Full Length Research Paper

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

M. Abdallah[1], A. S. Fouda[2], S.A. Shama[1] and E. A. Afifi[1]

[1]Chemistry Department, Faculty of Science, Benha University, Benha, Egypt.
[2]Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt.

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, Indus-trial 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 disso-lution. Most of the well-known inhibitors are organic com-pounds 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 -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 com-pounds toward the corrosion of C-steel in 2M hydro-chloric acid solution using weight loss, and galvanostatic polarization techniques. Moreover, the effect of tempe-rature 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. Galva-nostatic polarization studies were carried out using PS remote potentiostat with Zum PS6 software for calculation of electroche-mical parameters. Three compartment cell with a saturated calomel electrode, and a platinum foil auxiliary electrode were used. Con-ductance measurements were carried out using YSI model 32 con-

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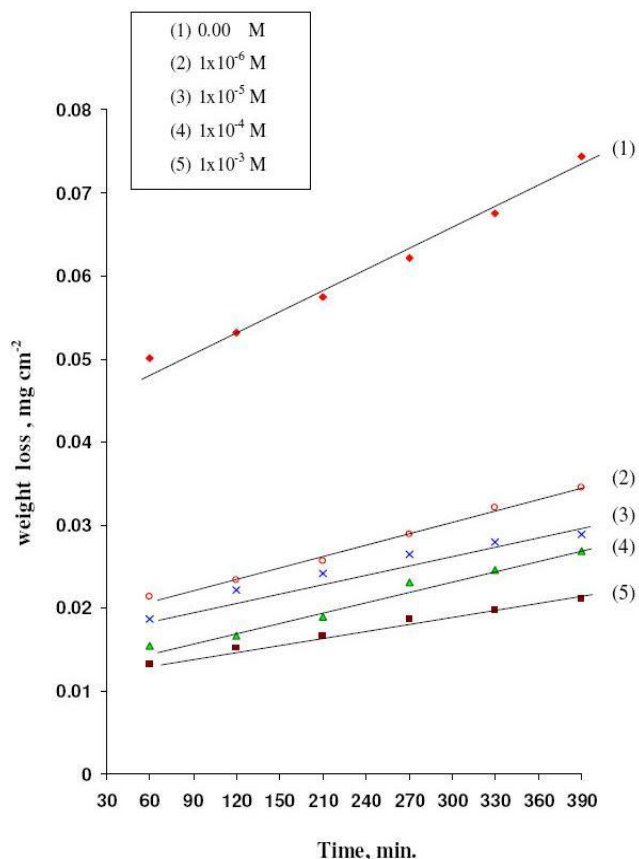*Corresponding author. E-mail: metwally552@hotmail.com.

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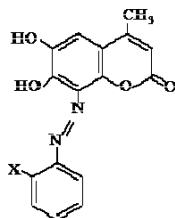
Where X= H (I), o-OCH₃ (II),o-OH (III), o- NO₂ (IV) and o- COOH (V).

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 concentrations 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 compounds 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 parameter surface coverage (θ) which represents the part of the surface covered by the inhibitor molecules, were calculated using the following equations:

$$\% I.E = 1 - \frac{W_{add}}{W_{free}} \times 100 \qquad (1)$$

$$\theta = 1 - \frac{W_{add}}{W_{free}} \qquad (2)$$

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 θ are listed in Table (1).

It is obvious from Table 1, that the weight loss decreases 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).

$$R_{corr} = \frac{\Delta w}{St} \qquad (3)$$

Where Δw is the weight loss of metal, S is the surface area (cm²), 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).

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

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 θ for different concentrations of the studied compounds (I - V) at different temperatures are listed in Table (2). The degree of θ 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:

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

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:

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

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 desorption can be calculated from the reciprocal of anti logarithm of the intercept, listed in Table (3). The thermodynamic parameters for adsorption process. (ΔG)$_{ads}$, and entropy (ΔS)$_{ads}$ 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 Activation parameters (KJ mol^{-1})					Compound II Activation parameters (KJ mol^{-1})					Compound III Activation parameters (KJ mol^{-1})				
		K	$E_a°$	ΔH°	-ΔG°	ΔS°	K	$E_a°$	ΔH°	-ΔG°	ΔS°	K	$E_a°$	ΔH°	-ΔG°	ΔS°
10^{-3}	30	1.54x103	-10.78	12.44	25.47	18.50	1.39x10^3	-12.12	13.97	20.16	18.23	1.45x10^3	-11.21	12.82	23.53	18.34
	40	1.58x10^3			26.80	19.17	1.49x10^3			22.01	19.01	1.55x10^3			25.23	19.11
	50	1.61x10^3			28.01	19.83	1.58x10^3			23.71	19.78	1.59x10^3			26.59	19.80
	60	1.78x10^3			30.72	21.01	1.69x10^3			25.40	20.58	1.61x10^3			27.71	20.44
10^{-4}	30	1.65x10^4	-10.27	11.77	46.89	24.48	1.56x10^4	-11.49	12.87	42.37	24.33	1.56x10^4	-10.33	12.66	46.20	24.33
	40	1.68x10^4			48.08	25.32	1.65x10^4			44.05	25.28	1.62x10^4			47.60	25.23
	50	1.73x10^4			49.34	26.21	1.69x10^4			45.38	26.15	1.68x10^4			48.94	26.14
	60	1.78x10^4			48.10	26.29	1.72x10^4			46.63	27.02	1.71x10^4			50.30	26.99
10^{-5}	30	1.79x10^5	-9.88	10.43	67.95	30.47	1.63x10^5	-10.91	11.68	63.39	30.12	1.63x10^5	-10.00	11.88	66.76	30.23
	40	2.02x10^5			70.00	31.79	1.73x10^5			61.72	30.30	1.87x10^5			68.97	31.59
	50	2.09x10^5			71.26	32.90	1.79x10^5			66.81	32.49	1.91x10^5			70.15	32.66
	60	2.15x10^5			72.40	33.99	1.89x10^5			68.28	33.65	1.99x10^5			71.41	33.78
10^{-6}	30	1.88x10^6	-9.50	9.54	84.5	36.40	1.80x10^6	-9.88	10.85	79.6	36.29	1.81x10^6	-9.66	10.60	82.8	36.30
	40	2.05x10^6			86.3	37.82	1.92x10^6			81.5	37.65	1.90x10^6			84.3	37.62
	50	2.09x10^6			87.6	39.08	2.02x10^6			83.1	38.99	1.99x10^6			85.8	38.95
	60	2.15x10^6			88.8	40.37	2.05x10^6			84.4	40.24	2.07x10^6			87.2	40.27

Table 3. Contd.

Conc.	Temp	Compound IV Activation parameters (KJ mol^{-1})					Compound V Activation parameters (KJ mol^{-1})				
		K	$E_a°$	ΔH°	-ΔG°	ΔS°	K	$E_a°$	ΔH°	-ΔG°	ΔS°
10-3	30	1.87x10^3	-9.55	12.07	31.12	18.98	1.62x10^3	-9.60	12.25	29.80	18.63
	40	1.80x10^3			31.78	19.50	1.65x10^3			30.95	19.29
	50	1.91x10^3			33.25	20.29	1.81x10^3			32.63	20.14
	60	2.21x10^3			35.37	21.33	1.94x10^3			34.14	20.97
10^{-4}	30	2.18x10^4	-9.20	11.50	52.67	25.16	1.68x10^4	-9.33	11.78	50.99	24.51
	40	2.19x10^4			53.70	26.01	1.79x10^4			51.62	25.49
	50	2.22x10^4			54.73	26.88	1.85x10^4			52.81	26.39
	60	2.36x10^4			56.09	27.88	1.96x10^4			54.17	27.37
10^{-5}	30	2.30x10^5	-8.95	10.25	73.13	31.11	1.82x10^5	-9.02	10.30	70.95	30.52
	40	2.34x10^5			77.50	33.21	1.92x10^5			72.36	31.67
	50	2.44x10^5			75.44	33.32	2.05x10^5			72.94	32.85
	60	2.59x10^5			76.75	34.51	2.14x10^5			74.95	33.98
10^{-6}	30	2.39 x10^6	-8.44	9.12	90.5	37.00	1.87 x10^6	-8.75	9.30	88.3	36.38
	40	2.63 x10^6			92.3	38.47	1.98 x10^6			89.7	37.73
	50	2.76 x10^6			93.7	39.83	2.10 x10^6			91.3	39.09
	60	2.92 x10^6			95.1	41.22	2.26 x10^6			92.7	40.50

$$K = \exp \frac{-G_{ads}}{RT} \qquad (8)$$
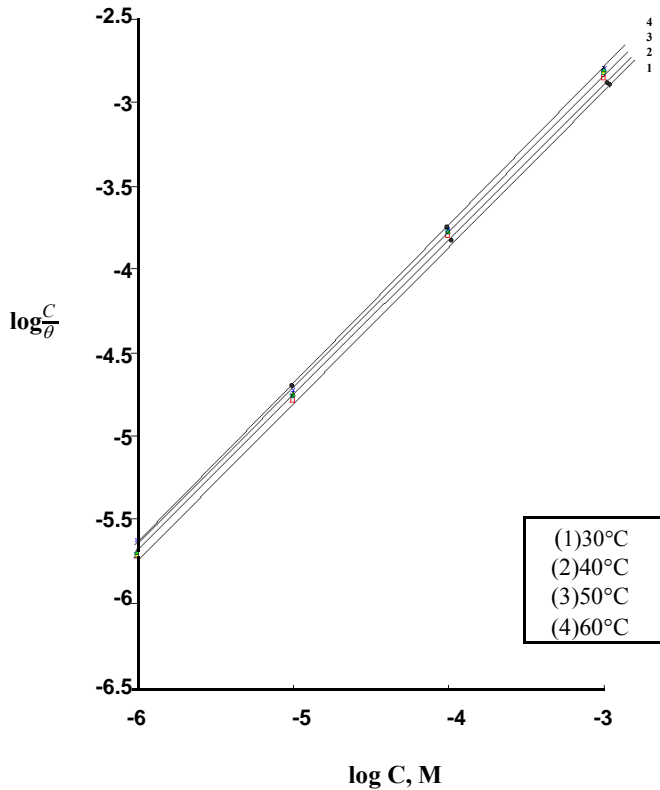
$$\Delta G = \Delta H - T\Delta S \qquad (9)$$

Figure 4. Langmuir adsorption isotherm plotted as log (C/θ) vs log C for corrosion of C-steel in 2M HCl containing different concentrations of compound (II) at different temperatures.
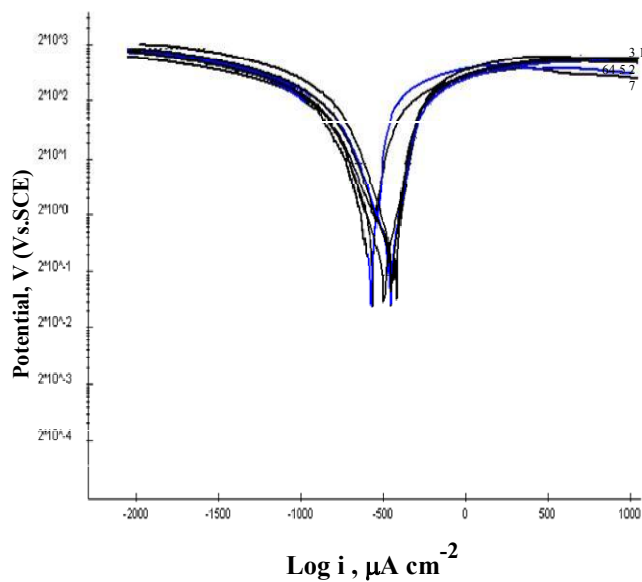

Figure 5. Galvanostatic polarization curves for the dissolution of carbon steel in 2M HCl in absence and presence of different concentrations of compound (II) at 30°C. (1) 2 M HCl; (2) 2M HCl +1x10^{-6} M compound II (3) 2M HCl +1x10^{-5} M; (4) 2M HCl +5x10^{-5} M; (5) 2M HCl +1x10^{-4} M ;(6) 2M HCl +5x10^{-4} M;(7) 2M HCl +1x10^{-3} M.

The calculated values of ΔG_{ads} and ΔS_{ads} over the temperature range from 30 to 60°C are given in Table (3). The negative values of ΔG_{ads} indicate the spontaneous adsorption of azo dye compounds on the surface of carbon steel. The value of ΔS_{ads} is decreased with decreasing of temperature. This supports the higher absorbability of azo dye compounds on the steel surface.

Galvanostatic polarization

Figure 5 shows typical anodic and cathodic polarization curves of carbon steel in 2 M HCl in absence and presence of varying concentrations of compound II. Similar curves (not shown) were obtained for the other compounds.

The values of cathodic ($_c$) and anodic ($_a$) Tafel constants were, calculated from the linear region of the polarization curves. The corrosion current density (I_{corr}) was determined, from the intersection of the linear part of cathodic, and anodic curves with stationary corrosion potential (E_{corr}).

The percentage inhibition efficiency (%IE) was calculated using the following equation:

$$\% \text{ IE} = \left(1 - \frac{I_{add}}{I_{free}}\right) 100 \tag{10}$$

Where I_{free} and I_{add} are the corrosion current densities in the absence and presence of inhibitors, respectively.

Table (4) shows the effect of the inhibitor concentrations on the corrosion parameters such as $_a$, $_c$, E_{corr}, I_{corr}, θ and %IE.

An inspection of the results presented in Table (4) reveals that, increasing the concentration of the additive compounds show the following:

i) The values of $_a$ & $_c$ are approximately constant, indicating the blocking of the available surface area of the metal by the inhibitor molecules. In other words, the adsorbed inhibitor molecule decreases the surface area available for, both metal dissolution, and hydrogen.

ii) Reaction without affecting the reaction mechanism (Khamis and Ateya, 1994).

iii) The corrosion potential (E_{corr}) shifted to more positive values, while the corrosion current I_{corr} decreases with increasing the inhibitor concentration, indicating the inhibiting effect of these compounds.

iv. The %IE calculated was found to increase with increasing the inhibitor concentration. The inhibition achieved by these compounds decreases in the following sequence:

II > III > I > V > IV

It is of interest to note that, the value of %IE given by galvanostatic polarization, are higher than those obtained

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} (μAcm^{-2})	$-E_{corr}$ mV	B_a mV dec^{-1}	B_c mV dec^{-1}	θ	%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 x 10^{-4}M Fe^{2+} with solution of 1 x 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.
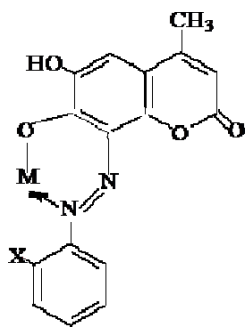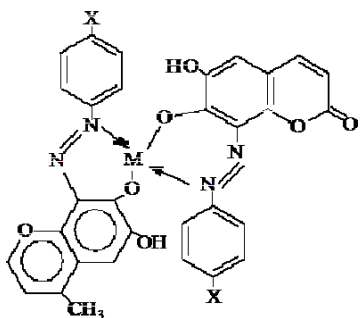

Structure I
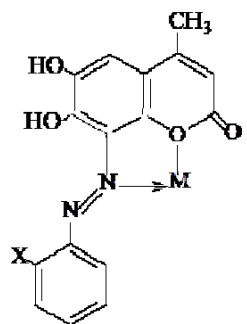
Structure II

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 galvanostatic polarization techniques decreases in the following order:

-OCH_3 > -OH > H > - COOH > - NO_2
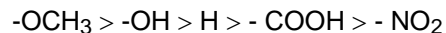
It is obvious from above sequence that, compounds containing electron donating groups are more efficient than compounds containing electron withdrawing groups. The electron donating groups enhance adsorption and increase the surface area covered by the compound and consequently, increase the inhibition 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.

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