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Experimental and Theoretical Study of Two Salen Type Schiff Base Compounds as Corrosion Inhibitors on Mild Steel in 0.5 M H_2SO_4 Media

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The effect of two synthesized salicylaldiminato Schiff base bis-(2-hydroxy-3-methoxy)-1,6-diaminohexane salicylaldimine (A) and bis-(2-hydroxy)-1,6-diaminohexane salicylaldimine (B) compounds on the corrosion inhibition of mild steel in 0.5 M H_2SO_4 has been studied by using electrochemical Tafel polarization technique at 25°C. The results show that these compounds revealed a good corrosion inhibition in 0.5 M H_2SO_4 media. The inhibition efficiency changes with the type of Schiff base and the inhibition efficiency for compound A is higher than for compound B. The adsorption of compounds A and B on the mild steel surface in 0.5 M H_2SO_4 obeys the Langmuir isotherm. The correlation between the molecular structures and corrosion inhibition efficiencies of compounds A and B has also been investigated using AMI semi-empirical calculations. The theoretical results have been compared with the experimental data and the relations between the inhibition efficiency and quantum parameters have been discussed. A good agreement between the inhibition efficiency of compounds A and B on mild steel in 0.5 M H_2SO_4 and theoretical data with some quantum chemical calculations on the structures of compounds A and B are found.

Key Words: Corrosion inhibition, Molecular orbital, Schiff base, AMI, Tafel polarization, Quantum chemical study.

INTRODUCTION

Corrosion inhibition was in early times a practical art. It has now reached sufficient maturity and attained scientific status as our understanding of the complex system of metal/electrolyte/inhibitor is becoming clear[1]. Studies on the corrosion of metals in organic medium have attracted considerable interest in recent years due to their wide applications[2–5]. A corrosion inhibitor is a chemical substance that can diminish the effect of a corrosion media through decreasing its rate of attack corrosion[6].

The Schiff base compounds derived from salicylaldehyde (salen) compounds

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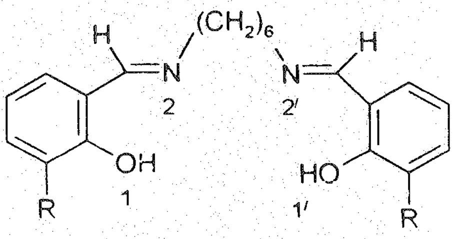
are known to form very stable complexes with the transition metal ions. The resulting salen complexes have attracted increasing attention, mainly in the area of binding small molecules. In general, Schiff base is a class of important compounds in medical and pharmaceutical field. They show biological activities including antibacterial[7, 8], anticancer[9, 10] and anticorrosion for mild steel in acid media[11]. Recently, several Schiff base compounds have been investigated as corrosion inhibitors for various metals and alloys in acidic media[12–14].

On the other hand, quantum chemical calculation has been performed on the structures of these compounds, and the electronic properties of the structures were studied by AMI[15] semi-empirical methods using a personal computer and some calculations were carried out on the structures of bis-(2-hydroxy-3-methoxy)-1,6-diaminohexane salicylaldimine **(A)** and bis-(2-hydroxy)-1,6-diaminohexane salicylaldimine **(B)** **(Scheme-1).**



R = OCH_3 Comp. A

R = H Comp. B

Scheme-1. Structure of Schiff base compounds **A** and **B**

Most Schiff base compounds employed as metal corrosion inhibitors protect the metal by forming a chelate on the metal surfaces. The efficiency of the inhibitor depends on the stability of the chelate formed. The efficiency of a Schiff base as an inhibitor depends on the structure of the inhibitor. The inhibitor molecule should have centres capable of forming bonds with the metal surface by electron transfer, in which the metal acts as an electrophile and the inhibitor acts as a Lewis base. In the structure of **A** and **B** Schiff base compounds, the nucleophilic centres are O atom in hydroxyl group and N atom in imine group with free electron pairs which are readily available for sharing with metal centes. The fact the Schiff bases can form chemisorbed films on metal surface provides a possibility of preparing self-assembled films.

In the present work, the relation between the experimental inhibition efficiency of two tetradentate Schiff base compounds **A** and **B** in 0.5 M H_2SO_4 solution and some theoretical quantum parameters (such as highest occupied molecular orbital or HOMO energy, lowest unoccupied molecular orbital or LUMO energy and charge density on coordination atoms of **A** and **B** molecules) have been discussed.

EXPERIMENTAL

The sample selected for study was mild steel with the following composition (in wt. %): C, 0.07; Si, 0.40; Mn, 0.05; P, 0.35; S, 0.03; Cu, 0.03; Al, 0.05 and Fe, balance. A mild steel rod with cross-area of 1 cm^2 was embedded in a teflon holder and used for electrochemical measurements. The mild steel was first polished with SiC abrasive paper grade 300–1200 and then rinsed with distilled water.

Impedance measurements were carried out at the open circuit potential (E_{oc}) using a computer-controlled potentiostat (PAR EG & G, Mode 263A) Princeton Model 1025 and frequency response analyzer Princeton Model 1025. In the conventional three-electrode assembly Pt foil auxiliary electrode and a saturated calomel reference electrode (SCE) and mild steel sample as working electrode were used. After immersion of the specimen, prior to the impedance measurement, a stabilization period of 30 min was observed, which proved sufficient for E_{oc} to attain a stable value. The alternating current frequency range extended from 100 kHz to 100 MHz and 10 mV peak-to-peak sine wave as the excitation signal.

Tafel polarization curves

The same equipment was used as for the impedance measurements, leaving the frequency response analyzer out of consideration. Quasi-potentiostatic polarization curves were obtained using a sweep rate of 1 mV s^{-1}. All potentials are reported *vs.* that of the SCE, unless mentioned otherwise.

RESULTS AND DISCUSSION

Electrochemical impedance spectroscopy (EIS): The corrosion behaviour of mild steel in acidic solution in the presence of **A** and **B** was investigated by the EIS method at 25°C after immersion for 30 min. The Nyquist plot was regarded as one part of a semi-circle.

The Nyquist plots of mild steel in inhibited and uninhibited acidic solutions containing various concentrations of **A** and **B** are shown in Figs. 1 and 2.

The impedance diagrams obtained are not perfect semi-circles and this difference has been attributed to frequency dispersion[16]. The charge transfer resistance, R_t values are calculated from the difference in impedance at lowest and highest frequencies.

The equivalent circuit after applying inhibitors is shown in Fig. 3. R_s is the solution resistance, R_t is the charge transfer resistance and C_{dL} is the double-layer capacitance.

To obtain the double layer capacitance (C_{dL}), the frequency at which the imaginary component of the impedance is maximum ($-Z_{max}$) is found and C_{dL} values are obtained from the equation[17].

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

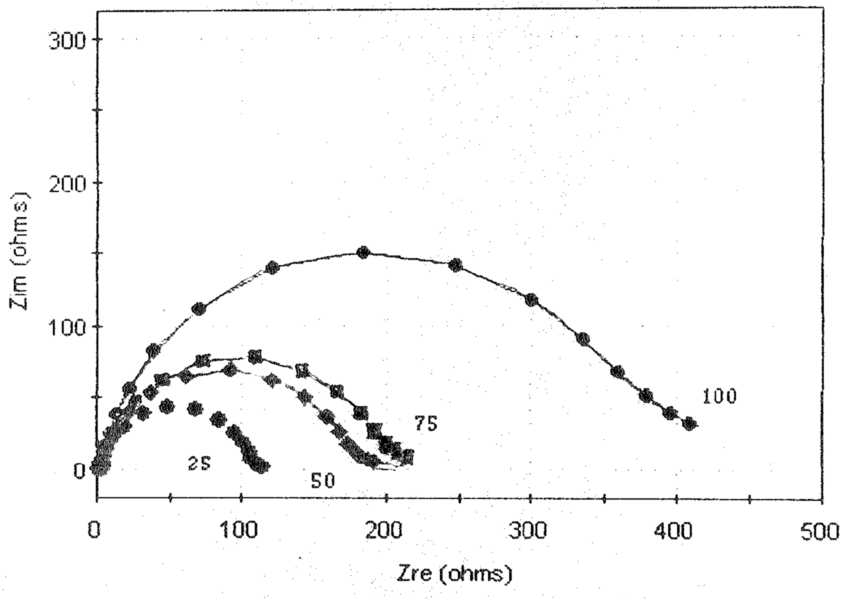


Fig. 1. The Nyquist plot for mild steel in 0.5 M H_2SO_4 in the presence of various concentrations of A (ppm) compound as inhibitor

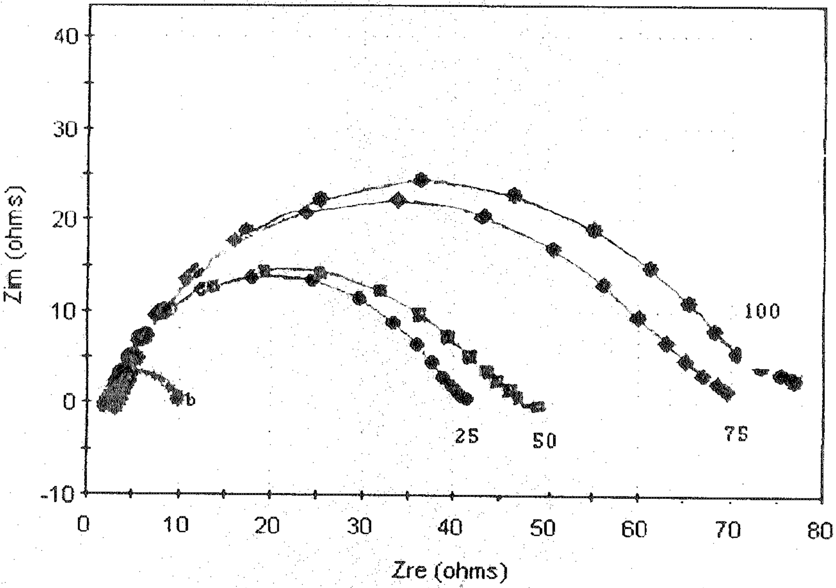


Fig. 2. The Nyquist plot for mild steel in 0.5 M H_2SO_4 in the presence of various concentrations of B (ppm) compound as inhibitor, b = blank

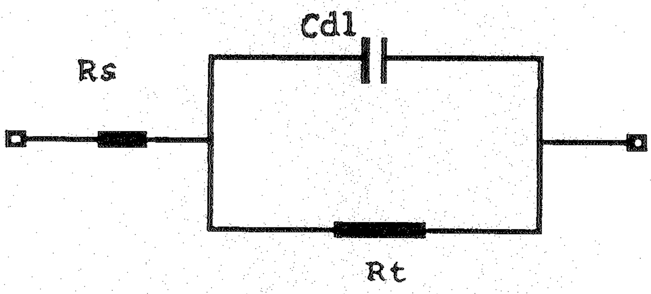


Fig. 3. The equivalent circuit

The inhibition efficiency of corrosion of steel is calculated by charge transfer resistance as follows:

$$\eta\% = \frac{R_{t_1} - R_{t_0}}{R_{t_1}} \qquad (2)$$

R_{t_0} and R_{t_1} are the charge transfer resistance values without and with inhibitor, respectively. The impedance parameters derived from these investigations are given in Tables 1 and 2. It is found (Table-1) that, as the **A** and **B** concentrations increase in the C_{dl} values is due to the adsorption of inhibitor on the metal surface. Similar behaviour is observed in both inhibitors.

TABLE-1
IMPEDANCE PARAMETERS AND INHIBITION EFFICIENCY FOR MILD STEEL IN 0.5 M H_2SO_4 CONTAINING DIFFERENT CONCENTRATIONS OF COMPOUND **A**

Concn. (ppm) of compound **A**	R_t (Ω cm^2)	C_{dl} (μF cm^2)	η (%)
Blank	10	1000	—
25 ppm	74	468	89.18
50 ppm	188	315	95.74
75 ppm	220	280	96.36
100 ppm	420	234	98.10

TABLE-2
IMPEDANCE PARAMETERS AND INHIBITION EFFICIENCY FOR MILD STEEL IN 0.5 M H_2SO_4 CONTAINING DIFFERENT CONCENTRATIONS OF COMPOUND **B**

Concn. (ppm) of compound **B**	R_t (Ω cm^2)	C_{dl} (μF cm^2)	η (%)
Blank	—	1000	—
25 ppm	39	770	79.48
50 ppm	46	600	82.60
75 ppm	67	470	88.06
100 ppm	74	420	89.20

Tafel polarization curves

Representative examples of Tafel polarization curves are shown in Figs. 4 and 5, whereas corrosion potential and current density are summarized in Table-2. Corrosion current densities were obtained from the polarization curves by linear extrapolation of the Tafel curves at points 100 mV more positive, respectively, more negative than E_{OC} to the open circuit.

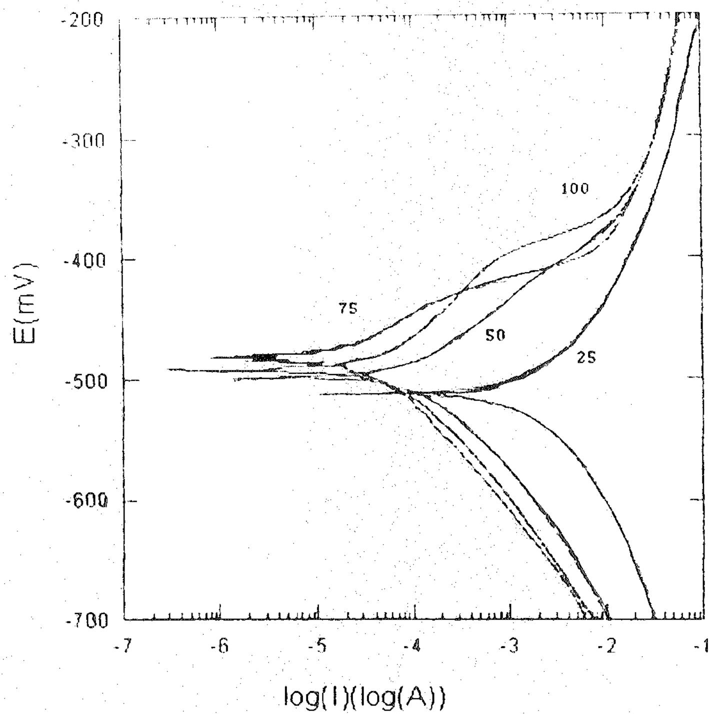


Fig. 4. The polarization curves for mild steel in 0.5 M H_2SO_4 with various concentrations of Schiff-base compound (A)

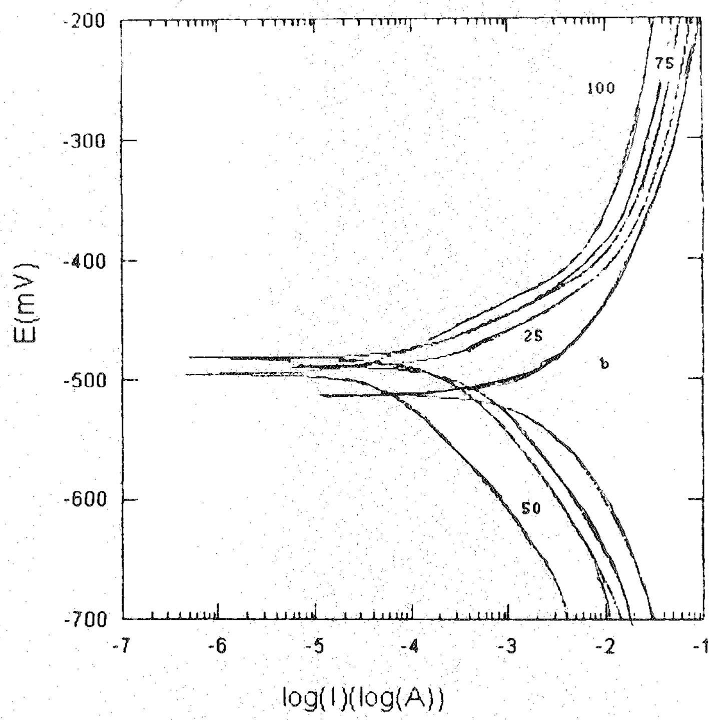


Fig. 5. The polarization curves for mild steel in 0.5 M H_2SO_4 with various concentrations of Schiff-base compound (B) (b = blank)

TABLE-3
TAFEL POLARIZATION PARAMETERS FOR CORROSION OF MILD STEEL IN 0.5 M H_2SO_4 WITH VARIOUS CONCENTRATIONS OF SCHIFF BASE COMPOUNDS (A AND B)

Compound	Conc. (ppm)	E_{corr} vs. SCE (mV)	I_{corr} (μA cm^{-2})	η (%)
	0	-512	1530	—
	25	–497	123	95.18
A	50	–490	72	97.17
	75	–492	64	97.50
	100	–482	16	99.30
	0	-512	1530	—
	25	–498	420	83.49
B	50	–480	261	89.76
	75	–484	223	91.29
	100	–482	190	92.53

Table-3 presents the values of the corrosion inhibition efficiency, for which the expression in this case is:

$$\eta_p\,(\%) = \frac{i_{corr_0} - i_{corr}}{i_{corr_0}} \times 100$$

where i_{corr} and i_{corr_0} are the corrosion current densities (A cm^{-2}), respectively, for the inhibited and the uninhibited situations. From the polarization data given in Table-3, it is observed that an increase in inhibitor concentration causes a positive shift in corrosion potential and decrease in corrosion current density.

The results of AC impedance and Tafel polarization techniques are in good agreement and these results are shown in Figs. 6 and 7.

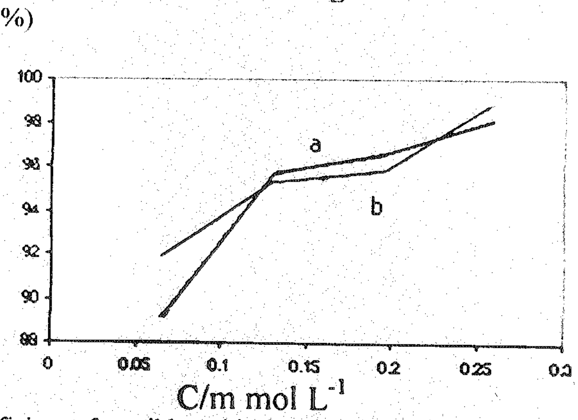


Fig. 6. Inhibition efficiency for mild steel in 0.5 M H_2SO_4 containing different concentrations of compound A: (a) polarization, (b) impedance

The interaction of surface-inhibitor can be estimated from the experimental data. The inhibitor efficiency depends on the type and number of active sites at the metal surface, charge density, the molecular size of inhibitor, the metal-inhib-

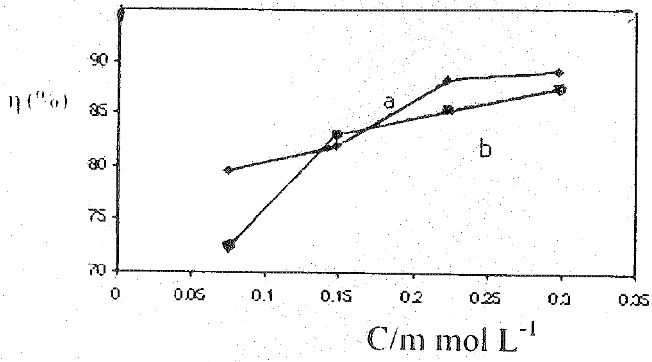


Fig. 7. Inhibition efficiency for mild steel in 0.5 M H_2SO_4 containing different concentrations of the inhibitor compound **B**: (a) polarization and (b) impedance

itor interaction and the metallic complex formation. The adsorption isotherm can give information of the metal-inhibitor interaction. If the adsorption of the inhibitor follows Langmuir isotherm, then the surface coverage degree is given by eqn. (2). The adsorption coefficient depends on temperature and its normal adsorption free energy[1].

$$\theta = \frac{bC_{inh}}{1 + bC_{inh}} \tag{3}$$

where b designates the adsorption coefficient. The degree of surface coverage (θ) for different concentrations of the inhibition in acidic media has been evaluated from electrochemical measurements using the equation[18]

$$\theta = \frac{C_{dl(\theta = 0)} - C_{dl\,\theta}}{C_{dl(\theta = 0)} - C_{dl(\theta = 1)}} \tag{4}$$

The surface coverage values (θ^{-1}) were tested graphically for fitting a suitable adsorption isotherm. The plot of $c_{inh}\,\theta^{-1}$ *vs.* c_{inh} yields a straight line proving that the adsorption of the **A** and **B** H_2SO_4 solutions on the mild steel surface obeys Langmuir adsorption isotherm.

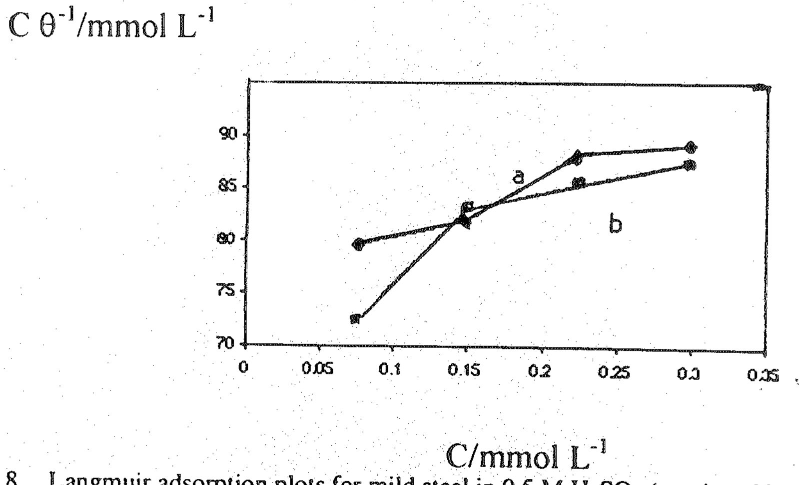


Fig. 8. Langmuir adsorption plots for mild steel in 0.5 M H_2SO_4 (a = **A** and b = **B**)

Theoretical Section

Corrosion inhibitors have been selected for years in a purely empirical manner. The calculations of their chemical structure and the investigation of the correlation between the molecular structure of the inhibitor and its inhibition action have been discussed by only a few authors[19, 20]. The knowledge of the effect of the chemical structure of a substance on its protective action would enable the synthesis of inhibitors with tailored properties.

In the previous works[21-23] a few groups of organic compounds using the semi-empirical calculations method were studied. In this work we want to continue some theoretical investigation on corrosion inhibitor effect of two asymmetrical tetradentate Schiff base compounds on mild steel in 0.5 M H_2SO_4 solution and then to compare between the theoretical and experimental data.

The calculations using the AMI quantum chemical method were carried out with the MOPAC 7.0 program[24]. The geometry of the molecules under investigation was determined by optimizing all geometrical variables (bond lengths and angles). Table-3 shows the structural quantum chemical parameters calculated by AMI semi-empirical method.

TABLE-3
CALCULATED QUANTUM CHEMICAL PARAMETERS FOR SCHIFF BASE COMPOUNDS A AND B BY USING AMI SEMI-EMPIRICAL METHOD

Compound	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	Calculated net charges on coordination atoms (N_2, N_2, O_1 and O_1)
B	–8.9428	–0.1842	8.7586	N: –0.234 O: –0.258
A	–9.2295	–0.3065	8.9230	N: –0.238 O: –0.282

The extent of energy change is inversely proportional to the difference in energy of the 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 approximate[25] interactions between frontier MO only, highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of both reactions are frequently considered, since the inverse dependence of stabilization energy on orbital energy difference ensures that terms involving the frontier MO will be larger than others.

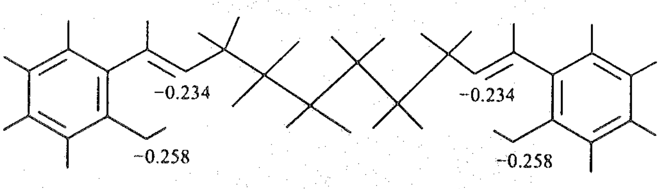
The negative charge density on coordination atoms in the structure of compound A is higher than compound B (Table-3 and Fig. 9).

An inhibitor does not only offer electrons to unoccupied *d*-orbital of metallic centre, it also accepts the electrons in the *d*-orbitals of metallic centre by using their anti-bond orbital to form a stable chelate.

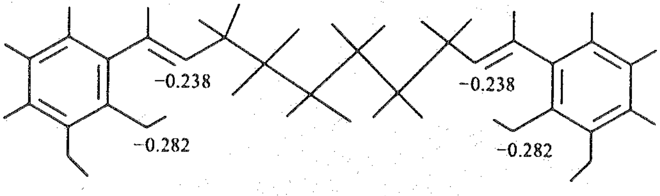
In the structures of A and B Schiff base compounds, the oxygen atom from hydroxyl groups and the nitrogen atom in the imine groups (C=N) could form a big π bond with metal center and the π* orbital of the Schiff base compounds A and B could also accept the electrons of *d*-orbitals of metallic centre to form feedback bonds, then produce more than one centre of chemical absorption action.

The experimental section (Table-3) shows that the Schiff base compound **A** is a better inhibitor than compound **B**.

The net charge density on N and O atoms for molecules **A** and **B** has been shown in Fig. 9. The greater inhibitor efficiency of the compound **A** is explained on the basis of the higher fractional negative charge calculated to be present on N and O atoms.



The optimized structure of **B** Compound



The optimized structure of **A** Compound

Fig. 9. Calculated net charges on N and O coordination atoms fo Schiff base compounds **B** and **A** by AMI semi-empirical method

Conclusions

1. From experimental data, it can be concluded that compounds **A** and **B** are good inhibitors for mild steel corrosion in 0.5 M H_2SO_4. The inhibition efficiency of **A** is better than that of **B** (Tables 1–3).

   In the present study, the inhibition of corrosion by Schiff base compounds **A** and **B** may be attributed to the adsorption on their molecules on the metal surface by interaction with π electrons of the azomethine (—C═N) and the —OH groups. For Schiff base compound **A** with an additional electron releasing —OCH_3 group, it gives a better protective action to metal surface than the Schiff base compound **B** (Fig. 9).
2. The inhibition efficiency value increases with the inhibitor concentration (Table-3).
3. The inhibition process corresponds to anodic mechanism for both compounds.
4. The adsorption of the Schiff base compounds obeys the Langmuir adsorption isotherm.
5. The electrochemical impedance spectroscopy and polarization curves are in good agreement.
6. The big negative charge (electron density) at the adsorption centres (N and O coordination sites for compounds **A** and **B**) gives rise to an increase in the inhibition effect of the respective compounds.
7. Table-3 and Fig. 8 show a good agreement between experimental and theoretical data, and compound **A** has a higher inhibition efficiency for mild steel in this condition.

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