



## Oxidation of 3-Methylindole by Potassium bromate in Acetic acid Medium - A Kinetic and Corrosion Investigation

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### Abstract

Kinetics of oxidation of 3-Methylindole by  $\text{KBrO}_3$  in aqueous acetic acid medium has been investigated. The reaction follows a total second order, first order each with respect to [3-Methylindole] and  $[\text{KBrO}_3]$ . The rate of the reaction was not affected by added  $[\text{H}^+]$ . Variation of ionic strength ( $\mu$ ) had no influence on the rate. Increase of percentage of acetic acid decreased the rate. Absence of any polymerization indicated a no radical pathway. Activation and thermodynamic parameters have been computed. A suitable kinetic mechanism based on these observations is proposed. The reactivity of  $\text{KBrO}_3$  towards 3-Methylindole was found to be higher than that with peroxomonosulphate and peroxodisulphate. The corrosive studies are performed using weight loss method by dipping the mild steel panels in 1M HCl solution.

**Keywords:** Kinetics, Mechanism, Oxidation, 3-Methylindole, Potassium bromate ( $\text{KBrO}_3$ ), Corrosion.

### 1. INTRODUCTION

Indole occurs in coal-tar, jasmine flowers and orange blossoms. Indole is an electron rich hetero-atomic, nitrogen containing compound which appears in various naturally occurring compounds such as alkaloids and tryptophan metabolites [1]. Tryptophan is an essential amino acid and as such is a constituent of most proteins; it also serves as a biosynthetic precursor for a wide variety of indole-containing metabolites, which are involved in a large and essential number of physiological functions.

Indoles and bromo indoles are compounds with high potential for applications in various domains, especially in the electrochemical industry as electro catalysts, anode materials in batteries, anticorrosion coating, and fast response potentiometric sensors [2]. These compounds have also attracted considerable attention in pharmacology, mainly because of their ability to develop antifungal and antibacterial agents. They also act as candidates for direct oxidation/reduction of biomolecules, and other biological activities [3]. Because of the very potent and diverse biological activity exhibited by various indole derivatives, this heterocyclic system has attracted considerable attention in chemistry, biology and medicine [4-5]. Hence, it is not surprising that indoles act as lead compounds and are key building blocks in numerous pharmaceuticals. Indole derivatives constitute an important class of therapeutic agents in medicinal chemistry including antihypertensive, antiproliferative, antiviral, antitumor, analgesic, anti-inflammatory, antimicrobial activities, etc. [6]. Although indole moiety is very small but is fascinated by scientists because of the diverse biological activities by not only indole but its various substituted derivatives as well. The indole moiety is present in many substances of biological occurrence. Its metabolism, in most cases, involves an oxidative pathway [7].

Among the various substituted indoles, Skatole or 3-Methylindole [3-MI] is taken for investigation. 3-Methylindole is also known as Skatole, a microbial fermentation product of tryptophan in the rumen cattle [8, 9]. The word skatole is derived from the Greek word skato, which means dung. This compound can be found in mammalian feces and has a sharp odour. Ironically, in low concentration, skatole has a flowery scent and is used in the manufacturing of perfumes. Another interesting fact about this molecule is that it has been found to cause pulmonary edema in goats, sheep and several rodents, such as mice and rats [10].

The oxidation of 3-Methylindole into 3-Methyloxindole was carried out by peracetic acid [11]. The oxidation of skatole by brominating agent gave bromo substituted 3-methyloxindole [12]. Oxidation of 3-Methylindole to indole-3-carboxaldehyde via indole-3-Methanol was carried out using an enzyme called Pseudomonas [13]. Oxidation of Indole-3-acetic acid (IAA) by PMS into 2-hydroxy indole-3-Methanol in aqueous acetonitrile medium was carried out by Chandramohan et al [14]. Muniyappan et al., investigated the kinetic study of oxidation of indole by PMS using various solvent medium like ethanol [15], acetonitrile [16] and acetone [17]. Skatole is a mildly toxic compound



The identity of the product was further confirmed from its FT-IR spectra (Fig .I) and HMNR (Fig .II). FT-IR (KBr) 3406, 1714 and 1675 cm<sup>-1</sup>, HNMR (DMSO) ppm = 6.0-8.0 (m, 5H, ArH, NH), 3.3 (S, 3H, C-H).

### 3. RESULTS AND DISCUSSION

Factors influencing the rate of oxidation of [3-Methylindole] by KBrO<sub>3</sub> such as effects of (i) [3-MI]<sub>0</sub>, (ii) [KBrO<sub>3</sub>]<sub>0</sub>, (iii) ionic strength ( $\mu$ ), (iv) [H<sup>+</sup>]<sub>0</sub>, and (v) dielectric constant have been studied. Rate and activation parameters were evaluated.

**(i). Effect of [3-Methylindole]<sub>0</sub>:** At a constant [KBrO<sub>3</sub>], [H<sup>+</sup>], [ $\mu$ ], and fixed percentage of acetic acid, kinetic runs were carried out with various initial concentrations of 3-Methylindole, which yielded [3-MI] dependent rate constants. The values of pseudo first-order rate constants  $k'$  (s<sup>-1</sup>) thus obtained were found to increase with [3-MI] (Table 1 & Fig. 1) over a range of [3-MI] used ( $2.0 \times 10^{-2}$  –  $4.0 \times 10^{-2}$  mol dm<sup>-3</sup>). This shows that the reaction obeys first order with respect to [3-MI]. This was confirmed by the linear plots of  $k'$ (s<sup>-1</sup>) vs [3-MI] passing through origin ( $r = 0.999$ ) (Fig. 2 ). Such a kinetic behaviour indicates the absence of any self-decomposition of KBrO<sub>3</sub>[23]. The value of  $k_2$  (mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>) was evaluated from the slope of  $k'$  (s<sup>-1</sup>) vs [3-MI] plots. The  $k_2$  (mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>) values thus obtained ( $r = 0.999$ ) from such plots were in agreement with the corresponding values calculated from the factor  $k'$  (s<sup>-1</sup>)/[3-MI].

**(ii) Effect of [KBrO<sub>3</sub>]<sub>0</sub>:** It is observed that the reaction rate was unaffected as evident from the constant slopes of log [KBrO<sub>3</sub>] vs time plots for various [KBrO<sub>3</sub>]<sub>0</sub> ( $1.0 \times 10^{-3}$  –  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup>) at fixed [3-Methylindole]<sub>0</sub>, [H<sup>+</sup>]<sub>0</sub>,  $\mu$ , and percentage of acetic acid (Table 2 (A) ) & Fig. 3). This observation confirms the first-order dependence of rate on [KBrO<sub>3</sub>].

**(iii) Effect of  $\mu$ :** The influence of ionic strength ( $\mu$ ) maintained by the addition of sodium per chlorate on the reaction rate was found to be negligible (Table 2 (B)). This shows that the reaction occurs between a neutral species namely the 3-Methylindole molecule and the mononegative ion BrO<sub>3</sub><sup>-</sup>, the active species of the oxidant under experimental condition.

**Table 1. Effect of concentrations of 3-Methylindole on the reaction rate at 303 K**

[3-MI] <sup>a</sup> (10 <sup>2</sup> mol dm <sup>-3</sup> )	$k'$ (10 <sup>4</sup> s <sup>-1</sup> )			
	293 K	298 K	303 K	308 K
2.0	3.1087	4.3408	6.0893	9.1477
2.5	3.8634	5.3929	7.6543	11.4670
3.0	4.6203	6.5182	9.1923	13.6336
3.5	5.4008	7.6255	10.6830	15.9006
4.0	6.1614	8.6803	12.1868	18.0078

<sup>a</sup>[KBrO<sub>3</sub>]:  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>, [H<sup>+</sup>]: 0.02 mol dm<sup>-3</sup>,  $\mu$ : 0.3 mol dm<sup>-3</sup>, Acetic acid: 50%.

**Table 2 (A). Effect of oxidant on reaction rate at 303 K**

[KBrO <sub>3</sub> ] <sup>b</sup> (10 <sup>-3</sup> mol dm <sup>-3</sup> )	$k'$ (10 <sup>4</sup> s <sup>-1</sup> )
1.0	9.1700
1.5	9.1507
2.0	9.1923
3.0	9.2170

5.0	9.1842
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<sup>b</sup>[3-MI]:  $3.0 \times 10^{-3}$  mol dm<sup>-3</sup>, [H<sup>+</sup>]: 0.02 mol dm<sup>-3</sup>,  $\mu$ : 0.3 mol dm<sup>-3</sup>, Acetic acid: 50%.

**Table 2 (B). Effect of [ $\mu$ ] concentration on the reaction rate at 303 K**

$\mu^c$ (mol dm <sup>-3</sup> )	$k'(10^4 \text{ s}^{-1})$
0.1	9.1591
0.2	9.0597
0.3	9.1923
0.4	9.2142
0.5	9.1269

<sup>c</sup>[3-MI]:  $3.0 \times 10^{-2}$  mol dm<sup>-3</sup>, [KBrO<sub>3</sub>]:  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>, [H<sup>+</sup>]: 0.02 mol dm<sup>-3</sup>, Acetic acid: 50%.

**Table 2 (C). Effect of [H<sup>+</sup>] concentration on the reaction rate at 303 K**

[H <sup>+</sup> ] <sup>d</sup> (mol dm <sup>-3</sup> )	$k'(10^4 \text{ s}^{-1})$
0.005	9.1834
0.010	9.2376
0.020	9.1923
0.050	9.2873
0.090	9.1918

<sup>d</sup>[3-MI]:  $3.0 \times 10^{-2}$  mol dm<sup>-3</sup>, [KBrO<sub>3</sub>]:  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>, [H<sup>+</sup>]: 0.02 mol dm<sup>-3</sup>, Acetic acid: 50%.

**Table 3. Effect of dielectric constant on the reaction rate at 293-303 K**

AcOH : H <sub>2</sub> O	$k'(10^4 \text{ s}^{-1})$		
	293 K	298 K	303 K
40 : 60	9.9410	11.4341	15.9852
45 : 55	5.8461	8.6471	12.7470
50 : 50	3.8900	5.8328	9.1923
55 : 45	1.6648	4.2141	6.4656

60 : 40	0.9377	2.2821	3.1295
65 : 35	0.1124	1.0414	1.8810

[3-MI]:  $3.0 \times 10^{-2}$  mol dm<sup>-3</sup>, [KBrO<sub>3</sub>]:  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>, [H<sup>+</sup>]: 0.02 mol dm<sup>-3</sup>,  $\mu$ : 0.3 mol dm<sup>-3</sup>

**Table 4. Effect of temperature on the reaction rate**

Temp (K)	$k_2$ ( $10^2$ mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup> )	SD
293	1.5446	±0.0023
298	2.1697	±0.0021
303	3.0538	±0.0064
308	4.5500	±0.0043

**Table 5. Thermodynamic parameters**

Thermodynamic parameters of Oxidation of 3-Methylindole		Activation Parameters
Energy of Activation ( $E_a$ )	kJ mol <sup>-1</sup>	53.7387
Enthalpy ( $\Delta H^\ddagger$ )	kJ mol <sup>-1</sup>	51.2646
Entropy ( $\Delta S^\ddagger$ )	JK <sup>-1</sup> mol <sup>-1</sup>	-104.9199
Free Energy ( $\Delta G^\ddagger$ )	kJ mol <sup>-1</sup>	83.0547

**(iv) Effect of [H<sup>+</sup>]:** The reaction rates measured at constant [3-Methylindole], [KBrO<sub>3</sub>],  $\mu$ , and percentage of acetic acid but with various [H<sup>+</sup>] ( $5 \times 10^{-3}$  –  $9 \times 10^{-2}$  mol dm<sup>-3</sup>) were found to be the same (Table 2 (C)). Such a kinetic behaviour indicates the nonexistence of any protonation equilibrium with respect to both KBrO<sub>3</sub> and 3-Methylindole under the present experimental conditions employed.

**(v) Effect of Dielectric Constant:** So as to determine the effect of dielectric constant (polarity) of the medium on rate, the oxidation of 3-Methylindole by KBrO<sub>3</sub> was studied in aqueous acetic acid mixtures of various compositions (Table 3). The data clearly reveals that the rate increases with decrease in the percentage of acetic acid, i.e. with increasing dielectric constant or polarity of the medium, and lead to the inference that there is a charge development in the transition state involving a more polar activated complex than the reactants [24], a neutral molecule (3-Methylindole), and a mononegative ion (BrO<sub>3</sub><sup>-</sup>) suggesting a polar (ionic) mechanism. Thus with decrease in concentration of acetic acid the  $\Delta S^\ddagger$  more and more negative hinting electrostriction due to more charge development at the activated complex.

**(vi) Rate and Activation Parameters:** The effect of temperature on  $k'$  (s<sup>-1</sup>) was studied in the range of 293–303 K and the results are shown in (Table 4). The Arrhenius plot of log  $k_2$  vs  $1/T$  was linear. From the above plot, the values of energy of activation ( $E_a$ ) were calculated (Fig.4 Fig and Table 5). The value of  $\Delta S^\ddagger$  was computed from Eyring equation. The large negative value of entropy of activation ( $\Delta S^\ddagger$ ) obtained is attributed to the severe restriction of solvent molecules around the transition state of higher charge and the cyclic nature of the intermediate[25].

## Stoichiometry

Solutions of 3-Methylindole containing an excess of  $\text{KBrO}_3$  were kept overnight at room temperature. Titrimetric estimation of the concentration of potassium bromate unconsumed and assuming that all the 3-Methylindole taken had reacted, the stoichiometry of 3-Methylindole: potassium bromate was found to be 1:2.

## Test for Free Radical Intermediates

The observed total second-order dependence of rate, beside first-order dependence each on both [3-MI] and  $[\text{KBrO}_3]$ , shows that the reaction involves a nonradical pathway. Moreover no polymer formation was observed when a freshly distilled acrylonitrile monomer was added to the deaerated reaction mixture indicating the absence of free radical intermediates.

Fig. 1. Variation of [3-MI] @ 303 K

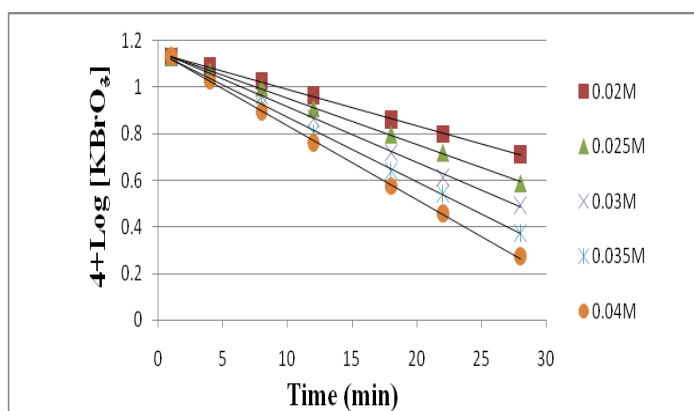


Fig. 2. Evaluation of  $k_2$

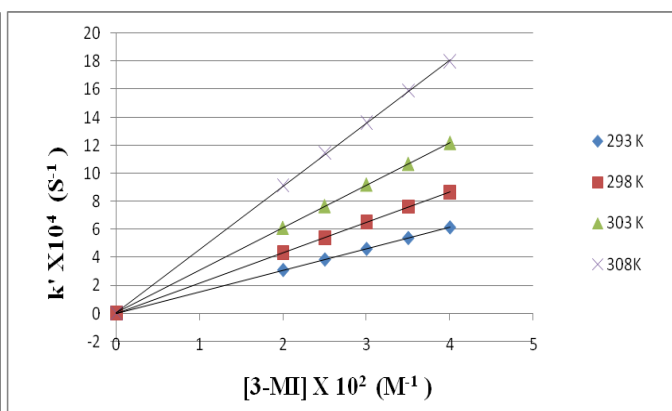


Fig. 3. Variation of  $[\text{KBrO}_3]$  @ 303 K

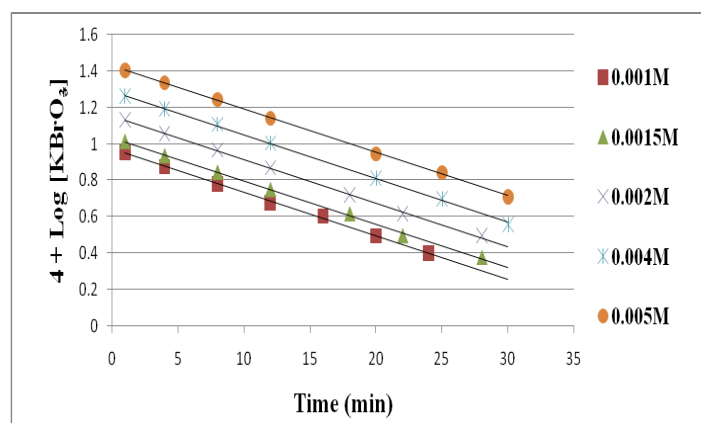
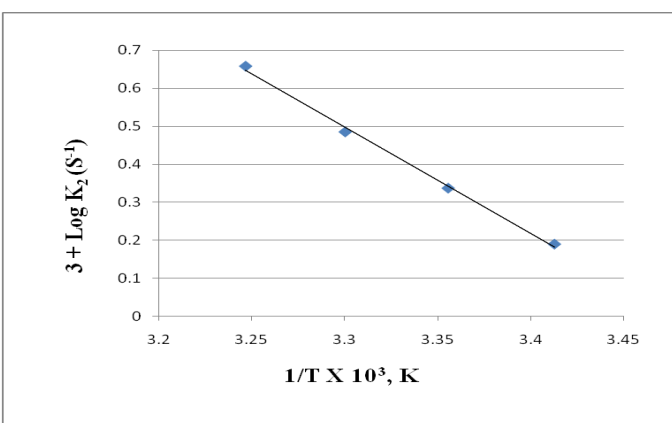


Fig. 4. Evaluation of  $E_a$



## Rate Law

In accordance with the above observations, the rate law for the disappearance of potassium bromate is given as follows:

$$-d[\text{Br (V)}]/dt = k_2 [\text{Br (V)}][3\text{-MI}]$$

$$\text{rate} / [\text{Br (V)}] = k'(s^{-1}) = k_2[3\text{-MI}]$$

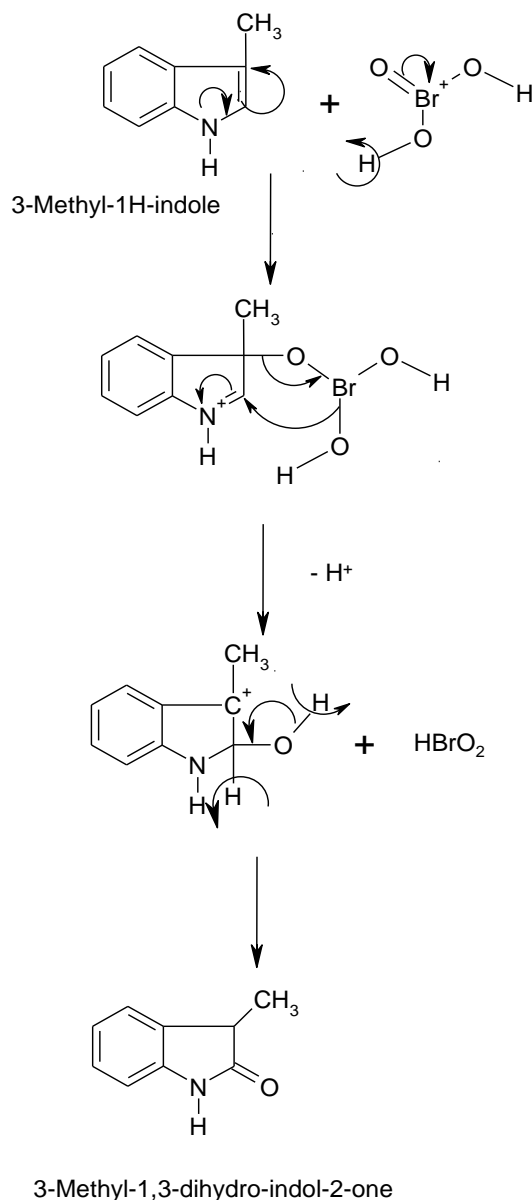
$$k^{-1} = k_2 [3\text{-MI}]$$

where  $k'$  = pseudo first order rate constant and  $k_2$  = second order rate constant.

## Mechanism

Based on the foregoing observations such as first-order dependence of rate each on [3-MI], [KBrO<sub>3</sub>], zero-order dependence on [H<sup>+</sup>], negligible effect of [μ], and the stoichiometry, the following mechanism is suggested:

Our results suggest that the reaction proceeds through an electrophilic attack of the oxidant (bromated ion) at nucleophilic site C-3 of 3-Methylindole by a mechanism involving nucleophilic displacement of bromated ion [26]. Presence of electron releasing methyl group increases the reaction rate. 3-Methylindole reacts with H<sub>2</sub>BrO<sub>3</sub> forming a bromated ester intermediate.



This intermediate breaks down fastly to produce 3-Methyloxindole as the product. The mechanism was supported by the observed rate laws, first order in oxidant, first order in substrate and second order in [H<sup>+</sup>]. This was further confirmed by the solvent influence on the reaction the rate was found to increase considerably upon increase in acetic acid content of the medium. This was due the fact the reaction was facilitated by the increase in polarity or nucleoplicity. The addition of acryonitrile, which is a good trapper of free radicals, did not have any retarding effect on the reaction. It indicates no free radical's participation in the reaction.

## Weight Loss Method of Corrosion Study

Weight loss measurements were done by hanging steel plate in a glass beaker containing 100 mL of corrosive media (1M HCl) without and with different concentration of inhibitor for an immersion time of 6 hours. The steel

plate was taken out and washed with tap water followed by distilled water dried and weighed accurately using digital balance of accuracy  $\pm 0.1$  mg at 303 K. All the experiments were carried out in static and aerated condition. Each measurement was repeated thrice for reproducibility and an average value was reported.

The  $\eta$  % (percentage inhibition efficiency) was calculated from the following relationship

$$\eta (\%) = \frac{W_0 - W}{W_0} \times 100$$

Where  $W_0$  and  $W$  are weight loss in the absence and presence of inhibitor.

The values of percentage inhibition efficiency ( $\eta$  %) and corrosion rate ( $\text{mg cm}^{-2} \text{h}^{-1}$ ) obtained from weight loss method at different concentrations of 3-MI and 3-MOI at 303K are summarized in Table. 6. It was clearly that the 3-MI and 3-MOI inhibits the corrosion of mild steel in 1 M HCl solution at all concentration was used in this study and the corrosion rate ( $C_R$ ) decreases continuously with increasing additive concentration at 303 K.

Table 6. Corrosion rate and inhibition efficiency ( $\eta$  %) values obtained from weight loss measurements.

Inhibitor	Concentration (M)	Wt. loss (mg)	$\eta$ %
Blank	0	60	-
3-Methylindole	$10^{-4}$	41.13	31.45
	$10^{-3}$	22.42	62.63
	$5 \times 10^{-3}$	17.79	70.35
	$10^{-2}$	9.1	84.83
3-Methoxyindole	$10^{-4}$	45.87	23.55
	$10^{-3}$	30.21	49.65
	$5 \times 10^{-3}$	25.20	58.00
	$10^{-2}$	19.22	67.96



Among the two tested compounds, the inhibition efficiency of 3-MI is more than that of 3-MOI. The adsorption of these inhibitor molecules on the iron surface can be explained on the basis of the donor acceptor interaction between  $\pi$ -electrons of donor atoms N, S and aromatic rings of the inhibitors and the vacant d orbitals of iron surface atoms [27].

#### 4. CONCLUSION

3-Methylindole and  $\text{KBrO}_3$  reaction involves of a ester intermediate, This intermediate breaks down to produce 3-Methyloxindole as the product. The mechanism was supported by the observed rate laws, first order in oxidant first order in substrate and second order in  $[\text{H}^+]$ . follows first order with respect to 3-Methylindole and  $\text{KBrO}_3$  and overall follows second order reaction. The results indicate that there is no ionic strength and  $[\text{H}^+]$ . From the data of the dielectric effect clearly reveals that the rate increases with decrease in the percentage of acetic acid. The corrosive studies are performed using weight lose method by dipping the mild steel panels in 1M HCl solution. It is very clear that the indole compounds inhibits the corrosion of mild steel at all concentration and corrosion rate ( $C_R$ ) decreases continuously with increasing additive concentration at 303 K.

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