Asian Journal of Chemistry Vol. 17, No. 1 (2005), 224–232

Investigation on Some Two Bidentate N,O-Schiff Base Ligands as Corrosion Inhibitors on Mild Steel in Sulfuric Acid Media

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The effect of two bidentate Schiff bases 4-methoxy phenyl-N-salicylidine (M_1) and 4-nitro-2-methoxy phenyle-N-salicylidine (M_2) on mild steel surfaces in 0.5 M H_2SO_4 acid using electrochemical impedance and Tafel polarization techniques has been studied. Results obtained reveal that M_1 and M_2 compounds are good inhibitors for mild steel in 0.5 M sulfuric acid media. The inhibition is in both cases of mixed anodic-cathodic nature. Change in impedance parameters (R_t and C_{dl}) are indicative of adsorption of these two bidentate Schiff-base ligands on metal surface leading to the formation of a protective film with inhibition efficiencies of around 93% at a concentration of 400 ppm at 25°C.

The adsorption of M_1 and M_2 derivatives on the mild steel surface in sulfuric acid follows the Langmuir adsorption isotherm. In order to study the ability of quantum chemistry to select corrosion inhibitors, quantum chemical calculations have been applied to these bidentate Schiff base ligands. The corresponding structures have been optimized and the energies and symmetries of their molecular orbitals have been calculated using the semi-empirical AM_1 semiempirical methods. The theoretical results obtained have been compared with the experimental data and have a good agreement with the others.

Key Words: Corrosion inhibitor, Quantum chemical calculation, Schiff bases, Mild Steel.

INTRODUCTION

The use of an inhibitor is one of the most practical methods for corrosion prevention[1]. Acid solution is also used in many manufacturing processes in different industries. Because acid solutions are aggressive, inhibitors are usually used to minimize the corrosive attack of metallic materials. Acid solutions containing inhibitors are used in industry where the most important problems are acid pickling, acid descaling and oil well acidizing. Some organic compounds were tested as corrosion inhibitors. The existing data show that most organic inhibitors act by adsorption on the metal surface. The nature of the metal and of the organic inhibitor has a decisive effect on the bond. Electrons transfer from

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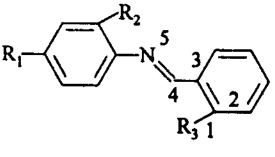
inhibitor to the metal is facilitated when the inhibitor molecule has an unshared lone pair of electrons on the donor atom. Availability of π electron due to the presence of multiple bonds or aromatic rings in the inhibitor molecule would facilitate electron transfer from the inhibitor to the metal[2].

The organic compounds, containing nitrogen, sulfur and oxygen atoms possessed π electrons due to the presence of multiple bonds or aromatic rings and free electron pairs on the nitrogen and oxygen atoms which can interact with *d*-orbital of iron to protective films[3]. These compounds should adsorb on the metal surface, have high adsorption energy on the metal surface and give protective films[4].

An important feature regarding practical applicability is that many Schiff bases can conveniently be synthesized from relatively cheap starting materials. The condensation product of an amine with a ketone or aldehyde having $R_2C{=}NR'$ as general formula are known examples of this category and have been investigated for the inhibition of acid corrosion of mild steel[5].

Shokry *et al.*[6] have studied the corrosion inhibition of mild steel in aqueous solution by symmetric Schiff base such as salop and salen. Desai *et al.*[5] have also investigated the inhibition effect of some other Schiff base compounds for mild steel in acid solutions. Both groups found that the inhibition efficiencies of these compounds are better than those of corresponding amines.

The formula of the Schiff bases M_1 and M_2 as iron corrosion inhibitors is shown in **Scheme-1.** Schiff-base ligands M_1 and M_2 were prepared in high yields (75–90%) via condensation of ethanolic solutions of aromatic aldehydes with aromatic amine[7]. Microanalyses (C, H, and N) were performed on a Perkin-Elmer analyzer, UV-Vis spectra were recorded in dimethylformamide (DMF) with a Beckman DU-7000 spectrometer and λ_{max} values were considered accurate to 0.1 nm. Infrared spectra were recorded as Nujol mulls using a Shimadzu DR-8001 FT-IR instrument. Also, the structures of two Schiff-base ligands were confirmed by using ^{1}H-NMR spectroscopy and mass spectrometry.



Compound	R_1	R_2	R_3
M_1	OCH_3	H	OH
M_2	NO_2	OCH_3	OH

Scheme-1

In the other part of this work the electronic properties for M_1 and M_2 structures by using a semi-empirical method have been studied. One of the best computer semi-empirical MOPAC[8] program packages is used to study the electronic structure and energy of ground state and excited state atoms, molecules, ions, first hyperpolarizability (β) and second hyperpolarizability (γ) etc.

Recently we have reported some quantum chemical calculations by using MOPAC 6.0 program[9, 10]. In this report, the properties of the electronic structures and symmetry of the MO levels for some Schiff base compounds as corrosion inhibitors for mild steel in 0.5 M H_2SO_4 media have been calculated.

In the present work, the effects of addition of M_1 and M_2 Schiff base compounds on the corrosion inhibition of mild steel in 0.5 M H_2SO_4 by using electrochemical impedance spectroscopy (EIS), Tafel polarization and semi-empirical methods have been studied.

EXPERIMENTAL

Mild steel with the following compositione was obtained commercially, (concentration in weight per cent): C (0.02), Si (0.26), Mn (0.07), Al (0.09) and P (0.02); remainder iron.

A mild steel rod with cross-sectional area of 1.00 cm^2 was embedded in epoxy resin and used for electrochemical measurements (as working electrode).

All specimens were mechanically polished on wet SiC paper (grade 300, 600 and 1200), rinsed with distilled water and ethanol.

All precursor chemicals were of analytical reagent grade (Merck or Fluka) and were used without further purification and double-distilled water was used throughout.

The inhibitors used in this study were synthesized using standard methods[7] and each was recrystallized twice from absolute ethanol and finally dried in air. Inhibitor concentrations of 100–400 ppm in 0.5 M H_2SO_4 solution at 25°C were applied. The prepared inhibitor solutions were used for all measurements.

The electrochemical impedance spectroscopy (EIS)

Impedance measurements were carried out at the $E_{corr.}$ (corrosion potential) after 30 min immersion in solution at 25°C with using electrochemical interface (EG&G model 263 A) and frequency response analyzer (Princeton model 1025). A conventional three-electrode cell assembly, platinum foil as the counter electrode, a saturated calomel electrode (SCE) as reference electrode and mild steel as working electrode, sine wave voltage (5 mV) peak to peak, at frequency range from 100 kHz to 0.1 Hz is applied.

Tafel Polarization

Measurements were carried out in a three-electrode assembly connected to the corrosion measurement system (EG&G model 263 A) using the M352W software for Tafel polarization and with sweep rate 1 mV/sec.

RESULTS AND DISCUSSION

Impedance spectra

Impedance spectra for mild steel in 0.5 M H_2SO_4 in the presence of different concentrations of M_1 and M_2 bidentate Schiff base ligands are shown in Figs. 1 and 2.

The Nyquist plots were regarded as one part of a semicircle. The impedance diagrams obtained are not perfect semicircles and this difference has been attributed to frequency dispersion[11]; for the frequency range applied for these measurements, no indications for mass transport control were observed, the absence of which is common to many corrosion situations. The charge transfer resistance (R_t) value is calculated from the difference in impedance at lower and higher frequency[12].

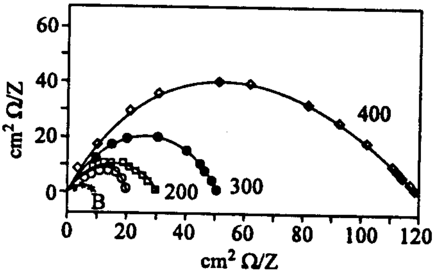


Fig. 1. Nyquist plots for mild steel in 0.5 M H_2SO_4 and containing different concentration M_1 compound (B = blank, R_t = 8 Ω cm^2)

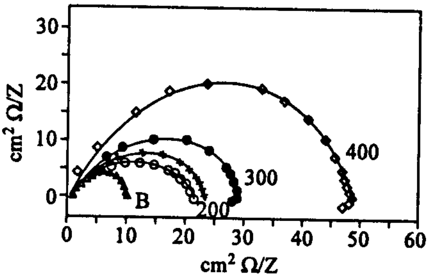


Fig. 2. Nyquist plots in 0.5 M H_2SO_4 for mild steel and different concentration M_2 compound (B = blank, R_t = 8 Ω cm^2)

To obtain the double-layer capacitance (C_{dl}), the frequency at which the imaginary component of the impedance in maximum ($-Z''_{max}$) was found and C_{dl} values were obtained[13] from equation (1).

$$f(-Z''_{max}) = \frac{1}{2\pi C_{dl} R_t} \quad (1)$$

The inhibition efficiencies (η) of corrosion of mild steel were calculated by charge transfer resistance as follows:

$$\eta(\%) = \frac{R_{t_0}^{-1} - R_{t_{inh}}^{-1}}{R_{t_0}^{-1}} \times 100 \quad (2)$$

where R_{t_0} and $R_{t_{inh}}$ are values of the charge transfer resistance (Ω cm^2) observed in the absence and presence of inhibitor.

The impedance parameters (R_t, C_{dl} and η) derived from these investigation are summarized in Table-1.

It is found from Table-1 that on increasing the concentration of M_1 and M_2 the R_t values increase but the C_{dl} values tend to decrease, which is attributed to the adsorption of inhibitor on the metal surface. The increase in the R_t value is due to increase in inhibition efficiency.

TABLE-1
IMPEDANCE PARAMETERS AND INHIBITION EFFICIENCY OF MILD STEEL IN 0.5 M H_2SO_4 FOR DIFFERENT CONCENTRATIONS OF M_1 AND M_2 COMPOUNDS

Inhibitor	Conc. (ppm)	R_t (Ω cm^2)	C_{dl} (μF cm^{-2})	η (%)
	Blank	—	982	—
M_1	100	18	654	57.7
	200	25	512	67.7
	300	48	442	83.1
	400	116	340	93.1
M_2	100	19	781	58.3
	200	22	602	61.7
	300	28	443	71.0
	400	46	431	82.5

Polarization curves

Tafel polarization curves for mild steel in 0.5 M H_2SO_4 at various concentrations of M_1 and M_2 are shown in Figs. 3 and 4.

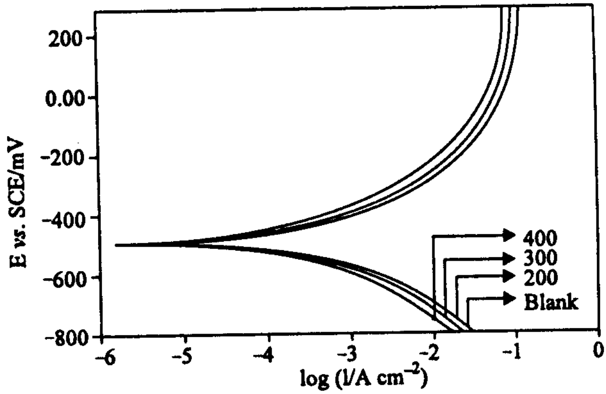


Fig. 3. Polarization curves for mild steel in 0.5 M H_2SO_4 (blank) and acid containing different concentrations of M_1 compound.

Corrosion current densities were obtained from the polarization curves by linear extrapolation of the Tafel curves at point ±50 mV than the values of $E_{corr.}$ (corrosion potential). The inhibition efficiencies for M_1 and M_2 compounds are defined equation (3).

$$\eta(\%) = \frac{I_{corr.} - I_{corr.\,i}}{I_{corr}} \times 100 \quad (3)$$

where $I_{corr.}$ and $I_{corr.\,i}$ are the corrosion current density values (A cm^{-2}) respectively in the absence and presence of inhibitor, whereas the corrosion potential, currer densities and η (%) are summarized in Table-2.

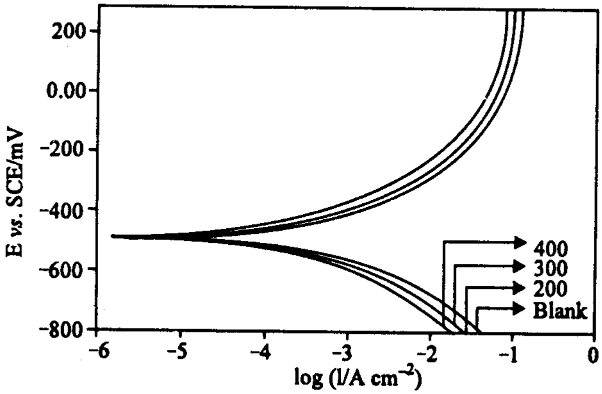


Fig. 4. Polarization curves for mild steel in 0.5 M H_2SO_4 (blank) and containing different concentrations of M_2 compound

TABLE-2
TAFEL POLARIZATION PARAMETER AND INHIBITION EFFICIENCY OF MILD STEEL IN 0.5 M H_2SO_4 FOR DIFFERENT CONCENTRATIONS OF M_1 AND M_2 COMPOUNDS

Inhibitor	Conc. (ppm)	$E_{corr.}$ (mV) vs (ESC)	$I_{corr.}$ (μA cm^{-2})	η (%)
	Blank	–509	1535	—
M_1	100	–485	710	53.3
	200	–512	569	61.8
	300	–498	283	81.1
	400	–491	108	92.2
M_2	100	–488	834	45.5
	200	–485	713	61.4
	300	–469	590	75.6
	400	–493	368	87.9

From these results, it can be concluded that the values of corrosion current density ($I_{corr.\,i}$) of mild steel in the inhibited solution were smaller than free solutions, and corrosion current decrease with increasing inhibitor concentration of M_1 and M_2 compounds. Also, inhibition efficiency η (%) increases with inhibitor concentration.

The polarization curve shows shift to lower current values, which results in inhibition of corrosion. On the other hand, corrosion rate decreases by increasing polarization of both the anode and the cathode; therefore M_1 and M_2 can be classified as inhibitors relatively mixed in 0.5 M H_2SO_4 (anodic cathodic inhibitor). It can be concluded that inhibition efficiencies obtained from electrochemical impedance spectroscopy measurements and polarization curves are in good agreement (Figs. 5 and 6).

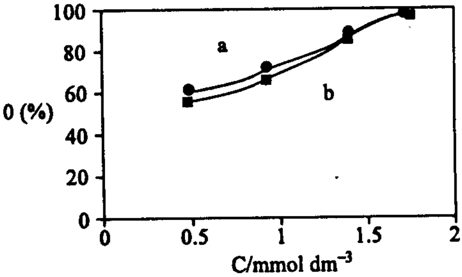


Fig. 5. Inhibition efficiency of M_1 in 0.5 M H_2SO_4 for mild steel: (a) Charge transfer resistance and (b) Polarization curve

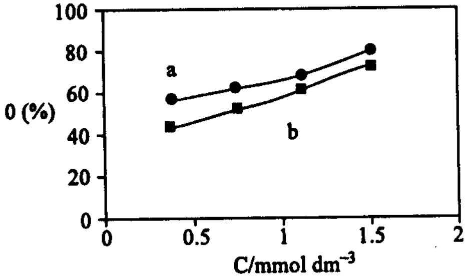


Fig. 6. Inhibition efficiency of M_2 in 0.5 M H_2SO_4 for mild steel: (a) Charge transfer resistance and (b) Polarization curves

Adsorption isotherm

The adsorption of inhibitor is governed by residual charge on the surface of metal and by the nature and chemical structure of the inhibitor. The two main types of adsorption of organic inhibitor on a metal surface are physical (electrostatic) and chemisorptions. Langmuir showed the classical relationship between concentration and surface coverage.

$$\frac{\theta}{1-\theta} = kc \tag{4}$$

and equation (4) can be written with equation (5):

$$\frac{c}{\theta} = c + \frac{1}{k} \tag{5}$$

If one supposes that the adsorption of these inhibitors follows the Langmuir isotherm (the degree of surface coverage θ), it is given by equation (6) as

$$\theta = \frac{I_0 - I}{I_0 - I_m} \tag{6}$$

where I_m is the corrosion current of maximum efficiency. The plots of $C_{inh.}\theta^{-1}$ *vs.* $C_{inh.}$ yields a straight line; therefore the adsorption of M_1 and M_2 from H_2SO on the mild steel surface obeys Langmuir adsorption isotherm (Fig. 7).

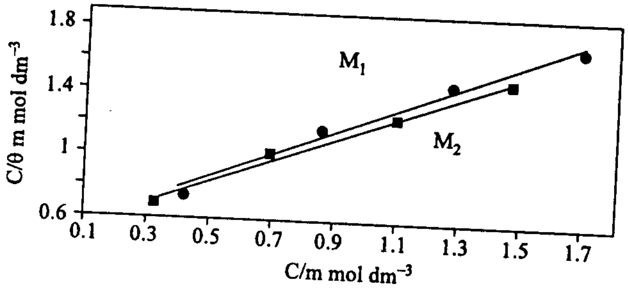
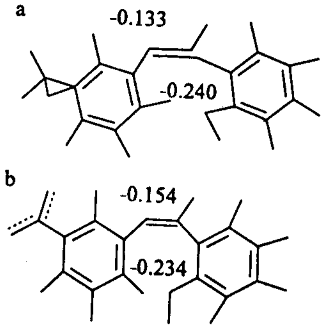


Fig. 7. Langmuir adsorption plots of M_1 and M_2 compounds for mild steel in 0.5 M H_2SO_4

Quantum chemical study

In calculations the experiments were carried out for two bidentate M_1 and M_2 Schiff base ligands. All calculations were performed using AM1[14] semi-imperical method at high precision. The HOMO-LUMO gap and Mulliken population analysis of the outermost MO's for M_1 and M_2 Schiff base ligands were performed using AM1 Hamiltonian.

So the geometrical variables (bond lengths, bond angles, point group, heat of formation and the energy level for all molecular orbitals) were calculated. The calculated atomic net charges for M_1 and M_2 have been shown in Scheme-2.



Scheme-2. (a) The coordinated atomic net charge for M_1 and (b) the coordinated atomic net charge for M_2 Schiff base ligands

It is an indication to note from the molecular calculations that the M_1 compound is a better inhibitor than the M_2 compound, because the interaction of MO (molecular orbital) results in a decrease of the energy of the lower energy orbital (LUMO) and an increase of the energy of the higher energy orbital (HOMO). The extent of energy change is indirectly proportional to the difference in energy of MO prior to interaction, and is directly proportional to the products of the MO coefficients at one site of interaction. According to Fukui's frontier orbital approximation[15], interaction LUMO of both reactants is frequently considered, since the inverse dependence of stabilization energy on orbital energy difference ensures that terms involving the frontier MO will be larger than the others.

The comparison of theoretical data with experimental data has shown a good agreement with the others. On the other hand, the data in Tables 1 and 2 and Tafel polarization curves (Figs. 3 and 4) have shown that the M_1 compound has greater inhibition efficiency than M_2.

Conclusions

1. The M_1 and M_2 compounds are good inhibitors for mild steel in 0.5 M sulfuric acid medium.
2. The inhibition efficiency value increases with the inhibitor concentration of M_1 and M_2 compounds.
3. The electrochemical impedance spectroscopy and polarization curves are in good agreement.
4. Tafel polarization curves indicate that both M_1 and M_2 compounds are of a mixed anodic-cathodic inhibitor.
5. The adsorption of M_1 and M_2 on the mild steel surface obeys a Langmuir isotherm.
6. The effects of Schiff base-metallocomplex on the corrosion of mild steel were investigated by corrosion measurements in 0.5 M H_2SO_4. The molecules of Schiff base metallocomplexes adsorbed on the surfaces of mild steels to depress the corrosion.
7. Theoretical data is in good agreement with experimental data.

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(*Received*: 9 March 2004; *Accepted*: 10 August 2004) AJC-3516