

THE INFLUENCE OF ETHYLENE GLYCOL ON THE KINETICS OF ATMOSPHERIC OXIDATION OF DISSOLVED SO₂ CATALYSED BY CoO IN ALKALINE MEDIUM.

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ABSTRACT :

The purpose of present work was to study the influence of Ethylene glycol on CoO catalysed autoxidation of S(IV) in alkaline medium has been studied for acidified atmospheric water. Based on the observed results and inhibition parameters following rate law and free radical mechanism has been proposed. The order of the reaction and rate constants were calculated and the reaction was found to be pseudo first order in all case. The effect of temperature and pH are also discussed. We report that Ethylene glycol is a good inhibitor for SO₂ Oxidation in the pH range 7.5 to 8.50. The value of apparent activation energy (E_a) was given by Arrhenius equation ($K = A \cdot e^{-E_a/Rt}$).

$$-\frac{d[S(IV)]}{dt} = \frac{(k_1 + k_2 [CoO]) [S(IV)]}{1 + B [E.G]}$$

Keywords: Kinetics; Inhibition; Catalysis; Ethylene glycol(E.G); SO₂; CoO; Sulfur(IV); Autoxidation.

INTRODUCTION :

Atmospheric oxidation of sulfur (IV) in the recent past and large number of studies carried out in aerosols and in bulk aqueous phase. The oxidation of SO₂ into acid sulphate is the major cause of atmospheric acid precipitation. It is generally agreed that the gas phase oxidation, including photochemical oxidation by ozone and hydrogen peroxide and oxidation by O₂ in aqueous phase catalysed by trace metal ions and by suspended particulate matter (SPM). Due to its surface activity they are the major contributors to the acid formation [1,2].

The transition metal ions play an important role in acidification of aqueous sulfur dioxide in acid rain chemistry. Transition metal ions and their complexes present in atmospheric liquid water are considered to be potential catalysts in the autoxidation of S(IV) oxides [3,4]. The atmospheric reactions of SO₂ and NO_x etc. are major acid rain precursors and responsible for acidification of various forms of atmospheric water [5]. Oxidation caused by O₂ aqueous

phase catalysed by dissolved trace metal ions and by suspended particulate matter. Which are produced in the atmosphere by photochemical reactions and oxidation by O₂ in aqueous phase catalysed by dissolved trace metal. The backbone of the atmospheric chemistry is made by the subsequent photochemical and thermal reaction of these species in gas and aqueous phases[6].

In this connection, the catalytic role of several metal oxides such as CoO [7], Co₂O₃[8], Ni₂O₃[9], CuO [10], MnO₂[11] and Cu₂O [12] in acidic medium has been examined in detail. In the case of the first five oxides, the kinetics agreed with the rate law (1).

$$-d[S(IV)]/dt = (k_1 + k_2[H^+]^{-1})[Catalyst] [S(IV)] \dots \dots \dots (1)$$

Where k_1 and k_2 are the rate constant for the autoxidation of HSO₃⁻ and SO₃²⁻ respectively.

An interesting feature of many radical reactions is rate inhibition by organics such as ethanol due to scavenging of oxysulfur radicals involved in radical autoxidation and details of mechanism are available in papers [13-18] and reviews [19-22]. The inhibiting effect of alcohol on the CoO, Co₂O₃ and Ni₂O₃ catalysed autoxidation reaction in alkaline medium and proposed a radical mechanism for CoO and Co₂O₃. Biglow [23], (1898) Aleya and Backstrom [24] studied the inhibiting effect of the aliphatic alcohol such as ethanol, isopropanol, secondary butanol and benzyl alcohol on the oxidation of sodium sulphite in alkaline conditions.

An interesting feature of many radical reactions is that, the reaction rate is inhibited by organics such as acetic acid, oxalic acid[25], alcohols[26], carboxylic acid[27] and ammonia, formic acid, aniline, benzamide, sodium benzoate[28-30], ascorbic acid[31], organic compounds[32], VOCs[33] and diesel truck particles[34].

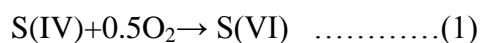
So far inhibiting effect of Ethylene glycol on the CoO catalysed autoxidation of aqueous sulfur dioxide is not studied. Very few studies available on the role of organics on the cobalt oxide catalysed autoxidation of S(IV) in aqueous heterogenous medium. In indian sub-continent, the pH of the rain water lies in the range 6.5-8.5. This necessitates the study of autoxidation of S(IV) in alkaline medium pH range 7.50 - 8.50 and the effect of Ethylene glycol has been studies in alkaline media to delineate the nature of the mechanism.

EXPERIMENTAL:

The experimental procedure was exactly the same as described earlier[35,36] and is briefly given here. All chemicals used were of reagent grade and their solutions were prepared in double distilled water. The reactions were conducted in 0.15-L Erlenmeyer flasks, open to air and to allow the passage of atmospheric oxygen. The flask was placed in a beaker, which had an inlet at the lower part and an outlet at the upper part for circulating thermostatic water for maintaining the desired temperature, $30 \pm 0.1^\circ\text{C}$. The reactions were initiated by adding the desired volume of standard Na_2SO_3 solution to the reaction mixture containing other additives such as buffer and catalyst oxide. The reaction mixture was stirred continuously and magnetically at 1600 ± 100 rpm to allow the passage of atmospheric oxygen and to save the reaction from becoming oxygen mass transfer controlled. The kinetics were studied in buffered medium, in which the pH remained fixed throughout the entire course of reaction. For this purpose, 10 cm^3 of buffer made from Na_2HPO_4 (0.08 mol L^{-1}) and KH_2PO_4 (0.02 mol L^{-1}) alkaline medium were used (total volume 100 m^3) for obtaining the desired pH. The kinetics were followed by withdrawing the aliquot samples periodically and titrating the unreacted S(IV) iodometrically in slightly alkaline medium as described earlier. The reproducibility of the replicate measurements was generally better than $\pm 10\%$. All calculations were performed in MS Excel.

PRODUCT ANALYSIS:

The qualitative tests showed Sulphate to be the only oxidation product. For quantitative analysis, the reaction mixtures containing catalyst and S(IV) in appropriately buffered solutions were constantly stirred for a sufficiently long time so as to ensure complete oxidation of Sulfur (IV). When the reaction was complete, CoO was filtered out and Sulphate was estimated gravimetrically by precipitating Sulphate ions as BaSO_4 using standard procedure[37]. The product analysis showed there recovery of Sulphate to be $98 \pm 2\%$ in all cases in agreement with Eq.(1)



RESULTS:

Preliminary Investigation:

The kinetics of both uncatalysed and CoO catalysed reaction were studied in alkaline medium in the pH range 7.5 to 8.50. In both cases, the kinetics was first order in [S(IV)] and the treatment of kinetics data is based on the determination of first order rate constant k_1 from $\log [S(IV)]$ versus time (t), plots as shown in Fig.1.

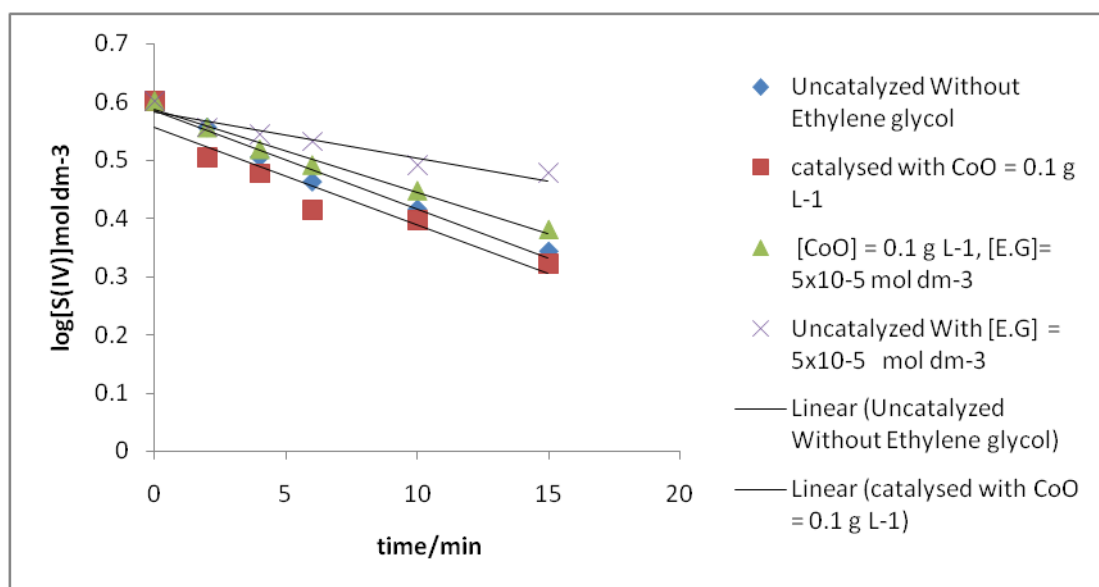


Fig.1.The disappearance of [S(IV)] with time in air saturated suspensions at [S(IV)] = $2 \times 10^{-3} \text{ mol L}^{-1}$, at 30°C and $\text{pH}=7.50$

Uncatalysed reaction: In this study the reaction was studied without adding CoO.

Dependence of sulphite:

The detailed dependence of the reaction rate on [S(IV)] was studied by varying it in the range 1×10^{-3} to $8 \times 10^{-3} \text{ mol dm}^{-3}$ at $\text{pH} = 7.50$, $\text{time} = 30^\circ\text{C}$ in phosphate buffer medium.

The kinetics was found to be pseudo first order in [S(IV)] as shown in Fig.1, $\log [S(IV)]$ v/s time plots were linear. The Value of first order rate constant, k_1 are given in Table- 1, are seen to be independent of [S(IV)] and are in agreement with the rate law (2):

$$-d[S(IV)]/dt = k_1[S(IV)] \dots \dots \dots (2)$$

Table-1: The values of k_1 for uncatalysed reaction at different $[S(IV)]$ at pH = 7.50 and

Time = 30°C

| | | | | | |
|--------------------------------------|-------|-------|-------|-------|-------|
| S(IV) mol L⁻¹ | 0.001 | 0.002 | 0.004 | 0.006 | 0.008 |
| 10⁴ k₁s | 6.837 | 6.496 | 6.332 | 6.706 | 6.117 |

[Ethylene glycol] dependence:

The major aim of this study was to examine the effect of organic inhibitors on the reaction rate, Ethylene glycol was chosen as the one organic compound. On increasing the concentration of Ethylene glycol from 3×10^{-6} to $5 \times 10^{-3} \text{ mol L}^{-1}$, the rate of reaction decreased. However, the nature of the $[S(IV)]$ dependence in presence of Ethylene glycol did not change and remained first order. The first order rate constant k_{inh} ,

Were defined by rate law(3)

$$-d[S(IV)]/dt = k_{inh}[S(IV)] \dots \dots \dots (3)$$

The values of k_{inh} decreased with increase in Ethylene glycol in agreement with the rate law.

$$k_{inh} = k_1/(1+B[E.G]) \dots \dots \dots (4)$$

Where B is inhibition parameter for rate inhibition by Ethylene glycol.

The equation (4) on rearrangement becomes-

$$1/k_{inh} = 1/k_1 + B[E.G]/k_1 \dots \dots \dots (5)$$

In accordance with Eq.(5), the plot of $1/k_{inh}$ versus $[E.G]$ found to be linear with a non zero intercept, Fig.2.

Table-2: The values of k_{inh} at different $[E.G]$ at pH = 7.50, time= 30°C

| | | | | | | | | | |
|------------------------------------------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| [E.G]mol dm⁻³ | 3×10^{-6} | 7×10^{-6} | 2×10^{-5} | 5×10^{-5} | 8×10^{-5} | 4×10^{-4} | 6×10^{-4} | 3×10^{-3} | 5×10^{-3} |
| 10⁴ k_{inh} s⁻¹ | 7.73 | 4.76 | 3.83 | 3.01 | 2.70 | 2.03 | 1.69 | 0.78 | 0.52 |
| 1/k_{inh} s | 1294 | 2101 | 2611 | 3322 | 3704 | 4926 | 5917 | 12820 | 19230 |

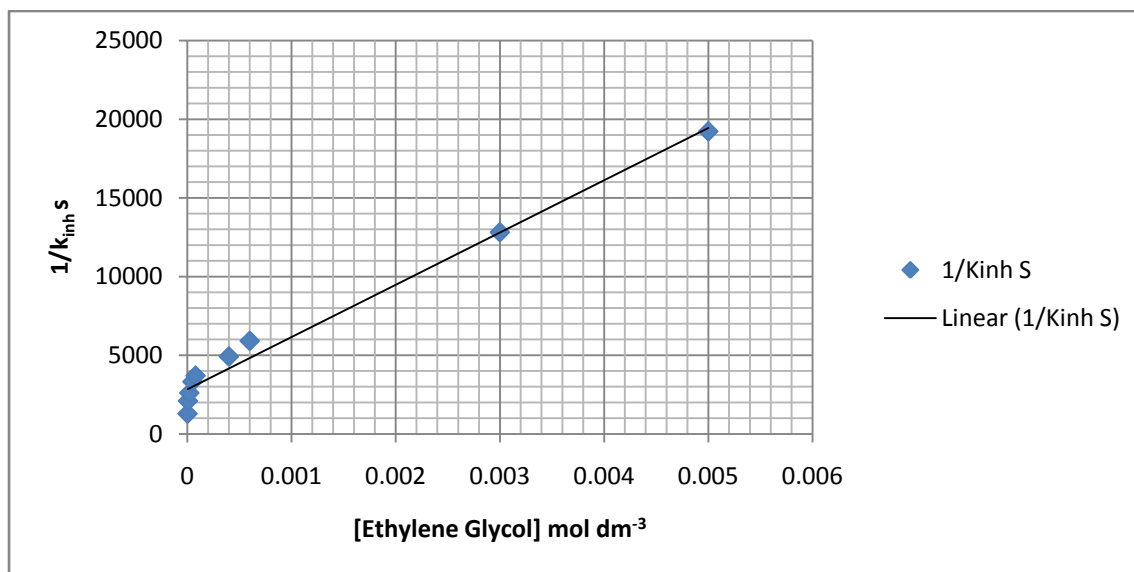


Fig.2. Effect of Ethylene glycol at $[S(IV)] = 2 \times 10^{-3} \text{ mol L}^{-1}$ and at 30°C , in phosphate buffered medium.

At pH =7.50, and 30°C the values of intercepts $1/k_1$ and slope (B/k_1) were found to be $3.1 \times 10^3 \text{ s}$ & $3.2 \times 10^6 \text{ mol}^{-1} \text{ L s}$ From these values the value of inhibition parameter B was found to be $1.0 \times 10^3 \text{ mol}^{-1} \text{ L}$.

CoO - Catalysed reaction:

At first the kinetics of CoO catalysed reaction in the absence of inhibitor was studied.

[S(IV)] variation:

$[S(IV)]$ was varied from 1×10^{-3} to $10 \times 10^{-3} \text{ mol L}^{-1}$ at two different but fixed $[\text{CoO}]$ of 0.1 and 0.2 g L^{-1} was carried out at $\text{pH} = 7.50$ and $\text{time} = 30^\circ\text{C}$ the results show that first order in $[S(IV)]$ plots were linear.

[CoO] variation :

The effect of $[\text{CoO}]$ on the rate was studied and the values of first order rate constants k_{cat} for S(IV) autoxidation was determined at different $[\text{CoO}]$, $\text{pH} = 7.50$ and $\text{time} = 30^\circ\text{C}$. The results of k_{cat} are given in Table 3.

Table-3: The value of k_{cat} at different $[CoO]$ at $S(IV)] = 2 \times 10^{-3} \text{ mol L}^{-1}$, $pH = 7.50$, $time = 30^\circ C$

| | | | | | |
|-----------------------|------|------|-------|-------|-------|
| $[CoO](g L^{-1})$ | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |
| $10^4 k_{cat} s^{-1}$ | 7.06 | 9.87 | 12.30 | 16.11 | 20.33 |

$$-d[S(IV)]/dt = k_{cat}[S(IV)] = k_1 + k_2[CoO] [S(IV)] \dots \dots \dots (6)$$

$$K_{cat} = k_1 + k_2[CoO] \dots \dots \dots (7)$$

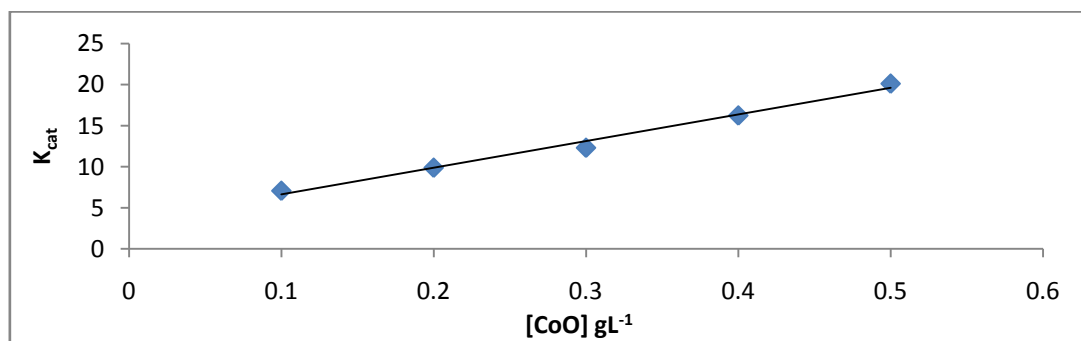


Fig. 3. Effect of CoO at $[S(IV)] = 2 \times 10^{-3} \text{ mol L}^{-1}$, $pH=7.50$ and $t= 30^\circ C$, in phosphate buffered medium.

Variation of pH:

Variation of pH in the range 7.50 to 8.50 in phosphate buffer medium was studied at $S(IV)=2 \times 10^{-3}$, $[CoO]=0.1 \text{ gL}^{-1}$, $[E.G]=5 \times 10^{-5}$ at $t=30^\circ C$ and the result show that be reaction is independent of pH (Table-3). The effect of [buffer] was examined by varying the concentration of both Na_2HPO_4 and KH_2PO_4 in such a way that the ratio $[Na_2HPO_4] / [KH_2PO_4]$ remained same, So that pH remained fixed. The values showed that the rate of the reaction to be insensitive to the buffer concentration.

Table-4: The k_{cat} values at different pH at $CoO=0.1gm$, $[E.G] = 5 \times 10^{-5}$, time = $30^{\circ}C$.

| | | | | |
|-----------------------|------|------|------|------|
| pH | 7.50 | 7.62 | 8.10 | 8.50 |
| $10^4 k_{cat} s^{-1}$ | 5.43 | 5.89 | 6.65 | 7.52 |

Rate law in the presence of Ethylene glycol:

A detailed study of dependence of rate on $[S(IV)]$, $[CoO]$ and pH on the reaction in the presence of Ethylene glycol revealed that the kinetics remain first order both in $[S(IV)]$ and $[CoO]$ and independent of pH in agreement with the following rate law. By increasing the Ethylene glycol concentration the rate decelerates *i.e.*, inhibition occurs.

The results are shown in Table and the effect of $[CoO]$ in the presence of Ethylene glycol is shown in Figure-3. The dependence of observed results for the reaction follows the following rate law. Eq.(8).

$$-d[S(IV)]/dt = (k_1+k_2[[CoO]) [S(IV)]/1 + B[E.G].....(8)$$

Where ,

$$k_{inh} = (k_1+k_2[CoO])/1+B[E.G] = k_{cat}/1 +B[E.G].....(9)$$

$$1/k_{inh} = 1+B[E.G]/k_{cat}.....(10)$$

$$1/k_{inh} = 1/ k_{cat} + B [E.G]/ k_{cat},.....(11)$$

A plot between $[CoO]$ vs first order rate constant is linear Figure-4.with intercept and slope.

Table-5. The Variation of CoO at $[E.G]=5 \times 10^{-5}$, $[S(IV)] = 2 \times 10^{-3} mol L^{-1}$, $t=30^{\circ}C$, pH = 7.50

| | | | | | |
|-----------------------|------|------|------|-------|-------|
| $[CoO](g L^{-1})$ | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |
| $10^4 k_{cat} s^{-1}$ | 5.43 | 8.06 | 9.51 | 10.22 | 14.70 |

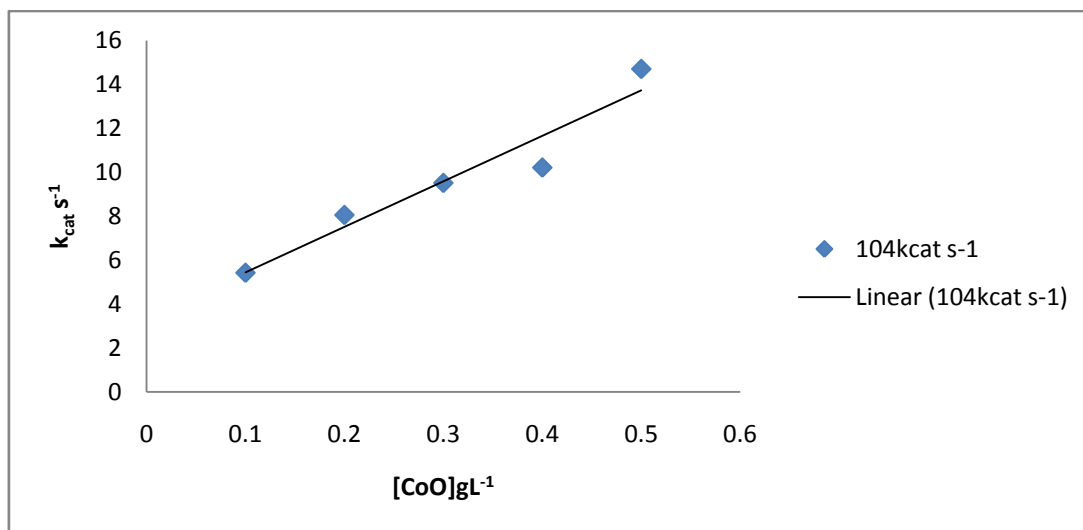


Fig. 4 .Effect of [CoO] at S(IV) = $2 \times 10^{-3} \text{ mol L}^{-1}$, [E.G] = 5×10^{-5} , pH = 7.50, and at 30°C, in phosphate buffered medium .

Table-6. The variation of [E.G] at [S(IV)] = $2 \times 10^{-3} \text{ mol L}^{-1}$, [CoO] = 0.1 g L^{-1} , time=30°C, pH = 7.50

| [E.G]mol dm ⁻³ | 3×10^{-6} | 7×10^{-6} | 2×10^{-5} | 5×10^{-5} | 8×10^{-5} | 4×10^{-4} | 6×10^{-4} | 3×10^{-3} | 5×10^{-3} |
|------------------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| $10^{-4} \text{ kinhs}^{-1}$ | 9.85 | 6.91 | 5.90 | 5.43 | 4.67 | 3.47 | 2.58 | 1.16 | 0.79 |
| $1/K_{inh}S$ | 1015 | 1447 | 1695 | 1842 | 2141 | 2882 | 3876 | 8621 | 12658 |

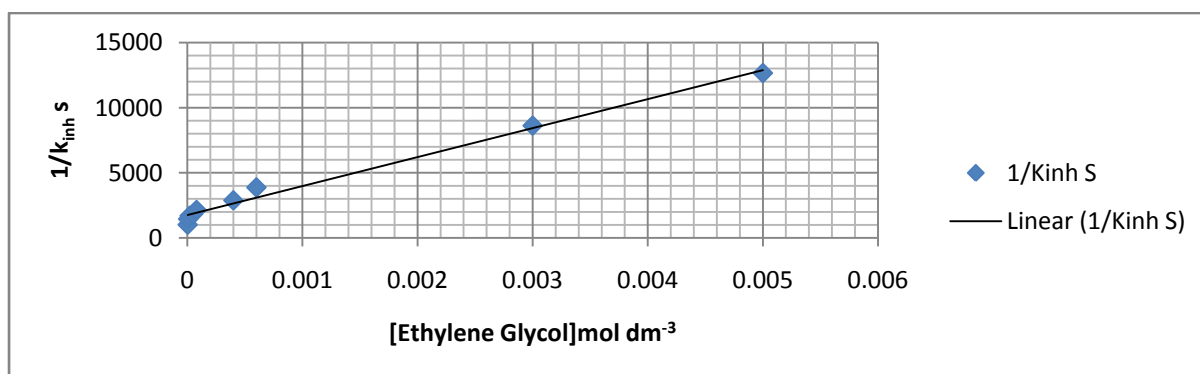


Fig. 5.Effect of [E.G] at S(IV) = $2 \times 10^{-3} \text{ mol L}^{-1}$, CoO= 0.1 g L^{-1} , pH = 7.50, and at 30°C, in phosphate buffered medium .

A plot between $1/k_{inh}$ vs $[E.G]$ is linear with intercept= $1/k_{cat}$ and slope= B/k_{cat} from the graph these value found to be 1.5×10^3 s and $3.2 \times 10^6 \text{ mol}^{-1} \text{ L s}$ respectively. From these values the values of inhibition parameter B can be calculated, inhibition parameter $B = \text{slope/intercept}$ that is $B = 2.1 \times 10^3 \text{ mol}^{-1} \text{ L}$.

Effect of temperature :

The values of k_{obs} were determined at three different temperatures in minute the range 30°C to 40°C . The results are given in table-7. These values yielded an apparent empirical energy of activation determined to be **21.63 KJ mol⁻¹**.

Table-7 Effect of temperature on k_{obs} air saturated suspensions at $[S(IV)] = 2 \times 10^{-3} \text{ mol L}^{-1}$, $[CoO] = 0.1 \text{ g L}^{-1}$, $[E.G] = 5 \times 10^{-5} \text{ mol L}^{-1}$, time= 30°C and pH = 7.50

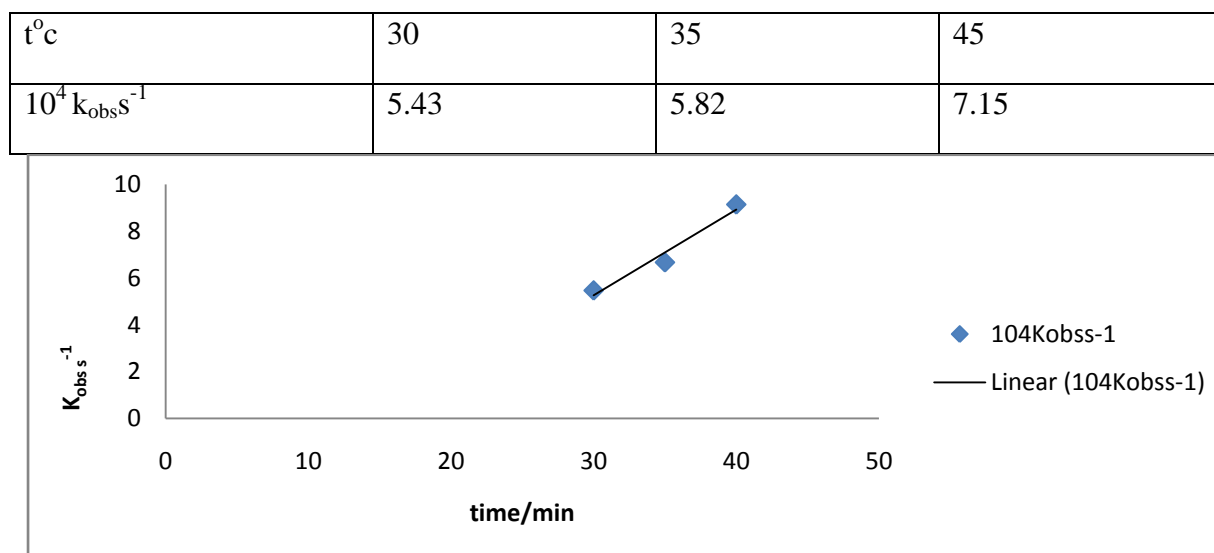
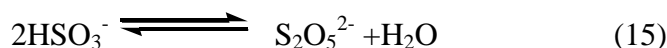
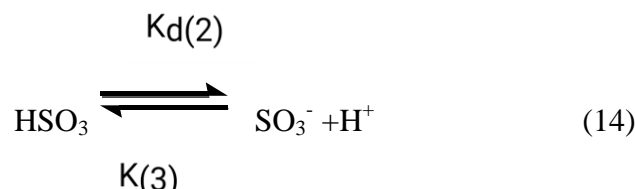


Fig.6. Effect of temperature at $[S(IV)] = 2 \times 10^{-3} \text{ mol L}^{-1}$, $[CoO] = 0.1 \text{ g L}^{-1}$, $[E.G] = 5 \times 10^{-5} \text{ mol L}^{-1}$, time= 30°C and pH = 7.50

DISCUSSION:

In aqueous solution SO_2 is present in four forms, $\text{SO}_2 \cdot \text{H}_2\text{O}$, HSO_3^- , SO_3^{2-} and $\text{S}_2\text{O}_5^{2-}$ Governed by the following equations.



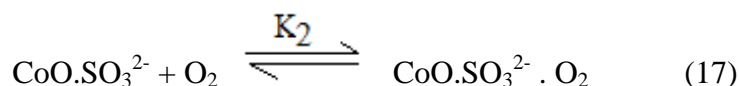


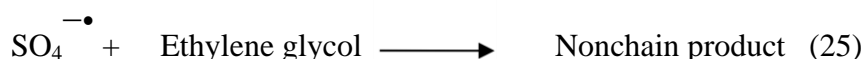
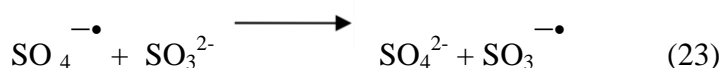
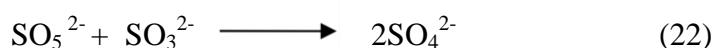
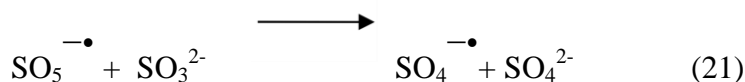
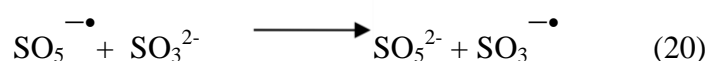
K_H is Henry's and K_1 , K_2 are acid dissociation constants, $K_{(3)}$ is the formation constant for $\text{S}_2\text{O}_5^{2-}$ at 25°C the values are $K_H = 1.23 \text{ mol L}^{-1} \text{ atm}^{-1}$, $K_{d(1)} = 1.4 \times 10^{-2}$, $K_{d(2)} = 6.24 \times 10^{-8}$ and $K_{(3)} = 7.6 \times 10^{-2}$. In this experimental study in pH range (7.5-8.5), S(IV) would be largely present as SO_3^{2-} .

Since the rate of reaction is nearly independent of pH, we have considered only SO_3^{2-} species to be reactive in the subsequently. In several transition metal oxide catalysed heterogeneous aqueous phase auto oxidation reactions of S(IV), the formation of surficial complexes by adsorption of S(IV) and O_2 on the particle surface and oxidation of S(IV) take place through the intervention of multiple oxidation states has been proposed.

In the present study, the dependence of oxygen shows that the formation of surficial complex by adsorption of O_2 on the particle surface of CoO through the fast step. In alkaline medium the rate of CoO catalysed reaction is highly decelerated by the addition of Ethylene glycol like that of ethanol reported by Gupta et al [38], this indicates the operation of a radical mechanism involving oxysulphur free radicals, like SO_3^- , SO_4^- and SO_5^- . The inhibition is caused through the scavenging SO_4^- by inhibitors such as ethanol and benzene etc.

Based on the observed results including the inhibition by Ethylene glycol, the following radical mechanism is proposed which similar to that proposed by Sameena et al. and Mudgal et al. [39]. In the ethanol inhibition of the CoO catalysed reaction.





In the mechanism, no role is assigned to O_2^- , which is also known to react with sulphur(IV) slowly. It may disproportionate to form H_2O_2 and O_2 or may be scavenged by impurities. By assuming long chain hypothesis and steady state approximation $d[\text{SO}_3^-]/dt$, $d[\text{SO}_4^-]/dt$, and $d[\text{SO}_5^-]/dt$ to zero. It can be shown that the rate of initiation is equal to the rate of termination.

$$k_1[\text{CoO}(\text{SO}_3^{2-})(\text{O}_2)] = \{k_7[\text{X}] + k_8[\text{E.G}]\}[\text{SO}_4^-] \dots \dots (26)$$

Since the reaction is completely stopped in the presence of [Ethylene glycol] at $1 \times 10^{-3} \text{ mol}^{-1}$, so the steps (18) and (22) appear to be unimportant. The contribution of propagation reaction (Eq. 21) been significant in the CoO catalysed. Reaction where the autoxidation reaction should have occurred even in the presence of high Ethylene glycol concentration But

this is not true and the reaction is completed seized in the presence of high concentration of Ethylene glycol. This led us to ignore the step (Eq.21) and assume only the rate of reaction given by equation- (27).

$$-d[S(IV)]/dt = R_{cat} = k_6[SO_4^-][SO_3^{2-}] \dots\dots\dots(27)$$

By substituting the value of (SO_4^-) we get

$$R_{cat} = \frac{k_6 k_1 [CoO \cdot SO_3^{2-} \cdot O_2][SO_3^{2-}]}{k_7[x] + k_8 [E.G]} \dots\dots\dots(28)$$

From equilibrium Eq. 13 and Eq. 14

$$R_{cat} = \frac{k_6 K_1 K_2 [CoO][S(IV)][O_2]}{\{1+k_1[S(IV)]k_7[x] + k_8 [E.G]\}} \dots\dots\dots(29)$$

At fixed O_2 , replacing $k_6 K_1 K_2 [O_2]$ by k^1 we get

$$R_{cat} = \frac{k^1 [CoO][S(IV)]}{\{1+k_1[S(IV)]k_7[x] + k_8 [E.G]\}} \dots\dots(30)$$

Since we observe a clean cut first order in $[S(IV)]$, The value of $K_1[S(IV)] \ll 1$ so the above rate law can be reduce to

$$R_{cat} = \frac{k^1 [CoO][S(IV)]}{k_7[x] + k_8 [E.G]} \dots\dots(31)$$

The calculated value of **inhibition constant B is $2.1 \times 10^3 \text{ mol}^{-1} \text{ L}$** . Therefore, it is concluded that Ethylene glycol acts as a free radical scavenger in the CoO catalysed autoxidation of aqueous sulfur dioxide in alkaline medium, and a free radical mechanism is operated in this system[40-46]

CONCLUSION:

The role of Ethylene glycol act as an inhibitor in CoO catalysed autoxidation of SO₂ in alkaline medium has been found and based on the observed results rate law a free radical mechanism has been proposed,

$$-d[S(IV)]/dt = (k_1+k_2[CoO])[S(IV)]/1 + [E.G]$$

Based on the experimental results, rate constants and orders of the reactions were determined .The reaction order in SO₂ was pseudo-first order for both reactions in the presence and absence of Ethylene glycol. The effect of pH on SO₂ oxidation in the presence of CoO and Ethylene glycol has been studied and found rate of the SO₂ oxidation independent of the pH change during the reaction .The effect of temperature of the solution on SO₂ oxidation catalysed by CoO in the presence of Ethylene glycol was discussed.

By the plotting a graph between logk v/s 1/T yield us an apparent empirical energy of activation 21.63 kJ mol⁻¹ for the reaction. Our results conclusively shows that Ethylene glycol studied here act as an inhibitor not a catalyst for SO₂ autoxidation.

The values of inhibition factor (B) for both uncatalsed and CoO catalysed autoxidation of SO₂ in the presence of Ethylene glycol are 1.0x10³ and 2.1x10³ respectively which coincide with earlier workers who found inhibition factors in the range of 10³-10⁴.

FUTURE SCOPE:

The results are useful for modeling rain water acidity and therefore a great use of meteorology and atmospheric chemistry. This study is important in understanding the mechanism of the atmospheric oxidation of S(IV) by O₂.Ethylene glycol is able to inhibit the oxidation of SO₂ so by using it in the atmosphere rain water acidity can be controlled.

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