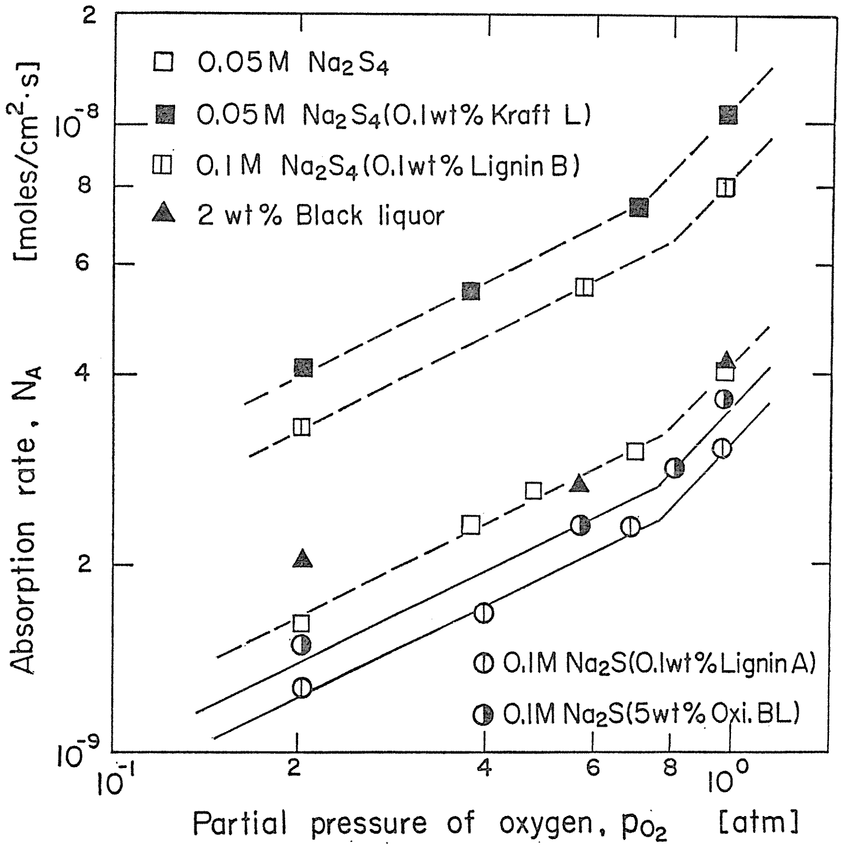

Fig. 6. Plot of N_A for both alkaline solutions of Na_2S and Na_2S_4 with/without lignins and for diluted black liquor as a function of the partial pressure of O_2.

4. 2. *Order with respect to sulfide ion*

Values of N_A/C_{Ai} obtained from the absorption runs using the pure oxygen are plotted in Fig. 7 against C_{Bo}, together with the $\phi-M$ curves calculated from Eq.

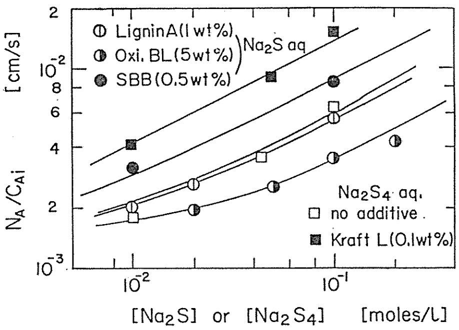

Fig. 7. Plot of N_A/C_{Ai} for alkaline solutions of Na_2S with additives ($pH=11.9\sim13.2$) and Na_2S_4 with/without lignin as a function of the sulfide concentration. The solid lines correspond to the ϕ-M curve with $m=1$ and $n=1$.

(9) by assuming $n=1$ and $\eta=1$. Here the curve was drawn by making it to match with the data points as well as a value of $N_A/C_{Ai}(\equiv k_L=1.45\times10^{-3}cm/s)$ at a smaller value of C_{Bo}. In Fig. 7, the data points fall well on the corresponding $\phi-M$ curves, being satisfied with $n=1$ for both S^{2-} and S^{4-}, even in the presence of lignins.

Furthermore, the value of η was examined in terms of Eqs. (11) and (12) with the observed value of ϕ. The results showed that the maximum deviation from unity was no more than 8%. In this calculation, a value of $1.85\times10^{-5}cm^2/s$ was used as the diffusivity of S_4^{2-} at 25℃, which was obtained on the same diaphragm cell with a Millipore filter as in the previous paper (*10*). Such a small deviation in the value of η suggests that the O_2 absorption systems used in the present study conform to a pseudo-mth-order reaction regime.

4. 3. Lignins content dependency of the rate of sulfide oxidation

Apparent rate of the sulfide oxidation would be given by an empirical expression.

$$-r=k[\text{Additive}]^{\alpha}[O_2]^{m}[S_x^{2-}]^{1.0} \qquad (m=0 \text{ or } 1) \qquad (14)$$

where k [Additive]$^{\alpha}$ represents the apparent $(m+1)$-th order reaction rate constant; [Additive] is the content of lignin ($wt\%$).

Apparent reaction order in the additives α can be found from the same matching method as in the determination of n. Figure 8 shows the additive content dependency of N_A/C_{Ai} for $0.1\,M$ Na_2S solutions at $p_{O_2}=0.975\,atm$, together with the $\phi-M$ curves using $m=1$ and $\alpha=1$ instead of n in Eq. (10), indicating that the apparent rates of the oxidation are directly proportional to each content of the additives. The BL solution also shows analogous behavior, owing to the existence of lignin compounds and sulfide ions in black liquors.

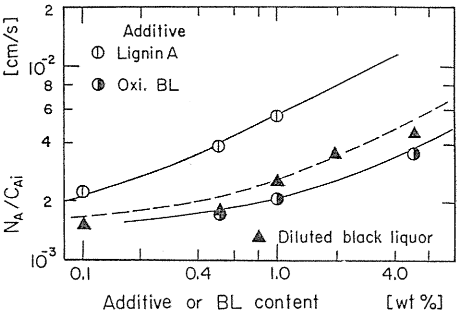

Fig. 8. Plot of N_A/C_{Ai} for 0.1 M Na_2S solution ($pH=12.5\sim13.3$) and diluted black liquor ($pH=10.5\sim12.8$) as a function of the additive content. The lines correspond to the ϕ-M curve with $m=1$ and $n=1$, wherein n is used instead of α of the reaction order in additive.

4. 4. *Apparent rate constants for sulfide oxidation*

Liquid phase reaction of sulfides with oxygen in the presence of lignin compounds was found to be first-order with respect to sulfide and also first-order in oxygen at concentrations higher than about $8\times10^{-4}M$. Several investigators (*2*, *3*, *7*) have reported the kinetics of sulfide oxidation with no additives, though the experimental conditions are different in each other. Chen and Morris (*3*) published an overall order of 1.9 with individual reaction orders 1.34 and 0.56 in S_x^{2-} and O_2, respectively; also O'Brien and Birkner (*7*) have given the order of 1.82 (1.02 in S_x^{2-} and 0.80 in O_2).

Here we can obtain the apparent rate constant for the sulfide oxidation as an index of the catalytic activity of lignins. The *2nd*-order reaction rate constants in the presence of lignins were determined from either the relation between M and C_{BO} for each matching line in Fig. 7 or Eq. (9) with the rate of O_2 absorption. The typical results for the sulfide solutions containing 0.1 *wt%* lignins and 1 *wt%* black liquor are summarized in Table 1.

According to Chen and Morris (*3*), thiosulfate was the principal product in laboratory solutions at a *pH* greater than 8.5, regardless of the sulfide to oxygen ratio. Being compared with their observation, the present results indicate that the oxidation rate of S^{2-} was increased owing to the addition of 0.1 *wt%* lignins by a factor of two to three orders of magnitude. From such a discussion, it can be concluded that lignin compounds are effective as a catalyst for the oxidation of alkaline sulfide solutions by oxygen, and therefore a certain lignin, e. g., kraft lignins have a potential applicability for treating wastewater containing sulfides.

Table 1. Apparent rate constants for oxidation of alkaline solutions of Na_2S and Na_2S_4 with/without lignin compounds, and of black liquor.

Additives	Content (*wt%*)	$k_{av}[m^3/kmol\cdot s]$ for $p_{O_2}>0.8\,atm$
Na_2S: initial conc.$=0.01\sim0.1M$; $pH=11.0\sim13.3$		
Dealkaline lignin (A)	0.1	1.47
Dealkaline lignin (B)	0.1	0.83
Chestnut SP waste	0.1	2.16
Red pine *MWL*	0.1	0.25
Kraft lignin	0.1	1.35
Oxidized black liquor	1.0	1.27
Na_2S_4: initial conc.$=0.01\sim0.1M$; $pH=13.0$		
No additive	0	16.6
Dealkaline lignin (B)	0.1	23.7
Kraft lignin	0.1	87.0
Black liquor: *BL* content$=0.1\sim5.0$*wt%*; $pH=10.5\sim13.2$		
$k_{av}=0.26[wt\%\cdot s]^{-1}$		

5. Conclusion

The rates of O_2 absorption in alkaline solutions of Na_2S and Na_2S_4 are significantly enhanced with addition of lignin compounds. The kinetics of the absorption was discussed on the basis of gas absorption accompanied by an irreversible chemical reaction.

The liquid phase oxidation of sulfides in the presence of lignins is first-order with respect to reduced sulfur species; whereas the apparent order in oxygen was found to change from zero-th to first at the O_2 concentration of *ca.* $8\times10^{-4}M$, provided that the Henry's law constants in the sulfide solutions were the same as that in water. Furthermore, the corresponding apparent rate constants for the sulfide oxidation were determined as an index of the catalytic activity of lignins.

Among the lignin compounds used in the present work, a chestnut sulfite pulp waste was the most effective to the sulfide oxidation. From the practical point of view, kraft lignins are likely to have a potential applicability to the oxidation of sulfides in an industrial wastewater.

Acknowledgment

The authors wish to thank Professor N. Terashima for a gift of lignins and useful suggestions during this work.

Nomenclature

A =gas-liquid contact area, cm^2
C =concentration in liquid phase, mol/l
D =diffusivity, cm^2/s
H =Henry's law constant in $C=Hp$, $mol/l\cdot atm$
k =second-order reaction rate constant, $l/mol\cdot s$
$k_{m,n}$ =$(m, n)th$-order rate constant, $(l/mol)^{m+n-1}s^{-1}$
k_L =liquid film mass transfer coefficient, cm/s
M =parameter defined by Eq. (10)
m =reaction order with respect to dissolved gas species
N_A =absorption rate of gas, $mol/cm^2\cdot s$
n =liquid phase stirring speed (s^{-1}), or reaction order with respect to liquid phase reactant
p =partial pressure, atm
r =reaction rate, $mol/l\cdot s$
t =contacting time, s

Greek symbols

α =reaction order with respect to additive
η =parameter defined by Eq. (11)
ν =stoichiometric coefficient
ϕ =enhancement factor for mass transfer without reaction

Subscripts

A =dissolved gas (O_2)

B =liquid phase reactant (S_x^{2-})
i =gas-liquid interface
O =liquid bulk
W =water

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