RESEARCH ARTICLE

Corrosion Inhibition Efficiency and Adsorption of Azo Schiff Base Chelate Surfactant at Carbon Steel in Hydrochloric Acid Interface

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Abstract

The aromatic Schiff base with azo linkage (CHMB) has been synthesized and characterized by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopic techniques. The compound (CHMB) has been evaluated as carbon steel corrosion inhibitor at different concentrations (0.1, 0.5, 1 and 5 mM) and different temperatures (298-318 K). The corrosion inhibition efficiency was studied by Potentiodynamic polarization. The effects of concentration and temperature on the inhibition efficiency were studied by Potentiodynamic polarization measurements, the results showed that increasing concentration of (CHMB) increases the inhibition efficiency while increasing the temperature decreases it, the highest corrosion inhibition efficiency, 93.58% was recorded with 5 mM of CHMB at 298 K in 1 M HCl. The adsorption process was found to obey Langmuir isotherm, and the adsorption thermodynamic parameters were studied.

Keywords: *Carbon steel, Corrosion inhibitors, Azo, Schiff base, Organic inhibitors.*

Introduction

In several industrial processes hydrochloric acid solution is widely used as an acid wash solution (cleaning, pickling, descaling) for removing rust and scale from a mild steel surface [1-3].This usually leads to serious metallic corrosion. To prevent their aggressiveness, use of an additive is the most effective and sensible approach to protect several metal and alloys against such type of acidic attack [4, 5]. A variety of additives are nowadays used to prevent metallic corrosion.

In this connection, organic com- pounds containing electron rich functional groups along with π-electrons inside their frameworks show better corrosion inhibition efficiency in such acid media. To date the existing results show that organic inhibitors adsorbed on the metallic surface either by physical or chemical adsorption or by both and eventually a protective layer is formed. Organic molecules having (i) N, O and S donor sites, (ii) unsaturated π-bonds, (iii) planar and conjugated aromatic rings are considered as effective adsorption centers,

because of their capability to donate available lone pair of electrons or acceptance of electrons in their low energy empty orbital's [6-9]. Thus compounds containing both nitrogen (N) and oxygen (O) in their structural unit exhibit greater inhibition performance compared to those possessing only one of these heteroatoms [10-12]. Among the reported organic inhibitors ones that contain imine (-C=N) [13-15] and/or azo (-N=N-) [16] groups in their structures.

In the present work we report the design, synthesis, and use of azo-Schiff compound as carbon steel corrosion inhibitor in 1.0 M HCl solution. The inhibitor is readily synthesized via two steps synthetic pathway from relatively inexpensive starting materials, it is designed to be rich with π-electrons, has azo (-N=N-), imine (-C=N) and carboxyl (-COOH) groups in its structure. The inhibition efficiency of these compounds was determined by using Potentiodynamic polarization. The thermodynamic parameters and activation of inhibitor were studied.

Experimental Detail

Materials

Tests were performed on carbon steel (CS) of the following composition: 0.3% C, 1.2% Mn, 0.05% P, 0.06% S, and the remainder is Fe.

Inhibitor

The target compound was synthesized via two steps as shown in Scheme 1. Compound 3 was synthesized according to a literature procedure [17], then 3 (10 mmol) was dissolved in (20 ml) methanol. 4-Aminobenzoic acid (10 mmol) was dissolved in absolute methanol (25 ml), the two solutions were mixed and catalytic amount of glacial acetic acid was added. The reaction mixture was subjected to reflux conditions for 6 hours. The product was collected by filtration and washed with hot methanol.
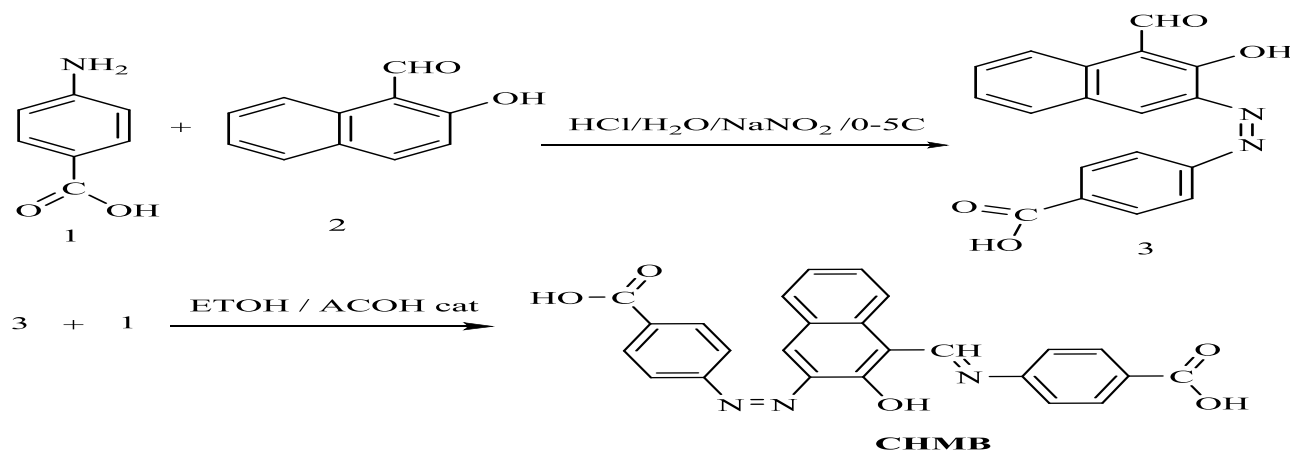
Scheme 1: Synthesis of CHMB

Result and Discussion

Structure Confirmation of the Synthesized Inhibitor

FTIR Spectroscopy

FTIR spectra of the synthesized compound showed the following absorption bands at 1637 cm^{-1} (C=N), 1689 cm^{-1} (C=O), 1603 cm^{-1} (aromatic C=C), 3425 cm^{-1} (O-H) and 1597 cm^{-1} (N=N) [18].FTIR spectra confirmed the expected functional groups in the synthesized.

^{1}HNMR Spectroscopy

^{1}HNMR spectra (400 MHz, DMSO-d$_6$) showed 9.31 ppm (s, 1H, N=CH), 7.15- 8.52 ppm (s, phenyl ring), 12.43 ppm (s, 1H, OH) and 13.00 ppm (s, 1H, COOH).

^{13}CNMR Spectroscopy

^{13}CNMR spectra (400 MHz, DMSO-d6) showed 167 ppm (carboxyl carbon), 120-138 ppm (aromatic carbon) and 164 ppm (-C=N).

Potentiodynamic Polarization Measurements

Potentiodynamic polarization measurements were carried out by three electrodes cell. Saturated calomel electrode Hg/Hg$_2$ Cl$_2$ was used as a reference electrode and Pt electrode was used as an auxiliary electrode. The carbon steel specimen was connected to the working electrode with exposure area of 1 cm^2. By the extrapolation of Tafel plots segments, the corrosion current density (I$_{corr}$) was measured. The inhibition efficiency (η %) was calculated according to equation (1) [19].

$$\% \, \eta = \left(\frac{I°corr - Icorr}{I°corr} \right) \times 100 \quad (1)$$

Where I°$_{corr}$ and I$_{corr}$ are uninhibited and inhibited corrosion current densities, respectively.Potentiodynamic polarization measurements were used to test the corrosion inhibition efficiency of carbon steel by the (CHMB) compound in 1M HCl. The experiments were carried out at different temperatures (298, 308 and 318 K), in presence of different concentrations of CHMB (0.10, 0.50, 1.00 and 5.00 mM).

Table 1 illustrates the measured parameters that include: corrosion potential (E$_{corr}$), corrosion current density (I$_{corr}$), cathodic and anodic Tafel slopes (ßc and ßa), inhibition efficiency (η %) and surface coverage (θ). The results indicate that increasing the

concentration increases the inhibition efficiency at each temperature, the maximum recorded inhibition efficiency was 93.58% in the presence of CHMB in 5 mM concentration at 298 K [20]. It was also found that increasing the temperature above 298 K decreases the inhibition efficiency, such decrement in the efficiency may be attributed to the desorption of CHMB molecules form

the adsorbed protective film on the metal surface. The displacement in the E_{corr} values that results from the presence of CHMB in the acidic solution was found to be less than 50 mV (Table 1); this indicates that CHMB acts as a mixed type inhibitor which inhibits both anodic and cathodic reactions simultaneously [21].Fig. 1 shows the obtained polarization curves.

Table 1: polarization parameters for carbon steel corrosion in 1M HCl in the presence of different concentrations CHMB at different temperatures

| θ	η%	β_a mv/Dec	β_c mv/Dec	I_{corr} µA/Cm²	CR mpy	- E_{corr} mV	Inhibitor Conc. mM	Tem. K
0	0	311.6	-302.7	31.03	13.63	446		298
0	0	364.9	-371.4	39.84	18.15	443	blank	308
0	0	344.9	-331.6	43.49	19.83	448		318
0.74	73.92	117.7	-104.3	8.09	3.69	461		298
0.71	70.78	163.9	-149	11.64	5.31	460	0.1	308
0.68	67.78	124.2	-121.4	14.01	6.39	452		381
0.83	83.11	77.9	-85	5.24	2.39	456		298
0.79	79.44	118.9	-125.9	8.19	3.73	456	0.5	308
0.75	74.75	111.7	-107.7	10.98	5.01	457		318
0.92	92.16	198.1	-113.1	2.43	1.11	409		298
0.85	84.86	131.3	-131.2	6.03	2.75	443	1	308
0.83	83.05	116.3	-120.6	7.37	3.36	505		318
0.94	93.58	155.9	-99.8	1.99	0.91	410		298
0.86	85.54	125	-130.8	5.76	2.63	462	5	308
0.82	82.32	116.3	-132	7.68	3.50	507		318
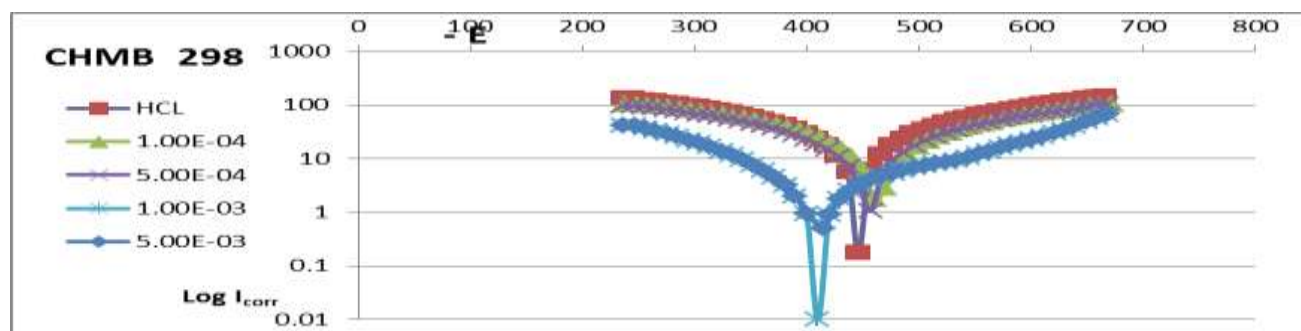
Fig. 1: Potentiodynamic polarization curves for carbon steel in 1 M HCl in the absence and presence of CHMB at 298 K

Effect of Temperature

The effect of temperature on the corrosion parameters of carbon steel in free and inhibited solutions of 1 M HCl was studied at a temperature range of 25-45 °C; Fig. 2 represents the influence of temperature on inhibition efficiency for corrosion of carbon steel in 1 M HCl in the absence and presence

of different concentrations of inhibitor (CHMB). Data revealed that the inhibition efficiency decreased with increasing temperature, indicating that the inhibitor was lower effective at higher temperature up to 45 °C [22]. This could be explained by weakness of Physisorption of adsorbed inhibitor on the carbon steel surface in first stage.
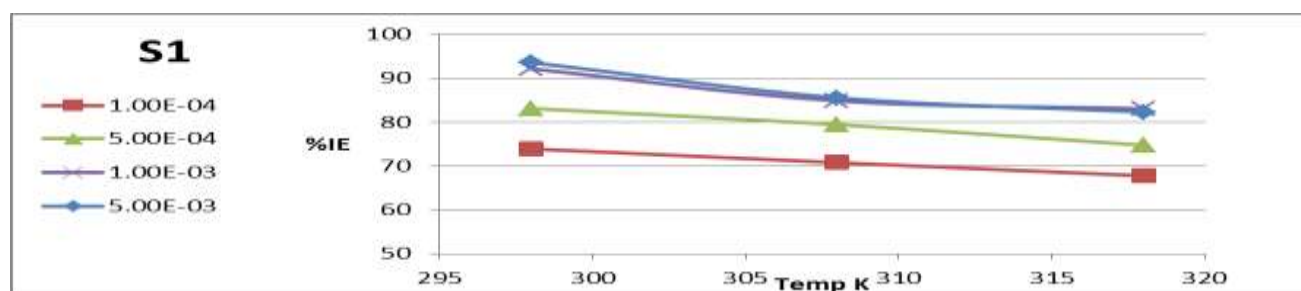
Fig. 2: Effect of the temperature on the inhibition efficiency was obtained for carbon steel in 1 M HCl in the presence of different concentrations of inhibitor (CHMB)

Adsorption Isotherm

The adsorption of organic molecules provides information about the interaction among the adsorbed molecules themselves as well as their interaction with the electrode surface. The degree of surface coverage (θ) for different concentrations of inhibitor molecules in 1 M HCl was calculated using the following equation [23]:

$$\theta = \left(\frac{I°corr - Icorr}{I°corr} \right) \quad (2)$$

Where $I°_{corr}$ and I_{corr} are uninhibited and inhibited corrosion current densities, respectively. The equation that fits our result is due to Langmuir isotherm and is given by the general equation [24]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (3)$$

Where C is the inhibitor concentration, K_{ads} is the adsorptive equilibrium constant and (θ) is the surface coverage. The surface coverage (θ) was tested graphically for fitting a suitable straight line with a correlation coefficient (R^2) equal to (0.9999--1) and a slope closed to 1 as seen in Table 2. This indicates that the adsorption of these inhibitors can be fitted to a Langmuir adsorption isotherm. The strong correlation of the Langmuir adsorption isotherm may confirm the validity of this approach. The equilibrium constant (K_{ads}) for the adsorption-desorption process of these compounds can be calculated from the reciprocal of the intercept. The adsorptive equilibrium constant (K_{ads}) values are listed in Table 2. It is clear that, the large values indicate a strong adsorption of the synthesized inhibitor on the surface of carbon steel in 1 M HCl at relatively higher temperatures. This may be due to the formation of co- ordinated bonds between the prepared inhibitor and the d- orbital of iron on the surface of steel.

Thermodynamic Parameters

The standard adsorption free energy ($\Delta G°_{ads}$) can be obtained according to the following equation 25]:

$$\Delta G°_{ads} = -R\ T\ \ln (55:5\ K_{ads}) \quad (4)$$

Where R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature, and the value 55.5 is the concentration of water in solution expressed in M .The negative values of $\Delta G°_{ads}$ indicate that the Adsorption of inhibitor molecule onto steel surface is a spontaneous process. Generally values of $\Delta G°_{ads}$ up to 20 k J mol^{-1} are consistent with the electrostatic interaction between the charged molecules and the charged metal (physical adsorption) while those more negative than -40 kJ mol^{-1} involve sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (chemisorptions) [26].Calculated $\Delta G°_{ads}$ values indicated that the adsorption mechanism of the prepared cationic surfactants on carbon steel in 1 M HCl solution is a chemical adsorption [27]. The adsorption heat can be calculated according to the Van't Hoff equation [28]:

$$\text{Log } K_{ads} = \frac{-\Delta Hads}{2.303\ RT} + \text{Cons} \quad (5)$$

Where $\Delta H°_{ads}$ and K_{ads} are the adsorption heat and adsorptive equilibrium constant, respectively. To obtain the standard enthalpy, plotting Log K_{ads} vs. 1/T (Fig. 3) yielded straight line according to Eq. (5) with slope equal to $-\Delta H°_{ads}/R$. The $\Delta H°_{ads}$ values were equal to 9.67 kJ mol^{-1} for CHMB. The positive values of $\Delta H°_{ads}$ indicated that the adsorption of investigated inhibitors on the carbon steel surface is endothermic. Entropy of inhibitor adsorption $\Delta S°ads$ can be calculated using the following equation [26]:

$$\Delta G°_{ads} = \Delta H°_{ads} - T\ \Delta S°_{ads}. \quad (4)$$

The obtained $\Delta S°_{ads}$ values were listed in Table 2. The positive values of $\Delta S°_{ads}$ mean that the adsorption process is accompanied by an increase in entropy, as was expected,

since the endothermic adsorption process is always accompanied by an increase of entropy which is the driving force for the adsorption of inhibitor onto the carbon steel surface [29].
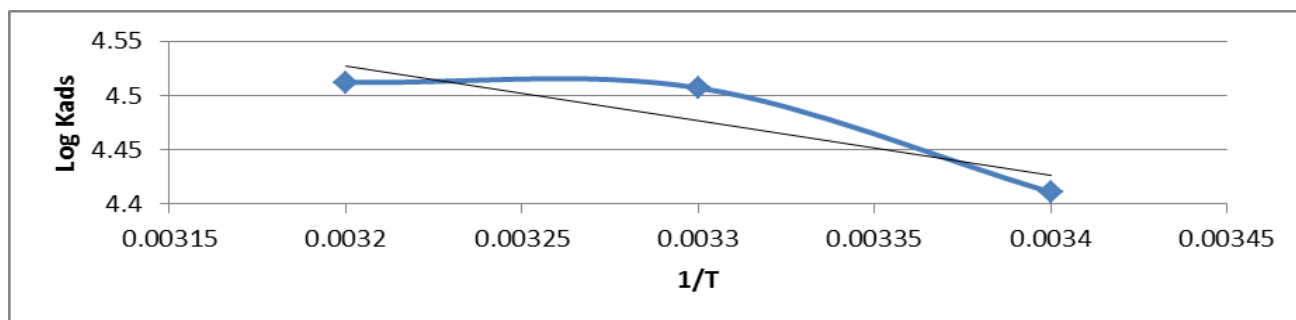

Fig. 3: The relationship between Log Kads and 1/T for carbon steel in 1 M HCl solution containing different concentrations of inhibitor

Table 2: Thermodynamic parameters of adsorption on carbon steel surface in 1 M HCl containing different concentrations of the synthesized inhibitor

Comp	T	slop	R^2	Log K_{ads}	ΔG^{o}_{ads} KJ.mol^{-1}	ΔH^{o}_{ads} KJ.mol^{-1}	ΔS^{o}_{ads} KJ.mol^{-1}
S1	298	1.1	0.9999	4.411	-35.11		0.085
	308	1.2	1	4.507	-36.85	9.67	0.088
	318	1.4	0.9999	4.512	-38.08		0.089

Conclusion

An aromatic azo-Schiff compound (CHMB) has been synthesized, the inhibition efficiency of CHMB for carbon steel corrosion in 1 M HCl was investigated, High inhibition efficiency was recorded (93.58% by Potentiodynamic) at 5.00 mM concentration. Thermodynamic studies proved that CHMB is adsorptive inhibitor and their adsorption process obeys the Langmuir's adsorption isotherm, and is spontaneous. The values of the standard free energies of adsorption indicate that inhibitors are adsorbed on carbon steel in 1 M HCl through chemical mechanism. Such high corrosion inhibition efficiency with such low concentration makes CHMB an excellent carbon steel corrosion inhibitor with environmental and economic advantages.

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