

Inhibition of Corrosion of Iron in Nitric Acid Solutions by 3-Phenylazolawsone Derivatives

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Abstract

The influence of 3-(3'-nitrophenylazo) lawsone and 3-(3'-methoxyphenylazo) lawsone on the corrosion rate of Iron in 1 mol L⁻¹ HNO₃ was investigated using weight loss method. It was observed that both the investigated derivatives behave as inhibitors. The inhibition efficiency increases with increasing inhibitor concentration, but decreases with increasing temperature. The adsorption of both the derivatives on Iron follows a Framkins adsorption isotherm. The influence of substituent group on the inhibition efficiency of the inhibitor was explained in terms of electron density cloud on both the derivatives. Further, kinetic parameters were determined and discussed. Finally the “inhibition co-efficient” of the inhibitors was evaluated.

Keywords: Iron; Corrosion inhibition; HNO₃; Phenylazolawsone derivatives; Kinetics; Inhibition co-efficient.

1. Introduction

Iron is widely used in many industries. During industrial process such as acid pickling, etching, acid cleaning, Iron is often made to come in contact with corroding solutions such as acidic and basic solutions [1 - 4]. Hence metal is prone to corrosion attack. The magnitude of corrosion of metal depends on the concentration of acidic and basic medium, operating temperature and period of contact etc [5 and 6]. Various workers have explained the interaction of these medium on the surface of Iron [7 - 14].

A useful method to protect metals deployed in service in corrosive environment is the addition of species to the solution in contact with the surface in order to inhibit the corrosion reaction and reduce the corrosion rate. A number of organic compounds [15 - 28] are known to be applicable as corrosion inhibitors in acidic environment. However there is no report on influence of 3-phenylazolawsone derivatives as corrosion inhibitors. As a part of our contribution to the growing interest of exploring inhibition of Iron, the present study investigates the inhibitive effect of 3-(3'-nitrophenylazo)lawsone and 3-(3'-methoxyphenylazo)lawsone on Iron in 1 mol L⁻¹ nitric acid, using weight – loss method in the temperature range of 25 - 40 °C.

2. Experimental

2.1. Materials Preparation

The experiments were performed with local commercial Iron obtained from Jindal Iron Limited, India. The inhibitor used were 3-nitro and 3-methoxy derivatives of 3-phenylazolawsone with chemical structure shown in Fig.1. Both the derivative were prepared, purified and identified according to the recommended method [29 and 30].

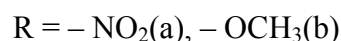
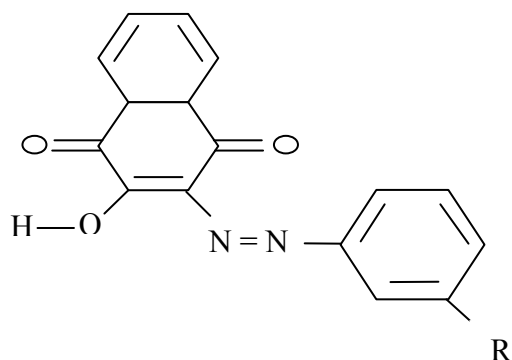


Fig. 1: Derivative (a and b)

Preparation of Inhibitor used

3-phenylazolawsone derivative were prepared by diazotization of aromatic primary amines and its coupling with lawsone.

Diazotization

3-nitroaniline and 3-methoxyaniline (0.01 mol L^{-1} each) was dissolved in minimum quantity of 2 mol L^{-1} HCl. The sodium nitrate (0.01 mol L^{-1}) in distilled water was added drop wise to 3-substituted anilines hydrochloride with constant stirring. The temperature of the reaction was maintained at 4°C .

Coupling with lawsone

Lawsone (0.01 mol L^{-1}) in pure ethanol was added to diazotized 3-substituted anilines with constant stirring in the presence of 23% sodium acetate at pH 6. After cooling, the solid product was washed with cold water, dried in vacuum and recrystallized to give 3-phenylazolawsone derivative (a and b). Formations of both derivatives were confirmed by elemental and spectral analysis. The Infra red (I.R.) spectra gave an absorption bands, (3551, 3426),

(1671, 1687), (1463, 1463), (1228, 1226) and (970, 968) cm^{-1} due to the $-\text{OH}$, $-\text{C}=\text{O}$, $-\text{N}=\text{N}-$, $-\text{C}-\text{O}$ and $-\text{C}-\text{N}=\text{NC}$ groups, respectively.

Stock solutions (10^2 mol L^{-1}) of derivatives (a and b) were prepared by dissolving an accurately weighed quantity of each derivative in 8.2% (v/v) hot ethanol – chloroform solvent mixture, then the required concentration ranging from 1.0×10^{-4} to $5.0 \times 10^{-4} \text{ mol L}^{-1}$ were prepared by dilution with doubly distilled water.

Nitric acid was prepared by diluting the appropriate volume of concentrated pure acid, with double distilled water and standardized with solution of sodium carbonate.

2.2. Chemical technique

Weight – loss method

Weight – loss measurements were conducted under total immersion condition in 200 cm^3 of test solutions maintained at $25 - 40^\circ\text{C}$. The test pieces were cut into $5\text{cm} \times 5\text{cm} \times 0.5 \text{ mm}$. They were first polished with a coarse paper and then with emery paper, degreased in alcohol, rinsed in double distilled water and finally dried in oven and weighed. The test pieces were suspended by hook at the edge of vessel and kept under the surface of test solution by about 2 cm. After 10 min. regular intervals of time, six test pieces were taken out of the test solutions, rinsed with double distilled water, dried as earlier and weighed again. The weight – loss at various time intervals for each set of six samples was taken on analytical balance to an accuracy of 5%.

3. Results and Discussion

[Fig. 2] and [Fig. 3] shows the weight – loss time plots for Iron in 1 mol L^{-1} nitric acid in presence and absence of various concentrations of derivatives (a and b) at 25°C . The plots are characterized by increase in weight – loss plots for added derivatives (a and b) containing system fall below that of the blank. These plots indicates that, the weight – loss of Iron depends on both type and concentration of added derivatives (a and b). Rise in bulk

concentration, consequently increases the surface coverage by the added derivatives (a and b) increases their inhibition efficiency toward Iron dissolution. The Table 1 and Table 2 shows that inhibition efficiency of added derivatives (a and b) increases with the increase of their concentration in 1 mol L^{-1} nitric acid solution. Hence, it is quite obvious that increase in surface area coverage by added derivatives (a and b) decreases the dissolution of Iron in 1 mol L^{-1} nitric acid. It is observed that the inhibition efficiency of added derivative (b) in 1 mol L^{-1} nitric acid solution, over all the concentration ranges is greater than the added derivative (a).

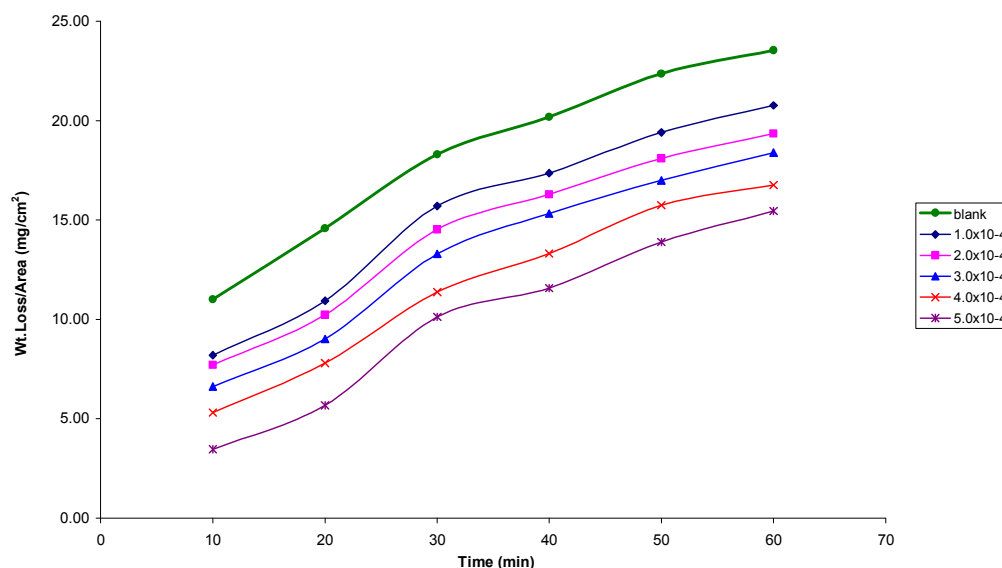


Fig. 2: Kinetics of corrosion of Iron in Nitric Acid: Effect of 3-(3'-nitrophenylazo)lawsone.

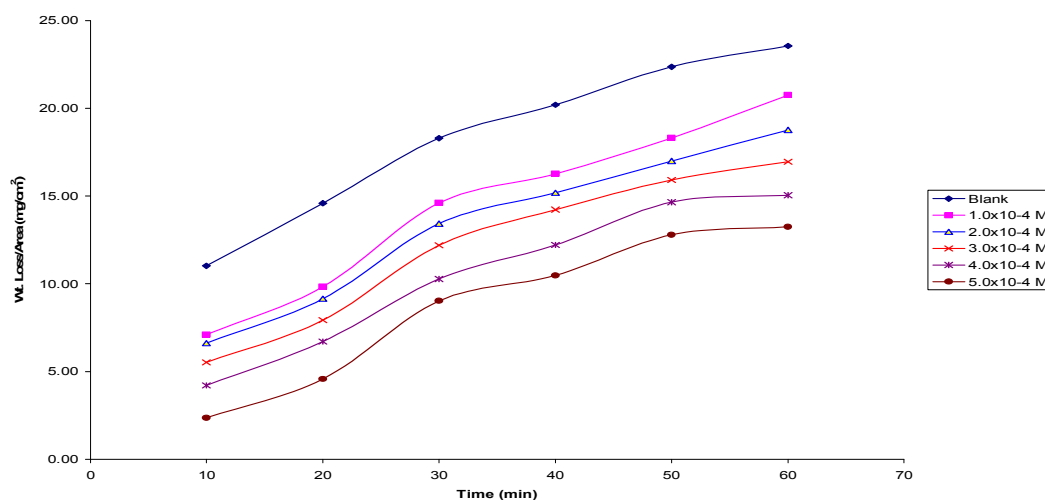


Fig. 3: Kinetics of corrosion of Iron in Nitric Acid: Effect of 3-(3'-methoxyphenylazo) lawsone.

Table 1: Kinetics of corrosion of Iron in Nitric Acid: Percentage

Inhibition of 3-(3'-nitrophenylazo)lawsone at 25 °C.

| Sr. No. | Time (min) | Inhibition Efficiency (%) | | | | |
|------------|---------------|------------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| | | 3-(3'-nitrophenylazo)lawsone | | | | |
| | | 1.0x10 ⁻⁴ M | 2.0x10 ⁻⁴ M | 3.0x10 ⁻⁴ M | 4.0x10 ⁻⁴ M | 5.0x10 ⁻⁴ M |
| 1 | 10 | 25.50 | 29.95 | 39.93 | 51.81 | 68.51 |
| 2 | 20 | 25.09 | 29.81 | 38.18 | 46.47 | 61.07 |
| 3 | 30 | 14.21 | 20.60 | 27.32 | 37.81 | 44.70 |
| 4 | 40 | 14.01 | 19.36 | 24.11 | 34.11 | 42.72 |
| 5 | 50 | 13.23 | 19.09 | 23.96 | 29.59 | 37.91 |
| 6 | 60 | 11.80 | 17.79 | 24.50 | 30.15 | 36.09 |

Table 2: Kinetics of corrosion of Iron in Nitric Acid: Percentage Inhibition of 3-(3'-methoxyphenylazo)lawsone at 25 °C.

| Sr. No. | Time (min) | Inhibition Efficiency (%) | | | | |
|---------|------------|--------------------------------|------------------------|------------------------|------------------------|------------------------|
| | | 3-(3'-methoxyphenylazo)lawsone | | | | |
| | | 1.0×10^{-4} M | 2.0×10^{-4} M | 3.0×10^{-4} M | 4.0×10^{-4} M | 5.0×10^{-4} M |
| 1 | 10 | 35.48 | 39.93 | 49.91 | 61.80 | 78.49 |
| 2 | 20 | 32.63 | 37.35 | 45.72 | 54.01 | 68.61 |
| 3 | 30 | 20.22 | 26.61 | 33.33 | 43.83 | 50.71 |
| 4 | 40 | 19.46 | 24.80 | 29.55 | 39.55 | 48.17 |
| 5 | 50 | 18.15 | 24.01 | 28.88 | 34.51 | 42.83 |
| 6 | 60 | 11.89 | 20.34 | 28.03 | 36.14 | 43.74 |

3.1. Adsorption considerations

The inhibition of Iron corrosion in the presence of the added derivatives (a and b) has been attributed to their adsorption onto the Iron surface and this is confirmed from the fit of the experimental data to various adsorption isotherms. It was found that the best fit was with Framkin's isotherm is $\Theta = k + (2.303/f) \log C$, where k is the constant and f is free energy of adsorption. When plot of Θ versus $\log C$ was plotted for the added derivatives (a and b), Framkin's isotherm is obeyed as shown in Table 3 and Fig.4.

Table 3: Kinetics of corrosion of Iron in Nitric Acid: Adsorption study of Inhibitors at 25 °C.

| Sr. No. | Concentration of Inhibitor (M) | log C | 3-(3'-nitrophenylazo) lawsone, θ | 3-(3'-methoxyphenylazo) lawsone, θ |
|---------|--------------------------------|---------|---|---|
| 1 | 1.0×10^{-4} | -4.0000 | 0.1180 | 0.1189 |
| 2 | 2.0×10^{-4} | -3.6989 | 0.1779 | 0.2034 |
| 3 | 3.0×10^{-4} | -3.5228 | 0.2450 | 0.2803 |
| 4 | 4.0×10^{-4} | -3.3979 | 0.3015 | 0.3614 |
| 5 | 5.0×10^{-4} | -3.3010 | 0.3609 | 0.4374 |

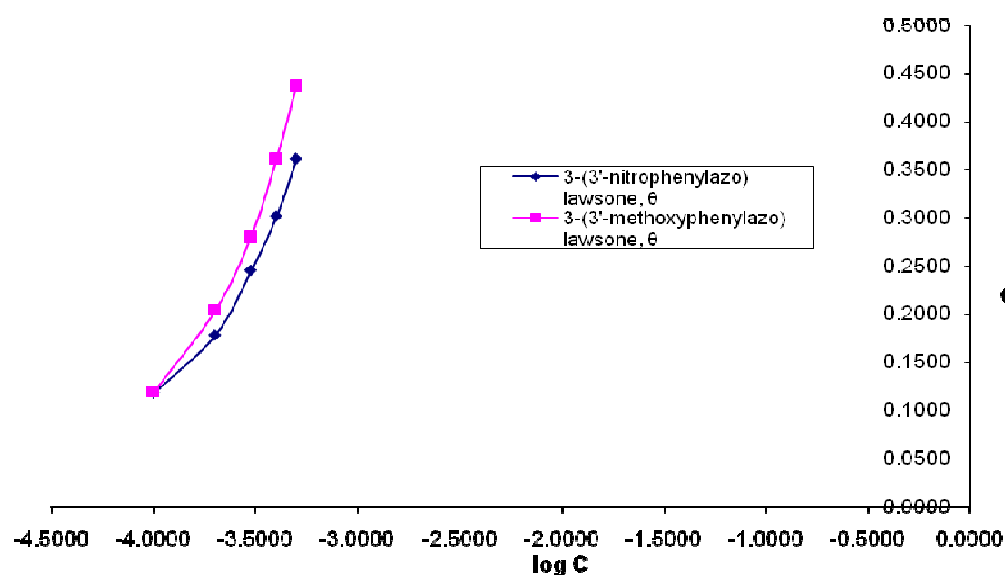


Fig.4: Kinetics of corrosion of Iron in Nitric Acid: Adsorption study of Inhibitors

3.2. Effect of temperature

The dissolution of Iron in 1 mol L^{-1} nitric acid increases by increasing temperature from 25 - 40 °C [Fig.5], the dissolution study was carried out in the presence of derivative (a and b) at $1.0 \times 10^{-4} \text{ mol L}^{-1}$ by weight – loss method over a temperature range of 25 - 40 °C. The weight-loss-time plots obtained in Fig. 6 and Fig. 7 in the presence of derivative (a and b) shows that the rate of Iron dissolution increases as temperature increases, but at lower rate than depicted in Fig. 5. It is observed that the inhibition efficiency of added derivatives (a and b) decreases with increasing temperature which shows that the adsorption of both derivative on the surface of Iron occurs through physical adsorption. Desorption takes place by increasing the system temperature. The activation energy, E_a^* , the enthalpy of activation, ΔH^* and entropy of activation, ΔS^* for the corrosion of Iron in 1 mol L^{-1} nitric acid solution in presence and absence of different concentration of both the derivatives were calculated using Arrhenius and transition – state equation of rate constant. The activation parameters obtained are given in Table 4. The result shows higher values of energy of activation E_a^* in presence of inhibitors. It also shows increase in inhibition efficiency, increases the energy of activation. It suggests exothermic nature of the dissolution process and dissolution of Iron in 1 mol L^{-1} nitric acid becomes difficult. Also, the entropy shows orderliness of inhibitor layers on the surface of Iron.

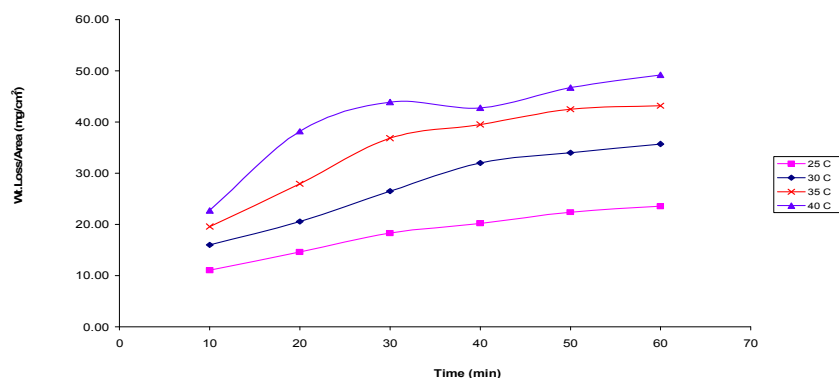


Figure 5: Kinetics of corrosion of Iron in Nitric Acid: Effect of Temperature.

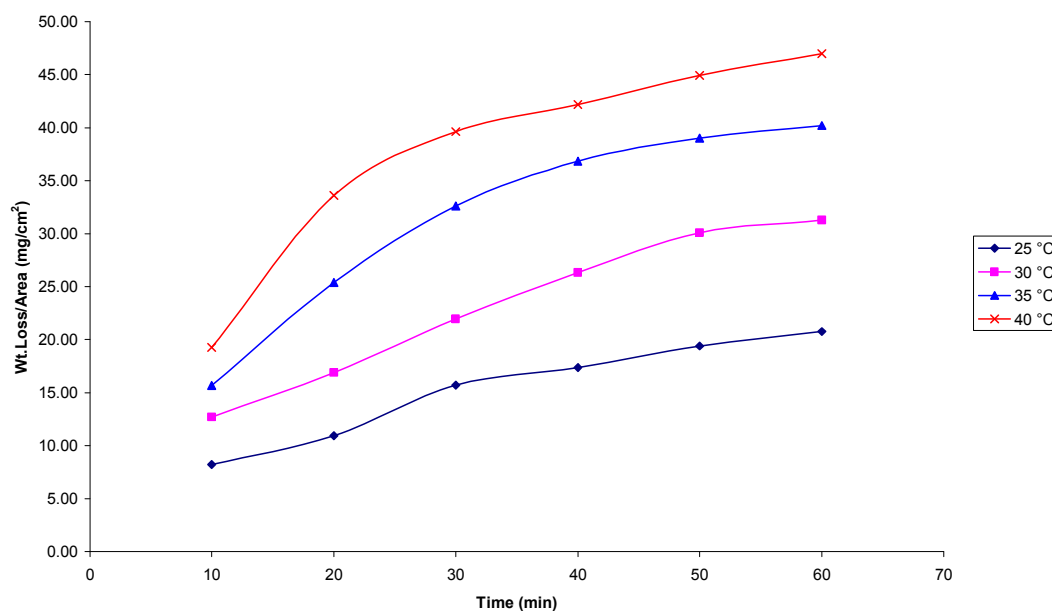


Figure 6: Kinetics of corrosion of Iron in Nitric Acid with 3-(3'-nitrophenylazo)lawsone: Effect of Temperature.

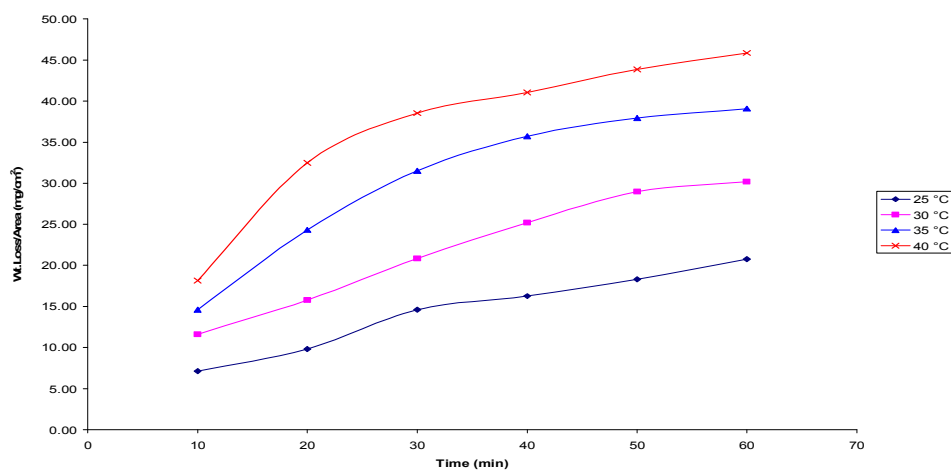


Figure 7: Kinetics of corrosion of Iron in Nitric Acid with 3-(3'-methoxyphenylazo)lawsone: Effect of Temperature.

Table 4: Kinetics of corrosion of Iron: Activation parameters.

| Sr. No. | Inhibitor | Energy of activation, E_a^* (KJ mole ⁻¹) | Entropy of activation, ΔS^* (J mole ⁻¹ K ⁻¹) | Enthalpy of activation, ΔH^* (KJ mole ⁻¹) |
|------------|------------------------------------|--|---|---|
| 1 | Blank | 12.64 | - 254.06 | 10.14 |
| 2 | 3-(3'-nitrophenylazo) lawsone | 48.76 | - 130.19 | 46.26 |
| 3 | 3-(3'-methoxyphenylazo) lawsone | 51.07 | - 122.70 | 48.57 |

3.3. Inhibition Co-efficient

In case of both the derivatives decrease in weight – loss (blank minus inhibitor) was calculated at various concentrations of these derivatives as in Table 5. These decreases in weight – loss were plotted versus concentration of both the derivatives. Straight lines were obtained as shown in Fig. 8. The slope of these lines could be considered as “Inhibition co-efficient”. It is observed that the “Inhibition coefficient” for 3-(3'-nitrophenylazo) lawsone (1.9×10^4) is greater than 3-(3'-methoxyphenylazo) lawsone (1.43×10^4), which shows that –methoxy derivative is more pronounced than the –nitro derivative.

Table 5: Kinetics of corrosion of Iron in Nitric Acid: Inhibition coefficient at 25 °C.

| Sr. No. | Concentration of Inhibitor (M) | Decrease in wt. loss/area/hr with respect to blank (mg/cm ²) | |
|------------|-----------------------------------|--|------------------------------------|
| | | 3-(3'- nitrophenylazo)lawsone | 3-(3'- methoxyphenylazo)lawsone |
| 1 | 1.00E-04 | 2.78 | 2.80 |
| 2 | 2.00E-04 | 4.19 | 4.79 |
| 3 | 3.00E-04 | 5.77 | 6.60 |
| 4 | 4.00E-04 | 7.10 | 8.51 |
| 5 | 5.00E-04 | 8.50 | 10.30 |

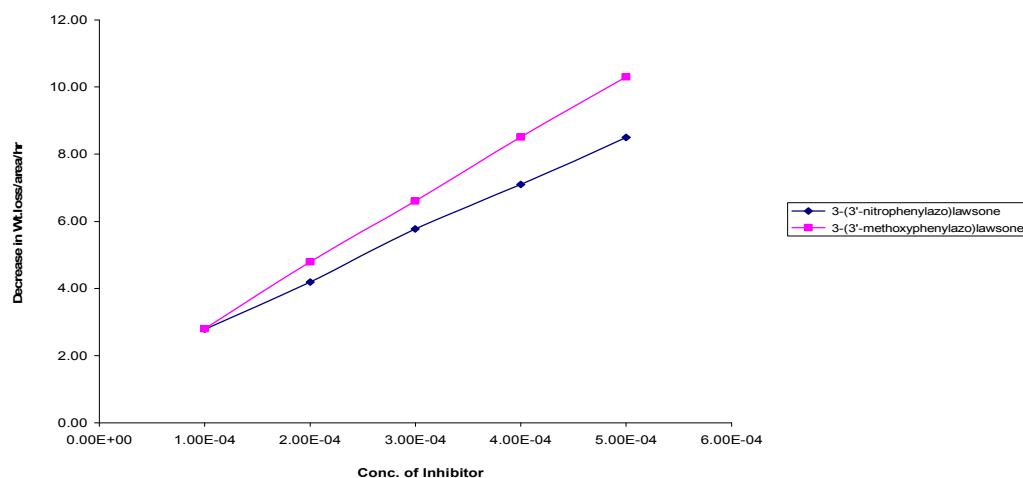


Fig. 8: Kinetics of corrosion of Iron in Nitric Acid: Inhibition Coefficient.

3.4. Chemical structure and mode of adsorption of Inhibitor:

The investigated inhibition of corrosion of Iron in 1 mol L⁻¹ nitric acid solution by derivatives (a and b) depend on concentration, type of metal, mode of adsorption of the inhibitors and condition of the surface. [Fig. 9] represents the proposed mode of adsorption of derivative (a and b) and indicates the adsorption centres in these derivatives. These derivatives get adsorbed through oxygen atom of the C₂ hydroxide group and co-ordination of the surface by β nitrogen atom of azo group. It is speculated that the mode of adsorption depends on affinity of Iron towards the electron cloud of the ring system. Iron has a greater affinity to adsorb benzene ring in flat orientation. Hence, the tested derivatives (a and b) get adsorbed in the flat orientation through oxygen atom of C₂ hydroxyl group and β – nitrogen of azo linkage. The 3-(3'-methoxyphenylazo) lawsone shows more inhibition efficiency than the 3-(3'-nitrophenylazo) lawsone. The adsorption character of reaction centre on the electron density of the ring may be due to the conjugation of the ring to the centre of adsorption. Derivative (b) has the more percentage inhibition efficiency; this is due to the presence of electron repelling m-methoxy group, which increases the electron charge density on the molecule. The percentage inhibition efficiency of derivative (a) is less as compared to derivative (b). This is due to the electron with drawing nature of the -nitro group. The inhibition by -nitro group depends on magnitude of its electron with drawing character.

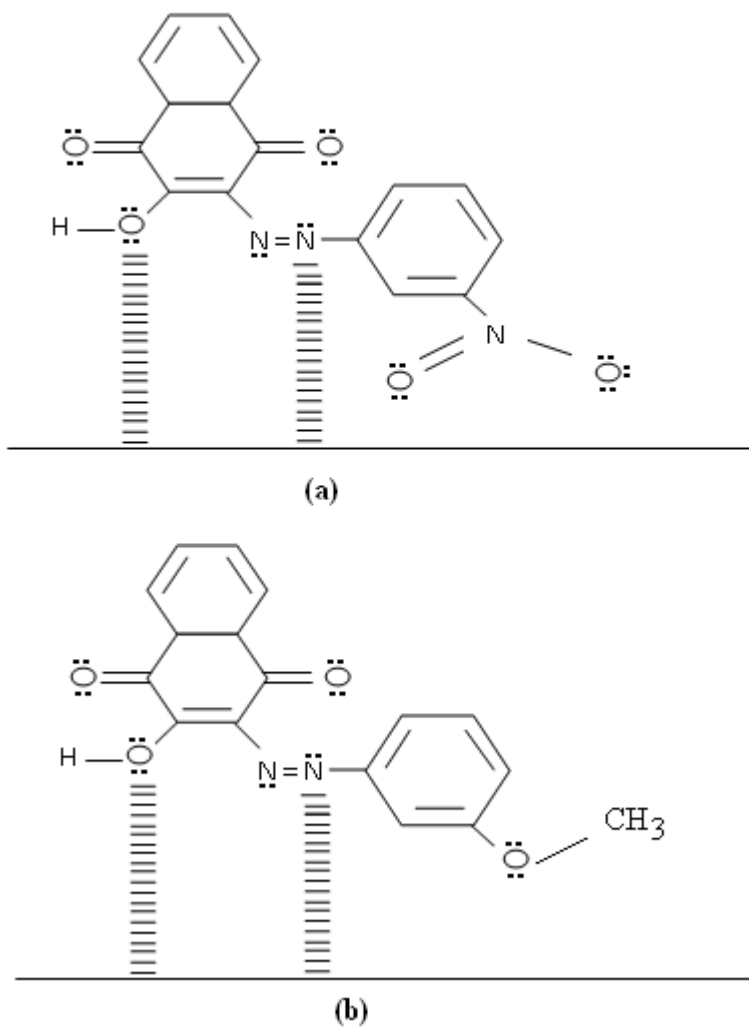


Fig. 9: Mode of adsorption of derivative (a and b)

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