*Full Length Research Paper*

# Azodyes as corrosion inhibitors for dissolution of C-steel in hydrochloric acid solution

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The effect of some mono azo dye compounds on the dissolution of carbon steel (type L-52) in 2 M hydrochloric acid solution was studied using weight loss and galvanostatic polarization techniques. The inhibition efficiency was found to increase with increasing inhibitor concentration and decreasing temperatures. Inhibition was explained by formation of insoluble complex adsorbed on the metal surface. The adsorption follows Langmuir adsorption isotherm. The formation of stable complex was studied by conductometric titration. The stiochiometric ratio was found to be 1:1; 1:2 for $Fe^{2+}$/ dye compounds and the mechanism of inhibition was explained in terms of these values. The thermodynamic functions of adsorption process was calculated and discussed.

**Key words:** Carbon steel, corrosion inhibitors, azo dyes, adsorption.

## INTRODUCTION

Acid solutions are widely used in industry, the most important fields of application being acid pickling, Industrial acid cleaning, acid descaling and oil well acidising, because of the general aggressiveness of acid solutions, the practice of inhibition is commonly used to reduce the corrosive attack on metallic materials. Inhibitors are generally used for this purpose to control the metal dissolution. Most of the well-known inhibitors are organic compounds containing nitrogen, sulphur and /or oxygen atoms. It has been observed that the most of the organic inhibitors act by adsorption on the metal surface (Abd El-Rehim et al., 1999).

The adsorption of corrosion inhibitor depends mainly on physico-chemical properties of the molecules such as functional group, steric factor, molecular size, molecular weight, molecular structure, aromaticity, electron density at the donor atoms and π-orbital character of donating electrons (Dehri and Ozcan, 2006; Hosseini et al., 2007; El-Naggar, 2007; Rosenfelld, 1981; Selvi et al., 2003), and also, on the electronic structure of molecules (Özcan, 2004; Granese, 1988; Granese et al., 1992; Fouda et al., 2004; Abdallah, 2003).

The aim of the present work is to study the inhibitive action of some newly prepared mono azo dye compounds toward the corrosion of C-steel in 2M hydrochloric acid solution using weight loss, and galvanostatic polarization techniques. Moreover, the effect of temperature on the dissolution of carbon steel, as well as, on the inhibition efficiency of the studied compounds was also investigated and some thermodynamic parameters were computed.

### Experimental method

The steel sample used (L-52) had the composition (wt%) 0.26 C, 1.35 Mn, 0.04 P, 0.05 S, 0.005 Nb, 0.02 V, 0.03 Ti and the remainder Fe. Coupons of steel with dimension of 1 x 3 x 0.2 cm were used for weight loss measurements. For galvanostatic studies a cylindrical rod embedded in araldite with an exposed surface area of 0.6 $cm^2$ was used. The electrode surface was polished with different grades of emery paper, degreased with acetone, and rinsed with distilled water. A.R. grade hydrochloric acid was used for preparing the corrosive solution.

For weight loss experiments, the cleaned C-steel coupons were weighed before and after immersion in 50 ml of the test solution for a period of time up to 6 h. The average weight loss for each two identical experiments was taken and expressed in mg $cm^{-2}$. The required temperature was adjusted using air thermostat. Galvanostatic polarization studies were carried out using PS remote potentiostat with Zum PS6 software for calculation of electrochemical parameters. Three compartment cell with a saturated calomel electrode, and a platinum foil auxiliary electrode were used. Conductance measurements were carried out using YSI model 32 con-

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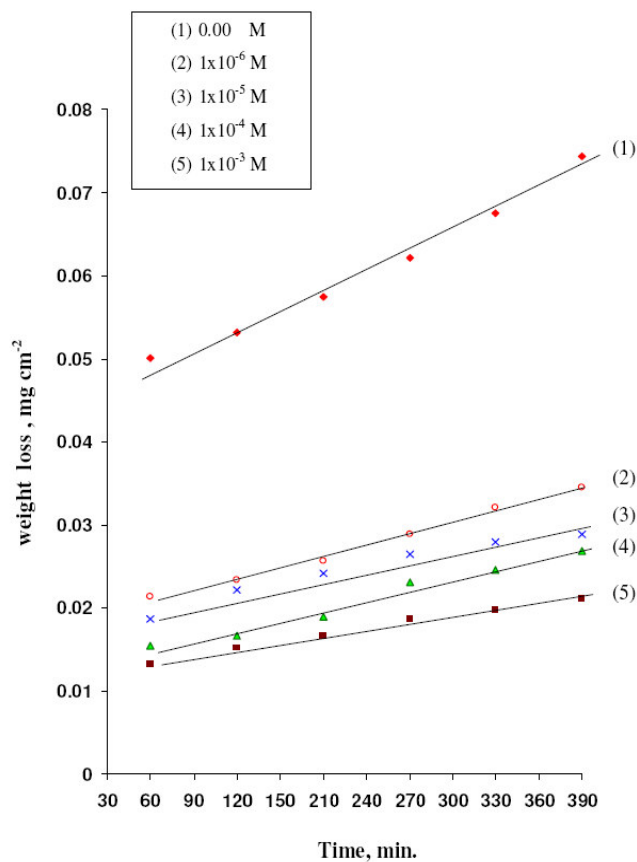*Corresponding author. E-mail: metwally552@hotmail.com.

**Figure 1.** Weight loss-time curves for the corrosion of C-steel in 2M HCl in absence, and presence of different concentrations of compound (II)

conductance meter of a cell constant 1.0.

The mono azo dye compounds used as inhibitors were prepared as described before (Moustafa et al., 1999) and has the following structure:-
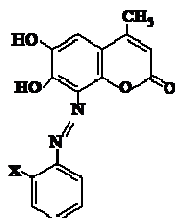


Where X= H (I), o-OCH₃ (II),o-OH (III), o- NO₂ (IV) and o- COOH (V).

## RESULTS AND DISCUSSION

### Weight loss measurements

Figure 1 shows the weight loss – time curves for C-steel coupons in the absence and presence of different con-centrations of compound (V) at 30°C. Similar curves were obtained for the other four compounds. It is clear that the

weight loss of carbon steel in presence of azo dye com-pounds varies linearly with time, and much lower than that obtained in the blank solution. The linearity obtained indicates the absence of insoluble film during corrosion, and that the inhibitors were first adsorbed onto the metal surface and thereafter, impede the corrosion process (El-Mahdy and Mohamed, 1995).

The percentage inhibition efficiency (%IE), and a para-meter surface coverage ($\theta$) which represents the part of the surface covered by the inhibitor molecules, were calculated using the following equations:

$$\% \text{I.E} = \left[ 1 - \frac{W_{add}}{W_{free}} \right] 100 \tag{1}$$

$$\theta = \left[ 1 - \frac{W_{add}}{W_{free}} \right] \tag{2}$$

Where $W_{free}$ and $W_{add}$ are the weight losses of C-steel in the absence and presence of inhibitors. The values of %IE and $\theta$ are listed in Table (1).

It is obvious from Table 1, that the weight loss de-creases as the concentrations of different compounds were increased. The order of inhibition efficiency of these compounds is:

II > III > I > V > IV
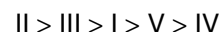
This behavior will be discussed later.

### Effect of temperature

The effect of rising temperature on the corrosion rate of C-steel in 2 M HCl in the absence, and presence of different concentrations of the azo dye compounds were studied using weight loss measurements. The corrosion rates $R_{corr}$ were calculated using the following equation (Bensajjay et al., 2003).

$$R_{corr} = \frac{\Delta w}{St} \tag{3}$$

Where $\Delta w$ is the weight loss of metal, S is the surface area ($cm^2$), and t is the exposed time (min). The data obtained are listed in Table (2).

Inspection of Table (2), reveals that the corrosion rate increases and hence %IE decreases as the temperature increases. This indicates that the rising of temperature decreases the inhibition process, and the highest inhibition efficiency is obtained at 30°C. The values of activation energy $E_a^*$ of the corrosion process were calculated using Arrhenius equation (Putilova et al.,1960).

$$\log R_{corr} = \log A - \frac{E_a^*}{2.303RT} \tag{4}$$

**Table 1.** Inhibition efficiency of mono azo dye compounds for corrosion of C-steel in 2M HCl solutions using weight loss method at 30°C.

| Inhibitor | Conc. M | Weight loss (mg cm$^{-1}$) | %I.E | θ |
|---|---|---|---|---|
| Compound (I) | 0.00   M compound (I) | 0.0744 | - | - |
| | 1x10$^{-6}$ M compound (I) | 0.0349 | 53.09 | 0.5309 |
| | 1x10$^{-5}$ M compound (I) | 0.0329 | 55.77 | 0.5577 |
| | 1x10$^{-4}$ M compound (I) | 0.0294 | 60.48 | 0.6048 |
| | 1x10$^{-3}$ M compound (I) | 0.0259 | 65.18 | 0.6518 |
| Compound (II) | 0.00   M compound (II) | 0.0744 | - | - |
| | 1x10$^{-6}$ M compound (II) | 0.0342 | 53.62 | 0.5362 |
| | 1x10$^{-5}$ M compound (II) | 0.0288 | 61.29 | 0.6129 |
| | 1x10$^{-4}$ M compound (II) | 0.0269 | 63.84 | 0.6384 |
| | 1x10$^{-3}$ M compound (II) | 0.0211 | 71.63 | 0.7163 |
| Compound (III) | 2M HCl +compound (III) | | | |
| | 0.00   M compound (III) | 0.0744 | - | - |
| | 1x10$^{-6}$ M compound (III) | 0.0335 | 54.97 | 0.5497 |
| | 1x10$^{-5}$ M compound (III) | 0.0298 | 59.94 | 0.5994 |
| | 1x10$^{-4}$ M compound (III) | 0.0272 | 63.44 | 0.6344 |
| | 1x10$^{-3}$ M compound (III) | 0.0231 | 68.95 | 0.6895 |
| Compound (IV) | 0.00   M compound (IV) | 0.0744 | - | - |
| | 1x10$^{-6}$ M compound (IV) | 0.0433 | 41.80 | 0.4180 |
| | 1x10$^{-5}$ M compound (IV) | 0.0421 | 43.41 | 0.4341 |
| | 1x10$^{-4}$ M compound (IV) | 0.0398 | 46.50 | 0.4650 |
| | 1x10$^{-3}$ M compound (IV) | 0.0332 | 55.37 | 0.5537 |
| Compound (V) | 0.00   M compound (V) | 0.0744 | - | - |
| | 1x10$^{-6}$ M compound (V) | 0.0347 | 53.3 | 0.533 |
| | 1x10$^{-5}$ M compound (V) | 0.0336 | 54.8 | 0.548 |
| | 1x10$^{-4}$ M compound (V) | 0.0301 | 59.5 | 0.595 |
| | 1x10$^{-3}$ M compound (V) | 0.0287 | 61.4 | 0.614 |

Where $R_{corr}$ is the rate of corrosion from weight loss, A is Arrhenius constant, R is the gas constant ant T is absolute temperature. Figure 2 represents Arrhenius plot (log $R_{corr}$ vs $\frac{1}{T}$ ) in presence and absence of different concentrations of compound V. Similar curves were obtained, for other compounds (not shown),  and the values of $E_a^*$ were obtained from the slope of the straight lines and are listed in Table 3. The increase of the activation energies in the presence of inhibitors is attributed to an appreciable decrease in the adsorption process of inhibitor, on the metal surface with increase in temperature and the corresponding increase in the reaction rate, because of the greater area of the metal that is exposed to the acid (Putilova et al., 1962).

**Adsorption isotherm**

The values of surface coverage $\theta$ for different concentrations of the studied compounds (I - V) at different temperatures are listed in Table (2). The degree of $\theta$ was found to increase, with increasing the concentration of the additives, and decrease with rise in temperature from 30 to 60°C. For a certain range of inhibitor concentrations, and temperatures when monolayer adsorption occurs on the steel surface, the Langmuir adsorption isotherm (Makhlouf and Wahdan, 1995) may express by:

$$\frac{\theta}{1-\theta} = AC \exp\left(\frac{-\Delta H}{RT}\right) \qquad (5)$$

Where A is independent constant, C is the inhibitor concentration and ΔH is the heat of adsorption. Equation (5) can be converted to the logarithmic scale:

$$\log\frac{\theta}{1-\theta} = \log A + \log C - \frac{\Delta H}{2.303\ RT} \qquad (6)$$

Figure 3 represents the relationship between $\log\frac{\theta}{1-\theta}$ vs $\frac{1}{T}$ at different concentrations of compound II, as an example. Similar curves were obtained for the other compounds (not shown) and the data obtained are listed in Table (3). Straight lines relationship was obtained. This means that, the adsorption of azo dye compounds on the C-steel, obeys Langmuir adsorption isotherm. The values of heat of adsorption ΔH, can be calculated form  the  slope

**Table 2**. The effect of temperature on the corrosion parameters of C-steel in 2M HCl containing different concentrations of inhibitor

| Conc. | Temp. °C | Free 2M HCl | Compound (I) | | | Compound (II) | | | Compound (III) | | | Compound (IV) | | | Compound (V) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Wt. loss | Wt. loss | IE | θ | Wt. loss | IE | θ | Wt. loss | IE | θ | Wt. loss | IE | θ | Wt. loss | IE | θ |
| $10^{-3}$ | 30 °C | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| | 40 °C | 0.0744 | 0.0254 | 65.18 | 0.6518 | 0.0211 | 71.63 | 0.7163 | 0.0231 | 68.95 | 0.6895 | 0.0332 | 55.37 | 0.5537 | 0.0287 | 61.4 | 0.614 |
| | 50 °C | 0.081 | 0.0296 | 63.45 | 0.6345 | 0.0268 | 66.91 | 0.6691 | 0.0288 | 64.44 | 0.6444 | 0.0358 | 53.82 | 0.5382 | 0.0321 | 60.37 | 0.6037 |
| | 60 °C | 0.0865 | 0.0326 | 62.08 | 0.6208 | 0.0315 | 63.58 | 0.6358 | 0.0321 | 62.89 | 0.6289 | 0.0397 | 52.36 | 0.5236 | 0.0387 | 55.26 | 0.5526 |
| | | 0.0934 | 0.0354 | 60.59 | 0.5059 | 0.0382 | 59.10 | 0.5910 | 0.0354 | 62.09 | 0.6209 | 0.0435 | 46.28 | 0.4628 | 0.0454 | 51.39 | 0.5139 |
| $10^{-4}$ | 30 °C | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| | 40 °C | 0.0744 | 0.0294 | 60.48 | 0.6048 | 0.0269 | 63.48 | 0.6384 | 0.0272 | 63.44 | 0.6344 | 0.0398 | 46.50 | 0.4650 | 0.0301 | 59.5 | 0.595 |
| | 50 °C | 0.081 | 0.0328 | 59.50 | 0.5950 | 0.0321 | 60.37 | 0.6037 | 0.0311 | 61.60 | 0.6160 | 0.0441 | 45.55 | 0.4555 | 0.0358 | 55.80 | 0.5580 |
| | 60 °C | 0.0865 | 0.0365 | 57.80 | 0.5780 | 0.0354 | 59.07 | 0.5907 | 0.0352 | 59.30 | 0.5930 | 0.0475 | 45.05 | 0.4505 | 0.0398 | 53.98 | 0.5398 |
| | | 0.0934 | 0.0411 | 55.99 | 0.5599 | 0.0393 | 57.92 | 0.5792 | 0.0389 | 58.35 | 0.5835 | 0.0538 | 42.39 | 0.4239 | 0.0459 | 50.85 | 0.5085 |
| $10^{-5}$ | | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| | 30 °C | 0.0744 | 0.0329 | 55.77 | 0.5577 | 0.0288 | 61.29 | 0.6129 | 0.0298 | 59.94 | 0.5994 | 0.0421 | 43.41 | 0.4341 | 0.0336 | 54.8 | 0.548 |
| | 40 °C | 0.081 | 0.0348 | 49.50 | 0.4950 | 0.0342 | 57.77 | 0.5777 | 0.0379 | 53.20 | 0.5320 | 0.0465 | 42.59 | 0.4259 | 0.0389 | 51.97 | 0.5197 |
| | 50 °C | 0.0865 | 0.0368 | 47.86 | 0.4786 | 0.0382 | 55.83 | 0.5583 | 0.0412 | 52.36 | 0.5236 | 0.0499 | 40.92 | 0.4092 | 0.0443 | 48.78 | 0.4878 |
| | 60 °C | 0.0934 | 0.0401 | 46.35 | 0.4635 | 0.0422 | 52.78 | 0.5278 | 0.0465 | 50.12 | 0.5012 | 0.0539 | 38.54 | 0.3854 | 0.0498 | 46.68 | 0.4668 |
| $10^{-6}$ | | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| | 30 °C | 0.0744 | 0.0349 | 53.09 | 0.5309 | 0.0345 | 53.62 | 0.5362 | 0.0335 | 54.97 | 0.5497 | 0.0433 | 41.80 | 0.4180 | 0.0347 | 53.3 | 0.533 |
| | 40 °C | 0.081 | 0.0384 | 49.50 | 0.4950 | 0.0389 | 51.97 | 0.5197 | 0.0384 | 52.59 | 0.5259 | 0.0498 | 38.51 | 0.3851 | 0.0402 | 50.37 | 0.5037 |
| | 50 °C | 0.0865 | 0.0411 | 47.86 | 0.4786 | 0.0411 | 49.47 | 0.4947 | 0.0411 | 50.05 | 0.5005 | 0.0551 | 36.30 | 0.3630 | 0.0454 | 47.51 | 0.4751 |
| | 60 °C | 0.0934 | 0.0448 | 46.35 | 0.4635 | 0.0454 | 48.17 | 0.4817 | 0.0435 | 49.89 | 0.948 | 0.0594 | 34.26 | 0.3426 | 0.0521 | 44.21 | 0.4421 |

of the straight line ($\dfrac{-\Delta H}{2.303\ R}$) and are given in Table (3). The negative values of ΔH reflect the exothermic behavior of azo dye compounds on carbon steel surface.

**Thermodynamic parameter**

The Langmuir adsorption isotherm may be formulated as:

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (7)$$

Where K is the equilibrium constant for adsorption process. Figure 4 represents, the plot of log $\dfrac{C}{\theta}$ vs

log C for compound II, as an example, adsorption isotherm. Similar curves were obtained for the other compounds (not shown).A straight lines with

unit slope value indicating that the adsorption of azodyes on C-steel surface follows Langmuir. From these results one can postulates that there is no interaction between the adsorbed species. The equilibrium constant (K) for adsorption de-sorption can be calculated from the reciprocal of anti logarithm of the intercept, listed in Table (3). The thermodynamic parameters for adsorption process. $(\Delta G)_{ads}$, and entropy $(\Delta S)_{ads}$ of the investigated compounds can be obtained from the thermodynamic relations:

**Table 3.** Activation parameters for the dissolution of C-steel in 2M HCl in the absence and presence of  different concentrations of inhibitors.

| Conc. | Temp | Compound I | | | | | Compound II | | | | | Compound III | | | | |
| | | Activation parameters (KJ mol⁻¹) | | | | | Activation parameters (KJ mol⁻¹) | | | | | Activation parameters (KJ mol⁻¹) | | | | |
| | | K | Ea° | ΔH° | -ΔG° | ΔS° | K | Ea° | ΔH° | -ΔG° | ΔS° | K | Ea° | ΔH° | -ΔG° | ΔS° |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $10^{-3}$ | 30 | 1.54x103 | -10.78 | 12.44 | 25.47 | 18.50 | $1.39 \times 10^3$ | -12.12 | 13.97 | 20.16 | 18.23 | $1.45 \times 10^3$ | -11.21 | 12.82 | 23.53 | 18.34 |
| | 40 | $1.58 \times 10^3$ | | | 26.80 | 19.17 | $1.49 \times 10^3$ | | | 22.01 | 19.01 | $1.55 \times 10^3$ | | | 25.23 | 19.11 |
| | 50 | $1.61 \times 10^3$ | | | 28.01 | 19.83 | $1.58 \times 10^3$ | | | 23.71 | 19.78 | $1.59 \times 10^3$ | | | 26.59 | 19.80 |
| | 60 | $1.78 \times 10^3$ | | | 30.72 | 21.01 | $1.69 \times 10^3$ | | | 25.40 | 20.58 | $1.61 \times 10^3$ | | | 27.71 | 20.44 |
| $10^{-4}$ | 30 | $1.65 \times 10^4$ | -10.27 | 11.77 | 46.89 | 24.48 | $1.56 \times 10^4$ | -11.49 | 12.87 | 42.37 | 24.33 | $1.56 \times 10^4$ | -10.33 | 12.66 | 46.20 | 24.33 |
| | 40 | $1.68 \times 10^4$ | | | 48.08 | 25.32 | $1.65 \times 10^4$ | | | 44.05 | 25.28 | $1.62 \times 10^4$ | | | 47.60 | 25.23 |
| | 50 | $1.73 \times 10^4$ | | | 49.34 | 26.21 | $1.69 \times 10^4$ | | | 45.38 | 26.15 | $1.68 \times 10^4$ | | | 48.94 | 26.14 |
| | 60 | $1.78 \times 10^4$ | | | 48.10 | 26.29 | $1.72 \times 10^4$ | | | 46.63 | 27.02 | $1.71 \times 10^4$ | | | 50.30 | 26.99 |
| $10^{-5}$ | 30 | $1.79 \times 10^5$ | -9.88 | 10.43 | 67.95 | 30.47 | $1.63 \times 10^5$ | -10.91 | 11.68 | 63.39 | 30.12 | $1.63 \times 10^5$ | -10.00 | 11.88 | 66.76 | 30.23 |
| | 40 | $2.02 \times 10^5$ | | | 70.00 | 31.79 | $1.73 \times 10^5$ | | | 61.72 | 30.30 | $1.87 \times 10^5$ | | | 68.97 | 31.59 |
| | 50 | $2.09 \times 10^5$ | | | 71.26 | 32.90 | $1.79 \times 10^5$ | | | 66.81 | 32.49 | $1.91 \times 10^5$ | | | 70.15 | 32.66 |
| | 60 | $2.15 \times 10^5$ | | | 72.40 | 33.99 | $1.89 \times 10^5$ | | | 68.28 | 33.65 | $1.99 \times 10^5$ | | | 71.41 | 33.78 |
| $10^{-6}$ | 30 | $1.88 \times 10^6$ | -9.50 | 9.54 | 84.5 | 36.40 | $1.80 \times 10^6$ | -9.88 | 10.85 | 79.6 | 36.29 | $1.81 \times 10^6$ | -9.66 | 10.60 | 82.8 | 36.30 |
| | 40 | $2.05 \times 10^6$ | | | 86.3 | 37.82 | $1.92 \times 10^6$ | | | 81.5 | 37.65 | $1.90 \times 10^6$ | | | 84.3 | 37.62 |
| | 50 | $2.09 \times 10^6$ | | | 87.6 | 39.08 | $2.02 \times 10^6$ | | | 83.1 | 38.99 | $1.99 \times 10^6$ | | | 85.8 | 38.95 |
| | 60 | $2.15 \times 10^6$ | | | 88.8 | 40.37 | $2.05 \times 10^6$ | | | 84.4 | 40.24 | $2.07 \times 10^6$ | | | 87.2 | 40.27 |

**Table 3.** Contd.

| Conc. | Temp | Compound IV | | | | | Compound V | | | | |
| | | Activation parameters (KJ mol⁻¹) | | | | | Activation parameters (KJ mol⁻¹) | | | | |
| | | K | Ea° | ΔH° | -ΔG° | ΔS° | K | Ea° | ΔH° | -ΔG° | ΔS° |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10-3 | 30 | $1.87 \times 10^3$ | -9.55 | 12.07 | 31.12 | 18.98 | $1.62 \times 10^3$ | -9.60 | 12.25 | 29.80 | 18.63 |
| | 40 | $1.80 \times 10^3$ | | | 31.78 | 19.50 | $1.65 \times 10^3$ | | | 30.95 | 19.29 |
| | 50 | $1.91 \times 10^3$ | | | 33.25 | 20.29 | $1.81 \times 10^3$ | | | 32.63 | 20.14 |
| | 60 | $2.21 \times 10^3$ | | | 35.37 | 21.33 | $1.94 \times 10^3$ | | | 34.14 | 20.97 |
| $10^{-4}$ | 30 | $2.18 \times 10^4$ | -9.20 | 11.50 | 52.67 | 25.16 | $1.68 \times 10^4$ | -9.33 | 11.78 | 50.99 | 24.51 |
| | 40 | $2.19 \times 10^4$ | | | 53.70 | 26.01 | $1.79 \times 10^4$ | | | 51.62 | 25.49 |
| | 50 | $2.22 \times 10^4$ | | | 54.73 | 26.88 | $1.85 \times 10^4$ | | | 52.81 | 26.39 |
| | 60 | $2.36 \times 10^4$ | | | 56.09 | 27.88 | $1.96 \times 10^4$ | | | 54.17 | 27.37 |
| $10^{-5}$ | 30 | $2.30 \times 10^5$ | -8.95 | 10.25 | 73.13 | 31.11 | $1.82 \times 10^5$ | -9.02 | 10.30 | 70.95 | 30.52 |
| | 40 | $2.34 \times 10^5$ | | | 77.50 | 33.21 | $1.92 \times 10^5$ | | | 72.36 | 31.67 |
| | 50 | $2.44 \times 10^5$ | | | 75.44 | 33.32 | $2.05 \times 10^5$ | | | 72.94 | 32.85 |
| | 60 | $2.59 \times 10^5$ | | | 76.75 | 34.51 | $2.14 \times 10^5$ | | | 74.95 | 33.98 |
| $10^{-6}$ | 30 | $2.39 \times 10^6$ | -8.44 | 9.12 | 90.5 | 37.00 | $1.87 \times 10^6$ | -8.75 | 9.30 | 88.3 | 36.38 |
| | 40 | $2.63 \times 10^6$ | | | 92.3 | 38.47 | $1.98 \times 10^6$ | | | 89.7 | 37.73 |
| | 50 | $2.76 \times 10^6$ | | | 93.7 | 39.83 | $2.10 \times 10^6$ | | | 91.3 | 39.09 |
| | 60 | $2.92 \times 10^6$ | | | 95.1 | 41.22 | $2.26 \times 10^6$ | | | 92.7 | 40.50 |

$$K = \exp \frac{-\Delta G_{ads}}{RT} \qquad (8)$$

$$\Delta G = \Delta H - T\Delta S \qquad (9)$$

**Table 4.** The values of corrosion parameters for the corrosion of carbon steel in 2M of HCl by galvanostatic polarization technique.

| Inhibitor | Concentration M | $I_{corr}$ ($\mu Acm^{-2}$) | $-E_{corr}$ mV | $B_a$ mV $dec^{-1}$ | $B_c$ mV $dec^{-1}$ | $\theta$ | %IE |
|---|---|---|---|---|---|---|---|
| Compound I | 0 M compound I | 1.970 | 530 | 200 | 160 | - | - |
| | $1x\,10^{-6}$ M compound I | 0.878 | 508 | 202 | 197 | 0.554 | 55.43 |
| | $1x\,10^{-5}$ M compound I | 0.8372 | 510 | 205 | 211 | 0.575 | 57.50 |
| | $5x10^{-5}$ M compound I | 0.8017 | 515 | 210 | 208 | 0.593 | 59.30 |
| | $1x10^{-4}$ M compound I | 0.7210 | 514 | 208 | 204 | 0.634 | 63.40 |
| | $5X10^{-4}$ M compound I | 0.6973 | 517 | 207 | 201 | 0.646 | 64.60 |
| | $1X10^{-3}$ M compound I | 0.5791 | 520 | 209 | 200 | 0.706 | 70.60 |
| Compound II | 0 M compound II | 1.970 | 530 | 200 | 160 | - | - |
| | $1x\,10^{-6}$ M compound II | 0.872 | 495 | 190 | 174 | 0.557 | 55.73 |
| | $1x\,10^{-5}$ M compound II | 0.717 | 498 | 201 | 188 | 0.636 | 63.60 |
| | $5x10^{-5}$ M compound II | 0.699 | 502 | 198 | 178 | 0.645 | 64.51 |
| | $1x10^{-4}$ M compound II | 0.6567 | 505 | 203 | 189 | 0.666 | 66.66 |
| | $5X10^{-4}$ M compound II | 0.629 | 508 | 205 | 201 | 0.680 | 68.07 |
| | $1X10^{-3}$ M compound II | 0.4921 | 510 | 201 | 198 | 0.750 | 75.02 |
| Compound III | 0 M compound III | 1.970 | 530 | 200 | 160 | - | - |
| | $1x\,10^{-6}$ M compound III | 0.844 | 510 | 188 | 197 | 0.571 | 57.15 |
| | $1x\,10^{-5}$ M compound III | 0.80 | 512 | 205 | 197 | 0.593 | 59.39 |
| | $5x10^{-5}$ M compound III | 0.731 | 514 | 201 | 188 | 0.628 | 62.89 |
| | $1x10^{-4}$ M compound III | 0.682 | 515 | 211 | 207 | 0.654 | 65.43 |
| | $5X10^{-4}$ M compound III | 0.632 | 518 | 205 | 205 | 0.679 | 67.91 |
| | $1X10^{-3}$ M compound III | 0.521 | 520 | 203 | 215 | 0.735 | 73.55 |
| Compound I V | 0 M compound I V | 1.970 | 530 | 200 | 160 | - | - |
| | $1x\,10^{-6}$ M compound IV | 1.07 | 511 | 210 | 203 | 0.456 | 45.68 |
| | $1x\,10^{-5}$ M compound IV | 1.031 | 517 | 205 | 200 | 0.476 | 47.66 |
| | $5x10^{-5}$ M compound IV | 0.981 | 514 | 198 | 202 | 0.520 | 50.20 |
| | $1x10^{-4}$ M compound IV | 0.942 | 518 | 204 | 199 | 0.521 | 52.18 |
| | $5X10^{-4}$ M compound IV | 0.871 | 518 | 207 | 203 | 0.557 | 55.78 |
| | $1X10^{-3}$ M compound IV | 0.782 | 519 | 211 | 220 | 0.603 | 60.30 |
| Compound V | 0 M compound V | 1.970 | 530 | 200 | 160 | - | - |
| | $1x\,10^{-6}$ M compound V | 0.882 | 503 | 202 | 194 | 0.552 | 55.22 |
| | $1x\,10^{-5}$ M compound V | 0.833 | 506 | 201 | 200 | 0.577 | 57.71 |
| | $5x10^{-5}$ M compound V | 0.773 | 510 | 210 | 215 | 0.607 | 60.76 |
| | $1x10^{-4}$ M compound V | 0.711 | 512 | 207 | 211 | 0.639 | 63.90 |
| | $5X10^{-4}$ M compound V | 0.667 | 511 | 211 | 198 | 0.661 | 66.142 |
| | $1X10^{-3}$ M compound I | 0.610 | 513 | 210 | 205 | 0.690 | 69.03 |

by weight loss measurements. These results may be due to the fact that, the electrochemical measurements were carried out on freshly prepared solutions.

**Mechanism of inhibition**

The inhibition action of mono azo compounds towards the corrosion of C-steel in 2M HCl, could be attributed to several factors including the structure, the number and types of adsorption sites, the nature of molecule, the metal surface, and the ability to form complexes (Fouda et al., 1986 ; Oguzie, 2005; Abdallah, 2004).

The inhibition mechanism of azo compounds under investigation is believed to be as a result of complex formation between $Fe^{2+}$ ion, and azo compounds. The formed complex is adsorbed on the metal surface and thereby isolating the metal from further corroding attack. To provide an evidence for formation of complex, the conductometric titration was carried out, to determine the stiochiometric ratio between $Fe^{2+}$ and azo dye compounds.

Conductometric titration was carried out by titrating 50 ml of $1 \times 10^{-4}M$ $Fe^{2+}$ with solution of $1 \times 10^{-3}M$ mono azo compound as titrant. The mono azo compounds used as

an inhibitor, have many centers for complex formation such as: the azo group (-N=N-), the o-substituted center, and the o-hydroxyl groups in the coumarine moiety. So the stiochiometric ratio of the metal complexes may be 1:1, 1:2 (M: L) (M = metal; L = ligand). This reflects that the great tendency of these compounds to adsorbed on the metal surface forming a protective film. For 1:1 metal /ligand complex, the ligand can react with $Fe^{2+}$ ion via two routes to give structure I and II.
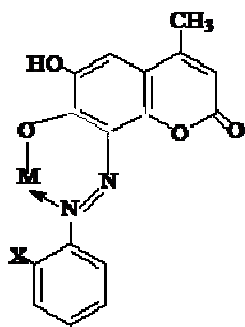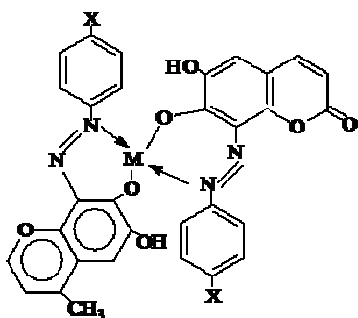


Structure I
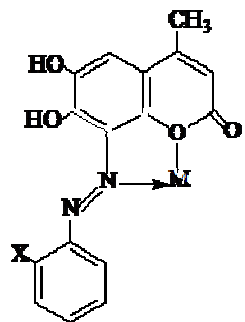


Structure II

In structure I, six membered ring is formed whereas in structure II, five membered ring is formed. Since six membered ring is more stable than five membered ring, thus structure I is the more preferably complex that is formed in case of 1:1 ($Fe^{2+}$/dye) complex formation. The expected structure of the complex formed in case of 1:2 ($Fe^{2+}$/dye) complex is structure III.



Structure III

The results indicated that the %IEs of mono azo dye compounds is more or less, dependent on the nature of constituents. The order of inhibition efficiency obtained from weight loss and polarization techniques decreases in the following order: II> III > I> V > IV.

The mono azo dye derivatives used in the present investigation, have an electron donating groups o-$OCH_3$ and –OH, and electron withdrawing group such –COOH and $NO_2$. The order of inhibition efficiency of the compounds studied, as given by weight loss and galvano-static polarization techniques decreases in the following order:

$$-OCH_3 > -OH > H > - COOH > - NO_2$$
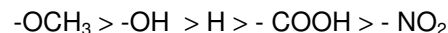
It is obvious from above sequence that, compounds containing electron donating groups are more efficient than compounds containing electron withdrawing groups. The electron donating groups enhance adsorption and increase the surface area covered by the compound and consequently, increase the inhibition efficiency. Compound II containing -$OCH_3$ group is more efficient than compound III containing –OH group.. -$OCH_3$ has a positive mesomeric effect (+M effect) and negative inductive effect (–I effect). So these groups are strong donating groups which facilitate the formation of stable complex, because it increases the electron density at the ring.

Compound IV containing –$NO_2$ group has the least inhibition efficiency, due to the electron withdrawing effect of –$NO_2$, which leads to decrease in electron density at the ring and hence the inhibition efficiency. Compound IV is less efficient than compound V due to that the large withdrawing effect of -$NO_2$, than the compounds containing –COOH group.

## Conclusions

1. Mono azo dye compounds inhibit the corrosion of carbon steel in 2 M HCl.
2. The inhibition efficiency of these compounds increased by increasing the electron donor characteristic of the substituted groups and decreasing of temperature.
3. The inhibition action of these compounds is attributed to adsorption of stable insoluble complex on the metal surface.
4. The adsorption of azo dye compounds on the carbon steel surface at different temperature was found to obey the Langmuir adsorption isotherm.
5. The stiochiometry of the expected Fe-azo dye compounds complexes was estimated by conductometric titration.

### REFERENCES

Abd El-Rehim SS, Ibrahim MAM, Khaled KF (1999). 4-Aminoantipyrine as an inhibitor of mild steel corrosion in HCl solution. J. Appl. Electrochem., 29: 593.
Abdallah M (2003). Corrosion behavior of 304 stainless steel in sulphuric acid solutions and its inhibition by some substituted pyrazolones Mater. Chem .Phys. 82: 786 .

Abdallah M  (2004). Corrosion inhibition of steel by 1-phenyl 5-mercapto 1,2,3,4- tetrazole in acidic environments Corros. Sci., 46: 1981.

Bensajjay F, Alehyen S, El-A Chouri M, Kertit S (2003). Corrosion inhibition of steel by 1-phenyl 5-mercapto 1,2,3,4- tetrazole in acidic environments.  Anti-corros. Meth. & Mater.., 50(6): 402.

El- Mahdy GA,  Mohamed SS (1995). Inhibition of acid corrosion of pure aluminium with 5-benzylidine-1-methyl-2-methyl thio-imidazole-4-one Corrosion, 51(6): 436.

Fouda AS, Mostafa HA, El-Taib F,  Elewady GY(2004). Synergistic influence of iodide ions on the inhibition of corrosion of carbon steel in sulphuric acid by some aliphatic amines Corros. Sci., 47: 1988-2004.

Fouda AS, Mousa M, Taha F, El-Neanaa A (1986). The role of some thiosemicarbazide derivatives in the corrosion inhibition of aluminium in hydrochloric acid. Corros. Sci., 26 : 719.

Granese SL (1988). Study the inhibition action of nitrogen containing compounds. Corrosion, 44: 322.

Granese SL, Rosales BM, Oviedo G, Zerbino JO (1992). The inhibition action of heterocyclic nitrogen organic compounds on Fe and steel in HCl media, Corros. Sci., 33: 1439.

Dehri I, Ozcan M (2006). The effect of temperature on the corrosion of mild steel in acidic media in the presence of some sulphur containing organic compounds .Mater. Chem and Phys. 98: 316.

Khamis K, Ateya M  (1994). Inhibition of acidic corrosion of aluminium by triazoline derivatives. Corrosion, 50 (2): 106.

Makhlouf MT, Wahdan MW (1995). Thermodynamic parameters of the synergistic effect of some thiols and halide ions on the acid corrosion of mild steel. Polish J. Chem, 69: 1042.

Moustafa ME, Issa YM, El-Hawary WF, Refaat M (1999). Synthesis and analytical application of the complexes of 4-methylesculetin azo compounds with some transition metal ions. Spectroscopy Lett. 32(5): 829.

Oguzie EE  (2005). Corrosion inhibition of mild steel in hydrochloric acid solution by methylene blue dye. Mater. Lett., 59: 1076.

Özcan M, Dehri I, Erbil M   (2004). Organic sulphur containing compounds as corrosion inhibitors for mild steel: Correlation between inhibition efficiency and chemical structure. App. Surf. Sci., 236: 155 .

Putilova I, Balezin S, Barannik V (1960). Metallic Corrosion Inhibitors, Pergamory Oxford.

Putilova IN, Balezin SA, Barannik V, Baba T (1962). Effect of organic inhibitors on the polarization characterstics of mild steel in acid solution. Corros. Sci., 2: 22.

Rosenfelld IL (1981). Corrosion Inhibitors. Mc Graw- Hill, New York .

El-Naggar MM (2007). Corrosion inhibition of mild steel in acidic medium by some sulfa drugs compounds. Corros.Sci. 49:2226 .

Selvi ST, Raman V, Rajendran N (2003). Corrosion inhibition of mild steel by benzotriazole derivatives in acidic medium J. Appl. Electrochem., 33: 1175.

Hosseini MG, Ehteshamzadeh M, Shahrabi T (2007). Protection of mild steel corrosion with Schiff bases in 0.5 M H2SO4 solution. Electrochim Acta, 52: 3680.