Investigation of Effects of Some Schiff Bases on Behaviour of Mild Steel in Acidic Medium

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This study investigated the effects on the behaviour of mild steel in 0.1 M HCl and 0.1M H_2SO_4 solution of the [4-(3-methoxy-salicylideneamino)-5-hydroxynaphthalene-2,7-disulfonic acid diisodium salt (L_1) and 4-(3-methoxysalicyaldimino)-5-hydroxy-6-(2-nitrophenylazo)-2,7-naphthalene disulfonic acid disodium salt (L_2) in different concentrations with current-potential and electrochemical impedance spectroscopy (EIS) techniques. Polarization curves revealed that Schiff bases are mixed type inhibitors. Adsorption of Schiff bases on mild steel surface is spontaneous and obeys Langmuir's isotherm. As a result, the inhibition efficiency of L_2 is higher than L_1 for the studied medium. Moreover, inhibition efficiency increases with increase in the concentration of the inhibitor.

Keywords: Schiff base, Inhibitor, Impedance spectroscopy, Acid corrosion, Mild steel.

INTRODUCTION

One of the common methods to protect metals from corrosion in acidic environments is to use inhibitors. Inhibitory effect depends on the metal surface and the ambient conditions. Therefore, type of inhibitor will vary depending on the circumstances. Attention is paid to two points in the selection of inhibitor. First, the inhibitor should be low cost. Second, the inhibitor should be easily synthesize, have easy solubility and a cloud of electrons on the aromatic ring, or long-chain compounds with electronegative atoms like N, O atoms[1,2]. To demonstrate the inhibitory properties of an organic substance, it should be adsorbable on a metal surface. Adsorption potential and electron density of the adsorption process of inorganic compound depend on the functional groups. Iron constitutes the metal coordination ligands with the atoms having a pair of the electrons such as nitrogen, oxygen and sulphur. The organic compounds known as acid inhibitors include N, S, P and O atoms, aromatic ring or triple bound. This type of inhibitory activity indicates an order for the atoms P > S > N > O. π molecular orbital of the Schiff base structure forms a stable bond with *d* orbital in the transition metal but this is not possible for an organic compound including an amino group[3-8]. There are a lot of research in the literature investigating the inhibitor effects of the Schiff base on the mild steel and the metals such as copper, iron and aluminium in an acidic medium[9-17]. Similarly, current study investigates the inhibitory effect of the two synthesized Schiff bases on the mild steel in the acidic medium[18,19].

EXPERIMENTAL

The Schiff bases[4-(3-methoxy-salicylideneamino)-5-hydroxynaphthalene-2,7-disulfonic acid diisodium salt (L_1) and 4-(3-methoxysalicylaldimino)-5-hydroxy-6-(2-nitrophenylazo)-2,7-naphthalene disulfonic acid diisodium salt (L_2) are used as the inhibitors in this study.

Synthesis of diazo compounds: Diazo compounds were synthesized and purified according to the literature[18].

Synthesis of Schiff base ligands: Schiff bases were synthesized according to literature[18,19]. The structure of the synthesized Schiff base ligands were measured by elemental analysis, FT-IR, UV-visible, mass and NMR spectra. Schiff bases and azo-Schiff base ligands of the formulae given in Fig. 1.
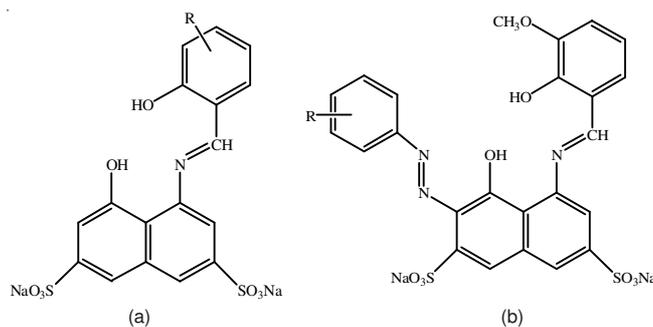

Fig. 1. (a) L_1 [R = 3-OCH$_3$], (b) L_2 [R = 2,5-dichlorine]

Electrochemical measurements: All electrochemical measurements were carried out by using HCH Instruments Electrochemical Work station device and software CHI 660 B model electrochemical analyser under computer control. For the measurements, a conventional three-electrode system with a platinum counter-electrode (area 1 cm²), a silver-silver chloride (Ag/AgCl) reference electrode and the working electrodes prepared from mild steel samples of the following chemical composition (wt. %) (C, 0.097, P, 0.32 S, 0.070, Si, 0.099, Mn, 0.459, Cr, 0.117, Ni, 0.137, Cu, 0.488, Mo, 0.054, Co, 0.004, Pb, 0.003, Sn, 0.018, Fe, 97.7) were used. The mild steel sample was embedded in PVC holder using epoxy resin with an exposed area of 0.5024 cm² as aworking electrode. The samples were polished by using different grits of wet emery papers. The working electrodes were cleaned with acetone, washed with distilled water and finally dried at room temperature before being immersed in the acid solution. All experiments were performed in atmospheric condition without stirring. The working electrodes were first immersed into the test solution for 0.5 h to establish a steady state open circuit potential.

To determine the polarization resistance of the working electrode from open circuit potential in the range of ± 20 m Vat a scan rate 0.1 mV s⁻¹ was polarized. The polarization resistance is determined by the slope of the graph. Polarization studies were performed with a scan rate of 1 mV s⁻¹ in the potential range from -250 to +200 mV relative to the corrosion potential. The Nyquist plots were recorded on instantaneous open circuit potentials for various exposure times in a frequency range from 105 to 10⁻³ Hz and 5 mV amplitude. By using the Z view software, the system behaviour was simulated and adjusted to a proposed equivalent circuit.

RESULTS AND DISCUSSION

The potentiodynamic polarization curves of mild steel in 0.1 M H₂SO₄ solution with various concentrations of Schiff bases L_1 and L_2 are shown in Fig. 2. The values of associated electro chemical parameters, *i.e.*, open circuit potential (E_{ocp}), corrosion current density (i_{corr}) and inhibition efficiency (IE %) were calculated from these curves and given in Table-1. The inhibition efficiency (IE %) was calculated from polarization measurements according to the relation:

$$IE\ (\%) = \frac{i_{corr} - i'_{corr}}{i_{corr}} \times 100 \qquad (1)$$

i_{corr} and i'_{corr} are the uninhibited and the inhibited corrosion current densities, respectively[17,20]. The values of current densities were obtained by the extrapolation of the current-potential lines to the corresponding corrosion potentials. The current-potential curves of the 0.1 M H₂SO₄ solution and various concentrations of L_1 and L_2 in the acid solutions were shown in Fig. 2.

The current-potential curves were obtained from the electrochemical parameters (Fig. 2) are given in Table-1. The current-potential curves of the 0.1 M HCl solution and various concentrations of L_1 and L_2 in the acid solutions were shown in Fig.3. The current-potential curves were obtained from the electrochemical parameters (Fig. 3) are given in Table-2.

Inhibitor	Concentration (M)	Rp (A/V) Ω	E_{cor} (V/Ag/AgCl)	b_a (mV/dec)	$-b_c$ (mV/dec)	μ_{cor} (μA/cm²)	IE₁* (%)	IE₂** (%)
Blank	0	68.3	-0.490	100.0	165.5	486.4	–	–
	1.0×10^{-4}	60.5	-0.485	82.6	138.6	309.0	-12.9	36.5
	2.5×10^{-4}	62.5	-0.485	89.7	153.2	389.5	-9.3	19.9
	5.0×10^{-4}	74.8	-0.482	60.5	125.6	221.4	8.7	54.5
L_1	1.0×10^{-3}	80.4	-0.498	117.0	173.0	422.0	15.0	13.2
	2.5×10^{-3}	225.9	-0.489	54.7	121.1	88.9	69.8	81.7
	5.0×10^{-3}	100.5	-0.479	48.0	115.5	148.4	32.0	69.5
	1.0×10^{-4}	95.2	-0.497	48.1	122.1	175.1	28.3	64.0
	2.5×10^{-4}	83.3	-0.498	55.3	128.1	223.1	18.0	54.0
L_2	5.0×10^{-4}	94.0	-0.500	58.6	127.7	119.9	27.3	75.3
	1.0×10^{-3}	150.8	-0.490	72.0	139.0	189.1	54.7	61.1
	2.5×10^{-3}	148.0	-0.469	66.0	127.8	57.3	53.9	88.2
	5.0×10^{-3}	486.1	-0.500	37.1	136.5	26.7	85.9	94.5

TABLE-1
ELECTROCHEMICAL PARAMETERS FOR MILD STEEL IN 0.1 M H₂SO₄ IN THE ABSENCE AND PRESENCE OF L₁ AND L₂

*Data obtained from linear polarization curves. **Data obtained from current-potential curves
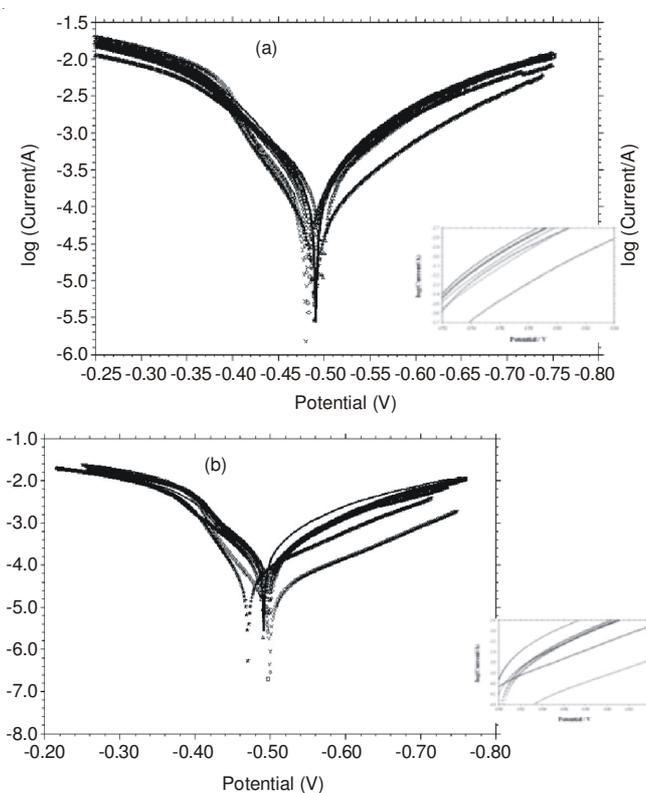
Fig. 2. (a) L₁; (b) L₂; 0.1 M H₂SO₄; Blank; ○: 1.0 × 10⁻⁴, □: 2.5 × 10⁻⁴, ◇: 5.0 × 10⁻⁴ △: 1.0 × 10⁻³*: 2.5 × 10⁻³ x: 5.0 × 10⁻³ current-potential curves

In the polarization curves obtained from the experimental data, corrosion potential shifted to more positive potentials when the inhibitors were added to the solutions. Shifting to more positive values of the corrosion potential indicates that the anodic branch is a bit more apparent than cathodic branch. L_2 appears to be more effective than L_1 in the working medium (Tables-1, 2). Inhibitory efficiency increases with the increasing concentration of inhibitor. When the concentrations of the added inhibitor to the acidic medium increase, the corrosion currents decrease. Also b_a and b_c obtained from the Tafel curves did not change significantly. Thus, studied inhibitor can be named as mixed type of Schiff bases[21].

TABLE-2
ELECTROCHEMICAL PARAMETERS FOR MILD STEEL
IN 0.1 M HCLIN THE ABSENCE AND PRESENCE OF L₁ AND L₂

Inhib-itor	Conce-ntration (M)	Rp (A/V) Ω	E_{cor} (V/Ag/ AgCl)	b_a (mV/ dec)	$-b_c$ (mV/ dec)	μ_{cor} (μA/ cm^2)	IE_1^* (%)	IE_2^{**} (%)
Blank	0	82.5	-0.516	119.0	154.4	358.5	–	–
L₁	1.0×10^{-4}	81.7	-0.514	119.3	161.1	389.9	-9.8	-7.1
	2.5×10^{-4}	88.4	-0.512	107.1	146.2	328.1	6.7	8.5
	5.0×10^{-4}	110.5	-0.519	115.3	162.7	338.0	25.3	5.7
	1.0×10^{-3}	103.6	-0.511	112.3	152.2	276.9	20.4	22.8
	2.5×10^{-3}	143.0	-0.505	99.2	142.0	183.0	42.3	49.0
	5.0×10^{-3}	137.0	-0.504	95.2	126.3	152.9	39.8	57.4
L₂	1.0×10^{-4}	97.4	-0.513	111.5	151.7	322.0	15.3	10.2
	2.5×10^{-4}	108.2	-0.509	100.8	136.6	232.0	23.8	35.3
	5.0×10^{-4}	151.8	-0.509	97.4	128.8	156.3	45.7	56.4
	1.0×10^{-3}	293.9	-0.484	63.0	114.1	31.7	71.9	91.1
	2.5×10^{-3}	252.0	-0.448	64.7	190.5	29.7	67.3	91.7
	5.0×10^{-3}	415.7	-0.485	83.0	118.0	18.9	80.1	94.7

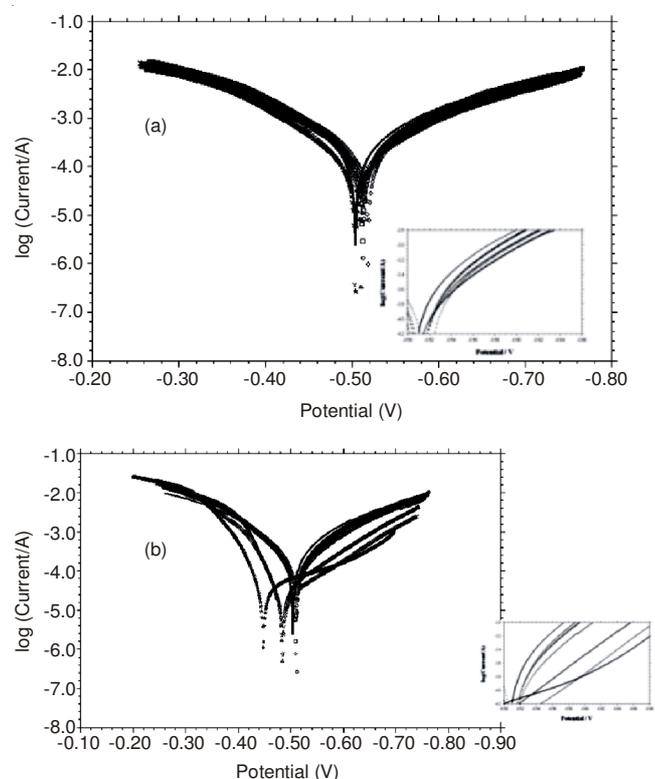*Data obtained from linear polarization curves. **Data obtained from current-potential curves

Fig. 3. (a) L₁; (b) L₂; 0.1 MHCl; Blank; ○: 1.0 × 10⁻⁴ □: 2.5 × 10⁻⁴ ◇: 5.0 × 10⁻⁴ △: 1.0 × 10⁻³,*: 2.5 × 10⁻³, x: 5.0 × 10⁻³ current-potential curves

Electrochemical impedance spectroscopy: The Nyquist curves of the 0.1 M H₂SO₄ solution and various concentrations of L₁ and L₂ in acid solutions were shown in Fig. 4.

In Fig. 4 the Nyquist plots of mild steel in 0.1 M H₂SO₄ solution is seen. The related representative log(freq)-log(Z) plot was included in the same Figure as inset. The electrochemical parameters obtained from the Nyquist curves (Fig. 4) are given in Table-3.

In Fig. 5, of the mild steel in Nyquist curves were obtained from 0.1 M HCl acidic environments. It is apparent from Figs. 4 and 5 that, the Nyquist plot of mild steel yields a slightly depressed semi-circular shape and only one time constant was observed in log(freq)-log (Z) plot. This observation indicates
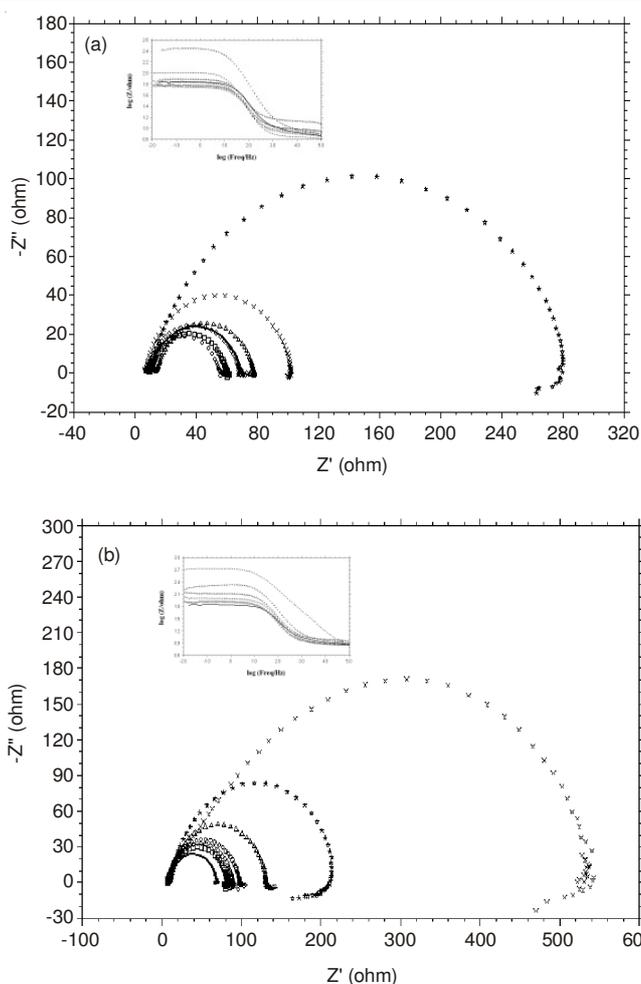

Fig. 4. (a) L₁; (b) L₂; 0.1 M H₂SO₄;c –: Blank; ○: 1.0 × 10⁻⁴ □: 2.5 × 10⁻⁴ ◇: 5.0 × 10⁻⁴ △: 1.0 × 10⁻³,*: 2.5 × 10⁻³, x: 5.0 × 10⁻³ Nyquist curves

that the corrosion of mild steel in 0.1 M H₂SO₄ solution and 0.1 M HCl solution are mainly controlled by a charge transfer process. According to electro chemical data, inhibitions efficiency of L₂ is more effective than L₁. Corrosion rate decreases with increasing concentration of inhibitor. When the concentrations of the inhibitors increase, $R_{p(imp)}$ values increase (Tables-3 and 4).

TABLE-3
POLARIZATION RESISTANCE, AND INHIBITOR EFFICIENCIES
FOR MILD STEEL IN 0.1 M H₂SO₄OBTAINED
USING THE IMPEDANCE METHOD

Inhib-itor	Conce-ntration (M)	$Rp_{(imp)}$ (Ω)	R_s (Ω)	Y_0 (Ω^{-1} cm^{-2}) (×10⁻⁶)	n	C_{dl} (μF cm^{-2})	IE_3 (%)
Blank	0	62.3	8.0	$2.28.10^{-4}$	0.786	76.0	–
L₁	1.0×10^{-4}	47.6	8.4	$2.43.10^{-4}$	0.848	112.1	-30.9
	2.5×10^{-4}	50.9	9.5	$2.40.10^{-4}$	0.836	104.4	-22.4
	5.0×10^{-4}	61.5	7.8	$2.35.10^{-4}$	0.846	111.6	-1.3
	1.0×10^{-3}	64.5	13.4	$2.18.10^{-4}$	0.833	95.9	2.3
	2.5×10^{-3}	274.6	8.5	$9.95.10^{-5}$	0.781	38.6	77.3
	5.0×10^{-3}	94.7	6.9	$1.81.10^{-4}$	0.881	106.1	33.7
L₂	1.0×10^{-4}	92.0	7.5	$1.48.10^{-4}$	0.839	67.1	32.3
	2.5×10^{-4}	75.1	7.5	$1.90.10^{-4}$	0.843	88.7	17.0
	5.0×10^{-4}	82.5	7.4	$1.56.10^{-4}$	0.853	75.5	24.5
	1.0×10^{-3}	123.6	9.6	$1.41.10^{-4}$	0.836	66.0	49.6
	2.5×10^{-3}	199.1	8.6	$9.41.10^{-5}$	0.830	42.4	68.7
	5.0×10^{-3}	621.9	5.7	$9.75.10^{-5}$	0.614	20.4	90.0

TABLE-4
POLARIZATION RESISTANCE AND INHIBITOR EFFICIENCIES
FOR MILD STEEL IN 0.1 M HCLOBTAINED
USING THE IMPEDANCE METHOD

Inhi-bitor	Concen-tration (M)	$Rp_{(imp)}$ (Ω)	R_s (Ω)	Y_0 (Ω^{-1} cm^{-2}) ($\times 10^{-6}$)	n	C_{dl} (μF cm^{-2})	IE_3 (%)
Blank	0	8.4	76.0	$1.55.10^{-04}$	0.833	66.0	–
L_1	1.0×10^{-4}	8.1	73.6	$1.64.10^{-04}$	0.850	77.4	-3.3
	2.5×10^{-4}	8.1	73.7	$1.51.10^{-04}$	0.863	75.8	-3.1
	5.0×10^{-4}	10.3	86.7	$1.25.10^{-04}$	0.856	59.9	12.3
	1.0×10^{-3}	10.3	78.9	$1.52.10^{-04}$	0.843	68.6	3.7
	2.5×10^{-3}	10.6	115.5	$1.34.10^{-04}$	0.840	62.2	34.2
	5.0×10^{-3}	8.7	118.7	$1.07.10^{-04}$	0.847	50.2	36.0
L_2	1.0×10^{-4}	8.4	80.7	$1.49.10^{-04}$	0.851	70.7	5.8
	2.5×10^{-4}	7.9	82.2	$1.56.10^{-04}$	0.849	73.8	7.5
	5.0×10^{-4}	8.6	115.6	$1.18.10^{-04}$	0.847	55.7	34.3
	1.0×10^{-3}	7.2	315.5	$7.53.10^{-05}$	0.818	34.1	75.9
	2.5×10^{-3}	6.5	366.8	$4.89.10^{-05}$	0.738	12.8	79.3
	5.0×10^{-3}	7.1	390.3	$9.50.10^{-05}$	0.688	24.1	80.5
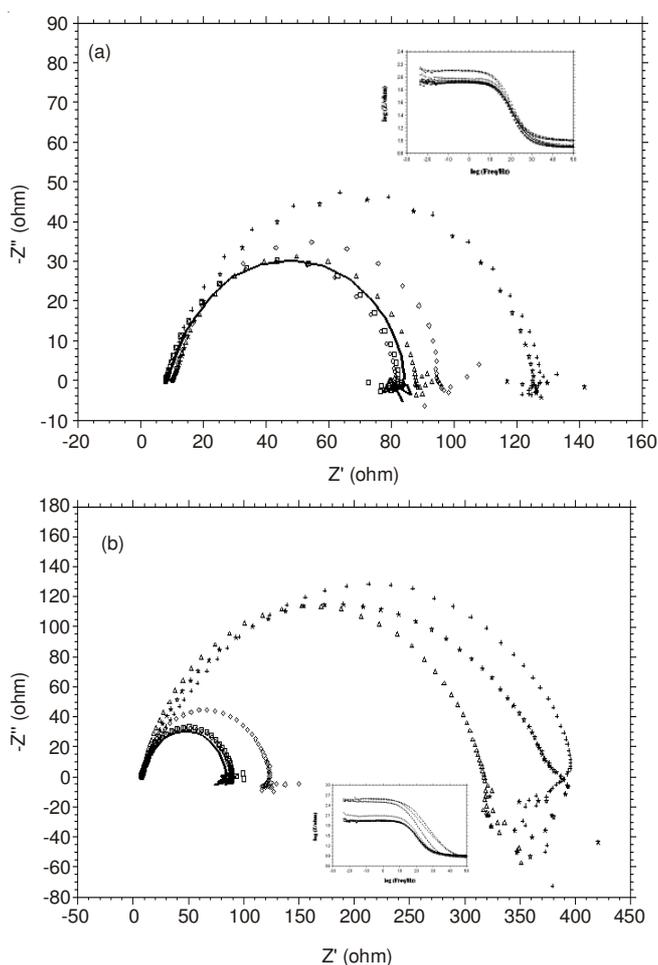
Fig. 5. (a) L_1; (b) L_2; 0.1 M HCl; –: Blank; O: 1.0×10^{-4} □: 2.5×10^{-4} ◇: 5.0×10^{-4} △: 1.0×10^{-3}, *: 2.5×10^{-3}, x: 5.0×10^{-3} Nyquist curves

The impedance data were fitted *via* Z view program to generate the electrical equivalent circuit diagram in Fig. 6 indicating a model the mild steel/solution interface. This includes the solution resistance, R1 and the constant phase element, CPE1 which is placed in parallel to charge transfer resistance element, R2. The R2 value is a measure of electron transfer across the surface and is inversely proportional to corrosion rate. The impedance Z of CPE1 is presented by eq. (2)[22,23]:
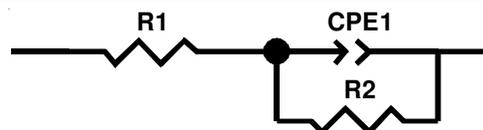

Fig. 6. Electrical equivalent circuit diagram used for modeling mild steel/solution interface

$$Z_{CPE1} = [Y_0(j\omega)^n]^{-1} \qquad (2)$$

where Y_0 is the magnitude of the C_{PE1}, n is the phase shift which can be explained as a degree of surface in homogeneity. ω is the angular frequency ($\omega = 2\pi f$, where f is the AC frequency) and j here is the imaginary unit. When the value of n is 1, the C_{PE1} behaves like an ideal double-layer capacitance (C_{dl}). Value of the C_{dl} decreases with increasing concentration of inhibitor due to the increased thickness of the electrical double layer or local reduction of the dielectric constant[24].

The inhibitor molecules are adsorbed to the metal surface indicates the increase in polarization resistance and decrease in double layer capacitance[23,25]. Thus, the corrosion inhibition process is based on the adsorption of the Schiff base molecules on the metal surface. Experimental results tested for their alignment with the Langmuir adsorption isotherm and Temkin adsorption isotherm. L_1 did not align with Langmuir and Temkin adsorption isotherms but L_2 with Langmuir and adsorption isotherm. Plots of the data for each isotherm showed that L_2 compounds agreed with the Langmuir isotherm[7,26,27]:

$$\frac{C_{(inh)}}{\theta} = \frac{1}{K_{(ads)}} + C_{(inh)} \qquad (3)$$

where K_{ads} is the adsorption equilibrium constant and θ_2 is the degree of surface coverage. C_{inh} is the inhibitor concentration. The adsorption isotherms obtained from linear polarization resistance data derived from the fractions of the surface coating and the inhibitor concentration values. The free energy of adsorption was calculated by using the following equations.

$$K = \frac{1}{55.5} \exp.\left(-\frac{\Delta G_{ads}}{RT}\right) \qquad (4)$$

In this equation, R value is 8.314 J mol^{-1} K^{-1} and T is 293 K. When ΔG_{ads} value is -20 kJ mol^{-1} or lower than this, interaction between the installed inhibitor molecules and the charged metal surface indicates physical adsorption. If adsorption free enthalpy is -40 kJ mol^{-1} or greater than this, the electron pair of the organic molecules are shared by the metal. Then, this chemical process is named as chemical adsorption[28-31]. The values of free energy of adsorption, ΔG_{ads}, are negative which reveals the spontaneity of adsorption process and stability of the adsorbed layer on the mild steel surface. The obtained values of the adsorption free energy, ΔG_{ads}, were -28.3 kJ mol^{-1} and -30.5 kJ mol^{-1} for studied compound L_2. These values point out that the adsorptions of compound occurs both physically and chemically[32].

Calculated K_{ads} values for L_2 are 2×10^3 in 0.1 M HCl and 5×10^3 in 0.1 M H$_2$SO$_4$. In literature, it was reported that the high K_{ads} values (> 100 M^{-1}) attribute to the stronger and more stable adsorbed layer formation on the metal surface[24,32,33].

Conclusion

In this study, two Schiff bases in 0.1 M HCl and 0.1 M H$_2$SO$_4$ acid mediums were studied in different inhibitor concentrations. L$_2$ inhibitory activity were high in both medium studied. According to the results obtained from the polarization curves of the Schiff bases were found to be a mixed type inhibitor. An equivalent circuit was suggested by using EIS results processed in Z view. L$_2$ has the best fit to the Langmuir adsorption isotherm. ΔG$_{ads}$ values are negative which reveals the spontaneity of adsorption process and the stability of the adsorbed layer on the mild steel surface.

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