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Corrosion Science 45 (2003) 2803–2817

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An investigation of chloride-substituted Schiff bases as corrosion inhibitors for steel

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Received 26 July 2002; accepted 6 March 2003

Abstract

Polarization and impedance measurements were performed on steel in deaerated 5% HCl solution with and without Schiff base additives within the concentration range 1×10^{-4} – 5×10^{-3} mol/dm³. The Schiff base compounds used were salicyldimine, R, *N*-(2-chlorophenyl)salicyldimine, 2Cl-R, *N*-(3-chlorophenyl)salicyldimine, 3Cl-R, and *N*-(4-chlorophenyl)salicyldimine, 4Cl-R. It was found that when the concentration of the inhibitors were increased the inhibitor efficiencies, η , also increased with increasing surface coverage. The results indicated that the ortho-substituted (2Cl-R) compound had the highest inhibition efficiency. All the Schiff base additives studied obeyed the Langmuir isotherm.

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Keywords: Steel; Acid media; Schiff base; Inhibitor; Polarization; Impedance

1. Introduction

The use of inhibitors is one of the most practical methods for protection against corrosion in acidic media [1]. HCl and H₂SO₄ are generally initiated as acidic media in the corrosion study of ferrous alloys. Most commercial inhibitor formulations include aldehyde and amines in their structure [2]. On the other hand most well

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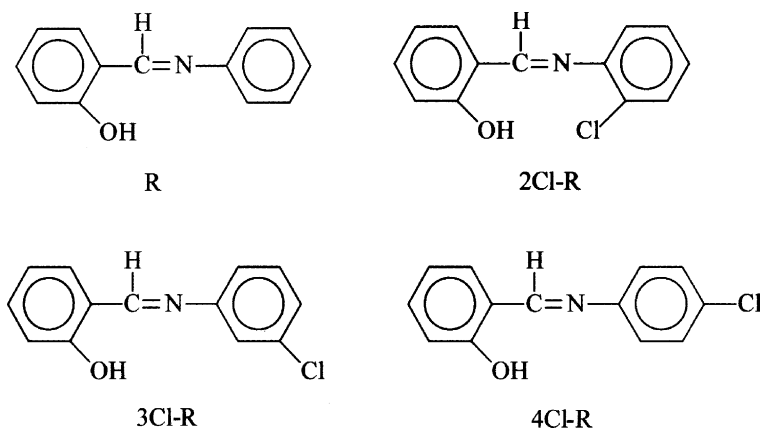


Fig. 1. Chemical structure of Schiff bases studied.

known acid inhibitors are organic compounds that contain N, S or O atoms [3–5]. Several Schiff bases have recently been investigated as corrosion inhibitors for various metals and alloys in acid media [6–10].

Due to the presence of the —C=N— group in the molecule, Schiff bases should be good corrosion inhibitors. Besides the imine group, substitution of different elements also affect the inhibition properties. The aim of study is to investigate the substitution effect of chloride ions on the inhibitive properties of salicylaldehyde on steel in 5% HCl acid solution. The chemical structures of the Schiff bases are given in Fig. 1.

2. Experimental apparatus and conditions

Electrochemical experiments were carried out in a Pyrex cell with three compartments. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum sheet as the counter electrode. The chemical composition of the working electrode, a steel rod embedded in epoxy, with a surface area of 0.097 cm^2 is given in Table 1.

The working electrode was mechanically polished with 1200 grit emery paper and $0.5 \text{ }\mu\text{m}$ alumina, washed in doubly distilled water and then placed in the test solution.

Table 1
Chemical composition (wt.%) of steel used as the working electrode

C	Mn	P	S	Fe
<0.3	0.35	0.03 max	0.03 max	Balance

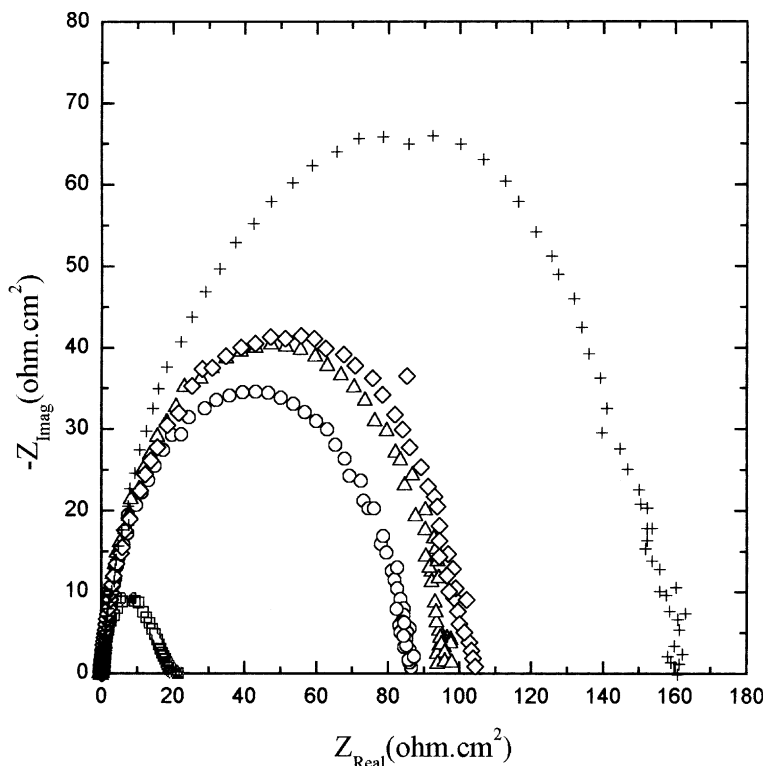


Fig. 2. Impedance plot obtained at 20 °C in 5% HCl in various concentrations of salicylaldimine, R. Key: (□) 5% HCl, (○) 5% HCl + 1×10^{-4} mol/dm³ R, (△) 5% HCl + 5×10^{-4} mol/dm³ R, (◇) 5% HCl + 1×10^{-3} mol/dm³ R, (+) 5% HCl + 5×10^{-3} mol/dm³ R.

The aggressive environment employed was an aqueous solution containing 5% HCl solution. The substances used were analytical grade reagents.

The Schiff base compounds used were generally synthesized by a condensation reaction between salicylaldehyde and the amine in question in ethanol and recrystallized in either ethanol or methanol. The amine compounds used were 2-chloroaniline, 3-chloroaniline and 4-chloroaniline. The resulting compounds were salicylaldimine, R, *N*-(2-chlorophenyl)salicylaldimine, 2Cl-R, *N*-(3-chlorophenyl)salicylaldimine, 3Cl-R, and *N*-(4-chlorophenyl)salicylaldimine, 4Cl-R (Fig. 1).

The potentiostatic polarization and impedance measurements were obtained on a VoltaLab 301 system complete with Pentium III PC and VoltaLab 4.0 software.

The impedance measurements were carried out in different solutions at the respective corrosion potentials with a sinusoidal potential perturbation of 5 mV. The preconditioning time for all the impedance measurements was 30 s and the frequency range was between 10000 Hz and 50 mHz. All the impedance measurements were taken at the respective corrosion potential and analyzed using Boukamp's Equivcrt Software [11].

All solutions were deaerated with argon for 30 min in the working cell prior to each experiment. The solutions were mixed vigorously with a magnetic stirrer. Before each experiment the electrode was immersed in the test solution for 20 min, which insured a reliable corrosion potential. The working temperature was 20 °C.

3. Results

3.1. AC impedance results

Figs. 2–5 show the complex plane display for steel in 5% HCl solution with and without the R, 2Cl-R, 3Cl-R or 4Cl-R additives between the concentration range 10^{-4} – 5×10^{-3} mol l⁻¹ at 20 °C. In general these circuits fall into the classical parallel capacitor resistor combination with the series resistance being that of the bulk solution. The influence of concentration of these additives shows the diameter of the semi-circles to increase with increasing additive concentration.

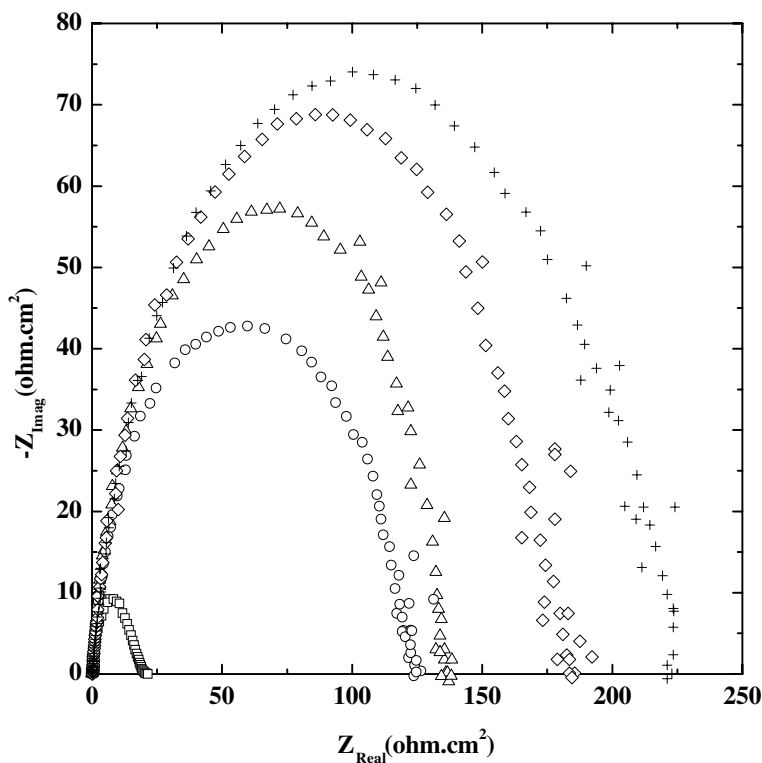


Fig. 3. Impedance plot obtained at 20 °C in 5% HCl in various concentrations of *N*-(2-chlorophenyl)salicyaldimine, 2Cl-R. Key: (□) 5% HCl, (O) 5% HCl + 1×10^{-4} mol/dm³ 2Cl-R, (Δ) 5% HCl + 5×10^{-4} mol/dm³ 2Cl-R, (◇) 5% HCl + 1×10^{-3} mol/dm³ 2Cl-R, (+) 5% HCl + 5×10^{-3} mol/dm³ 2Cl-R.

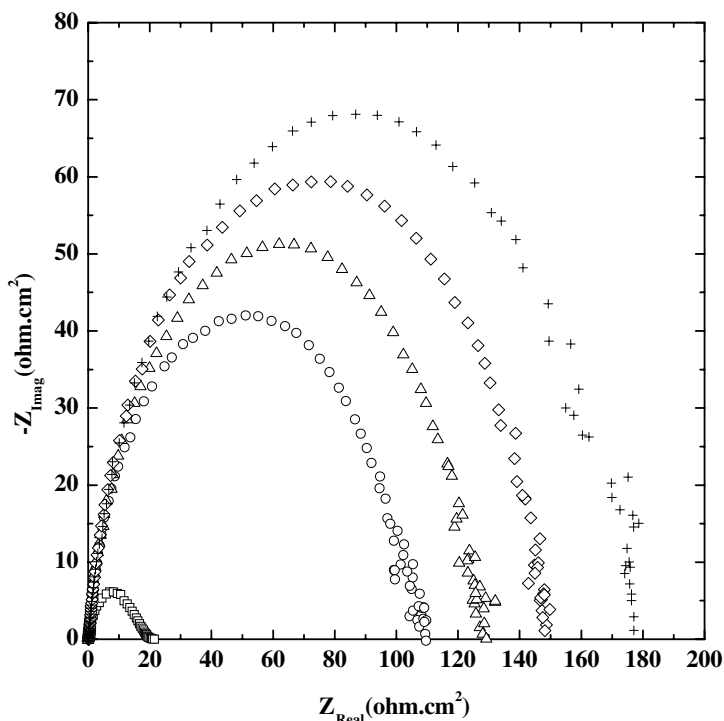


Fig. 4. Impedance plot obtained at 20 °C in 5% HCl in various concentrations of *N*-(3-chlorophenyl)salicyaldimine, 3Cl-R, Key: (□) 5% HCl, (○) 5% HCl + 1×10^{-4} mol/dm³ 3Cl-R, (△) 5% HCl + 5×10^{-4} mol/dm³ 3Cl-R, (◇) 5% HCl + 1×10^{-3} mol/dm³ 3Cl-R, (+) 5% HCl + 5×10^{-3} mol/dm³ 3Cl-R.

From Figs. 2–5, comparing the impedance behavior of steel in the solution with and without the inhibitor additive, the corrosion of steel is obviously inhibited in the presence of the additive. Quantitative results can be seen in Table 2. The inhibiting efficiencies of the additive are all higher than 80% and the inhibiting efficiency of the ortho-chloro substituted Schiff base (2Cl-R) with a concentration of 5×10^{-3} mol/dm³ is the highest, reaching a value of 94.8%.

3.2. Polarization results

In order to better define the action of different additives and concentrations on the corrosion process a series of anodic and cathodic polarization curves were recorded after an immersion of 20 min. Figs. 6–9 show the curves recorded in 5% HCl solution with and without inhibitor additive.

It is observed from the potentiostatic polarization curves (Figs. 6–9) that both cathodic and anodic curves show a lower current density in the presence of R, 2Cl-R, 3Cl-R and 4Cl-R additives than those recorded in the 5% HCl solution alone. This suggests that all the studied Schiff bases are mixed inhibitors and the inhibiting

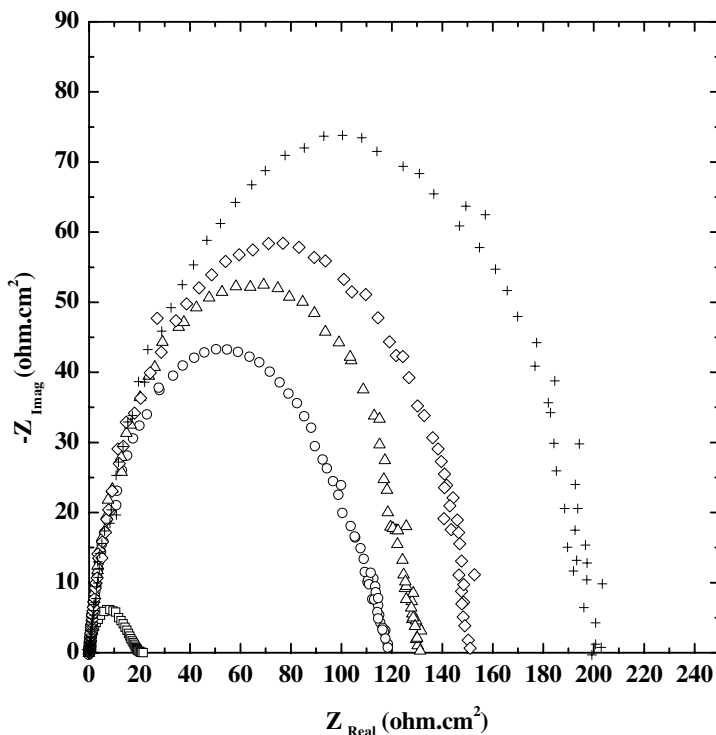


Fig. 5. Impedance plot obtained at 20 °C in 5% HCl in various concentrations of *N*-(4-chlorophenyl)salicyaldimine, 4Cl-R. Key: (\square) 5% HCl, (\circ) 5% HCl + 1×10^{-4} mol/dm³ 4Cl-R, (\triangle) 5% HCl + 5×10^{-4} mol/dm³ 4Cl-R, (\diamond) 5% HCl + 1×10^{-3} mol/dm³ 4Cl-R, (+) 5% HCl + 5×10^{-3} mol/dm³ 4Cl-R.

efficiency increases with an increase in the concentration of the additive. The results of Figs. 6–9 and the corrosion potentials shown in Table 2 clearly demonstrate that all the compounds under study reduce the corrosion current and render the corrosion potential more positive.

4. Discussion

The efficiency of an organic molecule as an inhibitor for metallic corrosion is dependent not only on the size of the molecule but also on the environment, nature of the metal, experimental parameters such as inhibitor concentration [12], molecular structure and nature of the substituent present in the molecule itself [13].

The electrochemical processes on the metal surface are likely to be closely related to the adsorption of the inhibitor [14,15], and as adsorption is known to depend on the structure of the inhibitor [16–19], the adsorption characteristics of the Schiff bases were also studied.

Table 2
Inhibitor efficiencies, η , and surface coverage, θ , calculated from Tafel and impedance plots for R, 2Cl-R, 3Cl-R, 4Cl-R in 5% HCl solution

Schiff base	E_{corr} (mV)	C (mol/dm ³)	i_{corr} (mA/cm ²)	R_s (m Ω cm ²)	R_p (Ω cm ²)	Inhibition efficiency (η) (%)	θ^a
No.	-530.1	–	1.2235	55.2	17.4	–	–
R	-510	1×10^{-4}	0.215	68.0	88	82.0	0.82
	-509	5×10^{-4}	0.191	70.0	95.9	84.0	0.83
	-507.8	1×10^{-3}	0.183	71.0	102.92	85.0	0.84
	-505.8	5×10^{-3}	0.106	70.0	169.6	91.3	0.91
2Cl-R	-507.0	1×10^{-4}	0.152	120.9	121.8	87.5	0.88
	-506.0	5×10^{-4}	0.1017	118.7	134.2	91.7	0.92
	-501.4	1×10^{-3}	0.0983	117.0	188.2	92.0	0.93
	-476.0	5×10^{-3}	0.0637	116.0	222.2	94.8	0.95
3Cl-R	-506.0	1×10^{-4}	0.1550	116.0	111.2	87.0	0.87
	-504.3	5×10^{-4}	0.1346	118.0	129.96	88.9	0.89
	-501.0	1×10^{-3}	0.1300	117.0	139.82	89.3	0.90
	-498.9	5×10^{-3}	0.1110	119.0	174.0	90.9	0.91
4Cl-R	-506.5	1×10^{-4}	0.153	117.0	117	87.4	0.87
	-505.0	5×10^{-4}	0.138	119.0	135.5	88.7	0.89
	-501.8	1×10^{-3}	0.130	118.0	153.2	89.3	0.90
	-490.4	5×10^{-3}	0.072	119.0	205.7	94.1	0.94

^a Results are the mean value of five experiments.

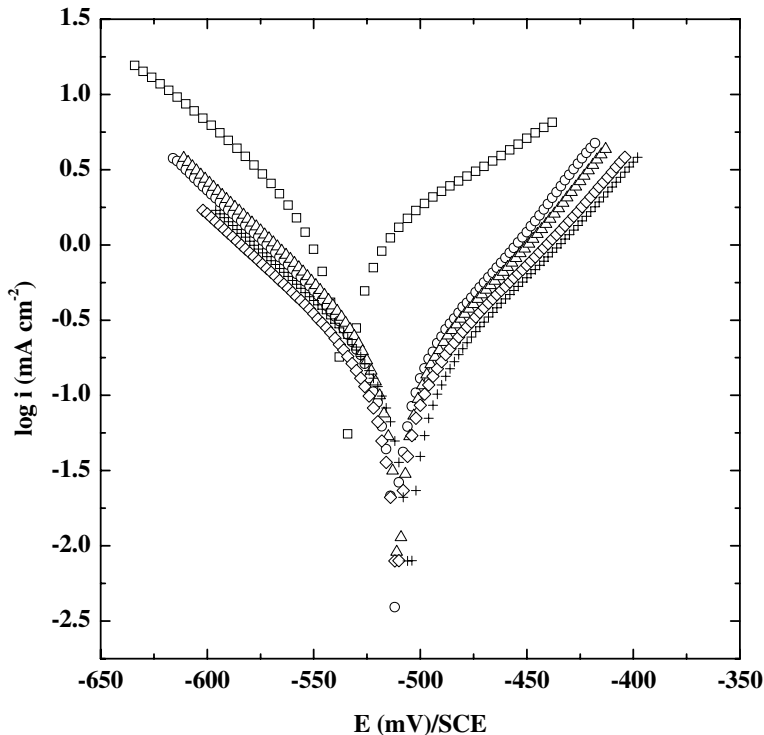


Fig. 6. Anodic and cathodic polarization curves obtained at 20 °C in 5% HCl in various concentrations of salicylaldimine, R. Key: (□) 5% HCl, (○) 5% HCl + 1×10^{-4} mol/dm³ R, (△) 5% HCl + 5×10^{-4} mol/dm³ R, (◇) 5% HCl + 1×10^{-3} mol/dm³ R, (+) 5% HCl + 5×10^{-3} mol/dm³ R.

Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions. The most frequently used isotherms are Langmuir, Frumkin and Temkin with the general formula,

$$f(\theta, X) \exp(-2\alpha\theta) = KC \quad (1)$$

where $f(\theta, X)$ is the configurational factor, θ is the degree of surface coverage, C is the inhibitor concentration in the electrolyte, X is the size ratio, α is the molecular interaction parameter, and K is the equilibrium constant of the adsorption process.

The inhibiting efficiency in Table 2 was calculated using the following formula [7–9],

$$\text{I.E.}(\%) = \frac{(i_{\text{corr}} - i'_{\text{corr}})}{i_{\text{corr}}} \times 100 = \frac{(R'_p - R_p)}{R_p} \times 100 \quad (2)$$

where i_{corr} is the corrosion rate in uninhibited solution and i'_{corr} is the corrosion rate in inhibited solution, R_p is the polarization resistance in uninhibited solution and R'_p is the polarization resistance in the inhibited solution. In the complex impedance plot

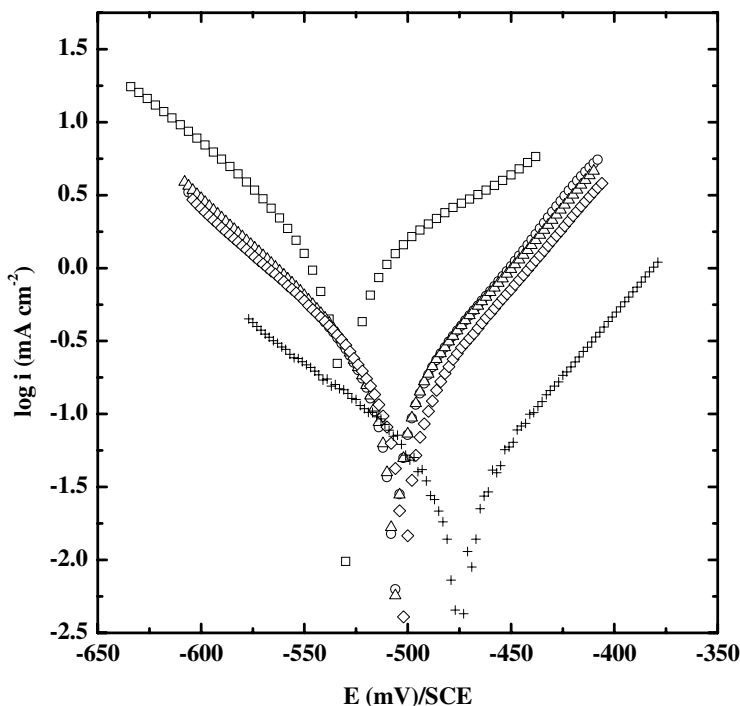


Fig. 7. Anodic and cathodic polarization curves obtained at 20 °C in 5% HCl in various concentrations of *N*-(2-chlorophenyl)salicylaldimine, 2Cl-R. Key: (□) 5% HCl, (○) 5% HCl + 1×10^{-4} mol/dm³ 2Cl-R, (△) 5% HCl + 5×10^{-4} mol/dm³ 2Cl-R, (◇) 5% HCl + 1×10^{-3} mol/dm³ 2Cl-R, (+) 5% HCl + 5×10^{-3} mol/dm³ 2Cl-R.

the value R_p represents the intersection point of the low-frequency semi-circle on the real axis, for $\omega \rightarrow 0$. In general the value of this intersection is used to obtain the apparent a.c. polarization resistance R_p . The corrosion currents i_{corr} and i'_{corr} were obtained from the intersection point of the linear portion of the anodic and cathodic tafel curves, 100 mV in the vicinity of the corrosion potential.

The surface coverage was calculated from the following formula from at least five experimental results and the mean values are also given in Table 2 [10].

$$\theta = \frac{(i_{\text{corr}} - i'_{\text{corr}})}{i_{\text{corr}}} \quad (3)$$

It is evident from Table 2 that all the examined Schiff bases are effective corrosion inhibitors in a 5% HCl solution. It is also observed that *N*-(2-chlorophenyl)salicylaldimine gives the highest inhibiting efficiency of 94.8% at a concentration of 5×10^{-3} mol/dm³. *N*-(3-chlorophenyl)salicylaldimine and *N*-(4-chlorophenyl)salicylaldimine give an inhibition efficiency of 90.9% and 94.1%, respectively, at a concentration of 5×10^{-3} mol/dm³. The inhibiting efficiency follows the order

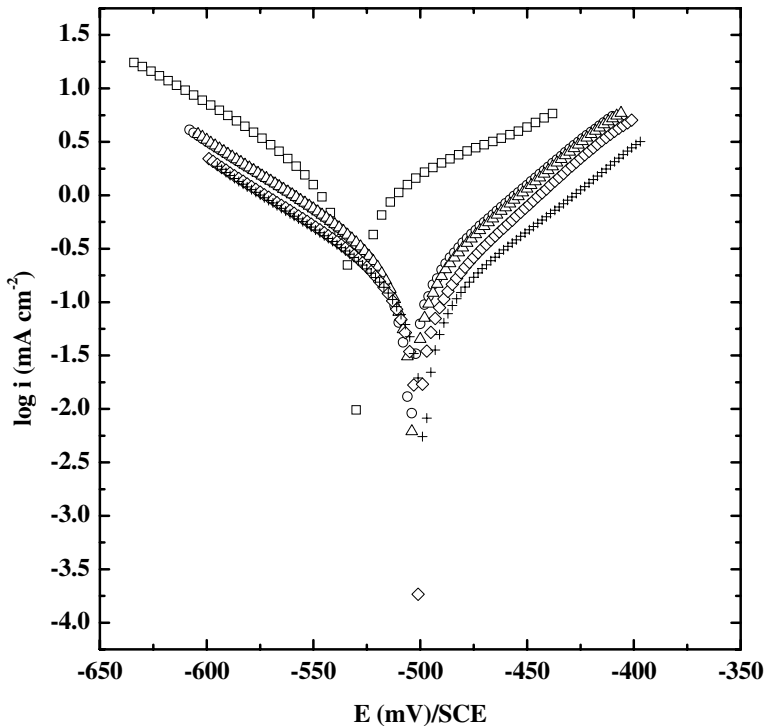


Fig. 8. Anodic and cathodic polarization curves obtained at 20 °C in 5% HCl in various concentrations of *N*-(3-chlorophenyl)salicyaldimine, 3Cl-R. Key: (□) 5% HCl, (○) 5% HCl + 1×10^{-4} mol/dm³ 3Cl-R, (△) 5% HCl + 5×10^{-4} mol/dm³ 3Cl-R, (◇) 5% HCl + 1×10^{-3} mol/dm³ 3Cl-R, (+) 5% HCl + 5×10^{-3} mol/dm³ 3Cl-R.

2Cl-R > 4Cl-R > 3Cl-R (Figs. 10 and 11). Substitution of chloride ions increases the inhibiting efficiency compared to the unsubstituted R.

As stated above, AC impedance and potentiostatic polarization results show the inhibiting efficiency to increase with increasing additive concentration.

In order to define the mechanism by which the inhibitor reacts with the metal surface, the concentration of the additives were varied from 5×10^{-3} to 1×10^{-3} mol/dm³ and different inhibiting efficiencies were obtained.

Starting with the Temkin isotherm;

$$\exp(-2a\theta) = KC \quad (4)$$

and rearranging this equation gives

$$\theta = -1/2a \ln K - 1/2a \ln C \quad (5)$$

According to Eq. (5) [20] the plot of θ (surface coverage) vs. $\ln C$ (inhibitor concentration) must be linear provided that the assumptions of the Temkin isotherm are valid. The same assumption is also true for the Langmuir isotherm.

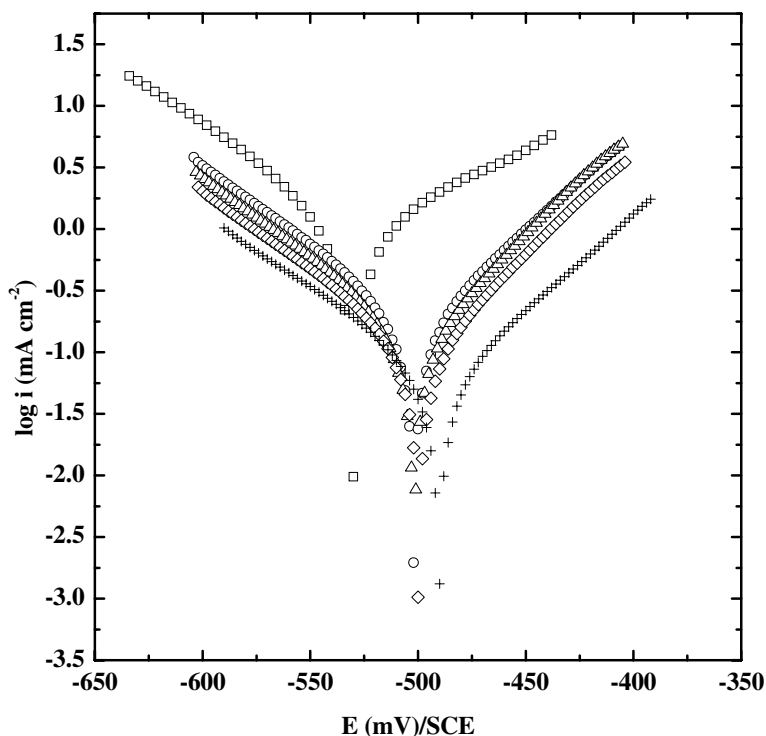


Fig. 9. Anodic and cathodic polarization curves obtained at 20 °C in 5% HCl in various concentrations of *N*-(4-chlorophenyl)salicyaldimine, 4Cl-R. Key: (□) 5% HCl, (○) 5% HCl + 1×10^{-4} mol/dm³ 4Cl-R, (Δ) 5% HCl + 5×10^{-4} mol/dm³ 4Cl-R, (◇) 5% HCl + 1×10^{-3} mol/dm³ 4Cl-R, (+) 5% HCl + 5×10^{-3} mol/dm³ 4Cl-R.

$$C/\theta = 1/K + C \quad (6)$$

Plotting C/θ against C gives straight lines for all the Schiff base molecules in question with unit slope values which obey the Langmuir isotherm. The fact that the lines are close to each other indicates inhibition to proceed through similar mechanisms (Fig. 12). The fact that the inhibiting efficiencies increase with increasing concentration suggests that the molecules may first be chemically adsorbed on the surface and cover some sites of the electrode surface, then probably form monomolecular layers, on which the insoluble product (by forming a complex) of the iron ions form and the inhibitor grows, thereby protecting these sites from attack by chloride ions. From these results it can be concluded that there is no interaction between the molecules adsorbed at the metal surface.

Iron is well known for its coordination affinity to nitrogen and oxygen bearing ligands [21,22]. Therefore adsorption of steel can also be attributed to coordination through phenolic –OH and C=N groups. Efficient adsorption may be due to either

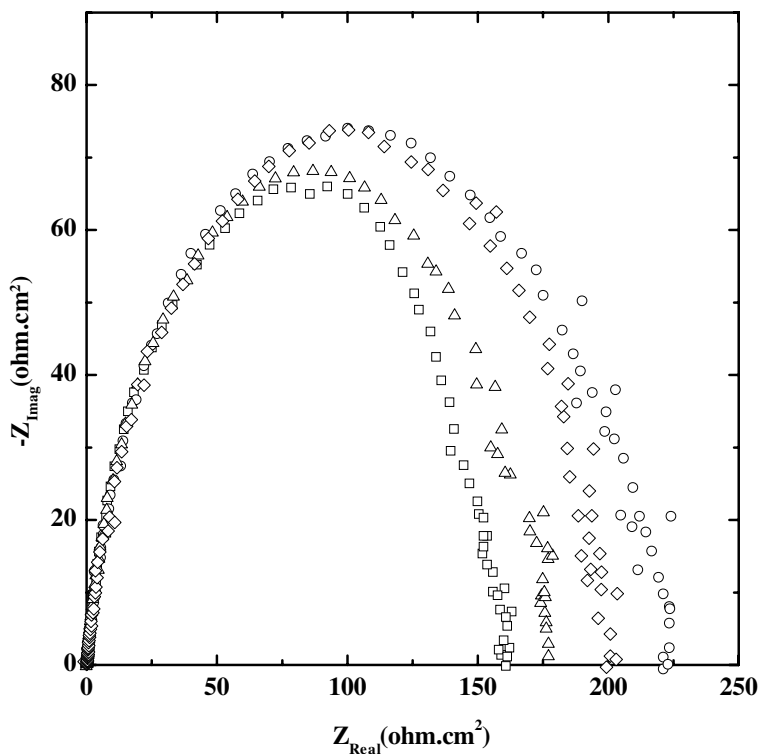


Fig. 10. Comparative impedance plot of 5×10^{-3} mol/dm³ salicyaldimine, R, *N*-(2-chlorophenyl)salicyaldimine, 2Cl-R, *N*-(3-chlorophenyl)salicyaldimine, 3Cl-R, and *N*-(4-chlorophenyl)salicyaldimine, 4Cl-R in 5% HCl. Key: (□) R, (Δ) 2Cl-R, (◇) 3Cl-R, (○) 4Cl-R.

the electronegative donor atom N, O and Cl or to the π electron of the aromatic system.

The ortho- > para- > meta-relationship in terms of inhibitor efficiency is due to the complexation and coordination effect. When an electron donor group, such as a Cl⁻ ion, is substituted in the ortho-position, the Schiff base tends to behave like a tridentate ligand in the form ONCl, which radically increases the complex formation constant. Iron(II) in this case tends to form a complex with the tridentate ligand in octahedral coordination [23,24]. Thus the main factor affecting the inhibition characteristics of 2Cl-R is the tridentate ligand which tends to form a mononuclear tridentate Fe(II) complex. Apart from this, the ortho-position is closest to the C=N group. The presence of the electron donating group in this position increases the electron density on the nitrogen of the C=N group [25].

On the other hand the para-position is similar to the ortho-position through resonance but is further away from the C=N group. The ligand tends to form a didentate structure in the form ON. In this case rather than formation of a tridentate

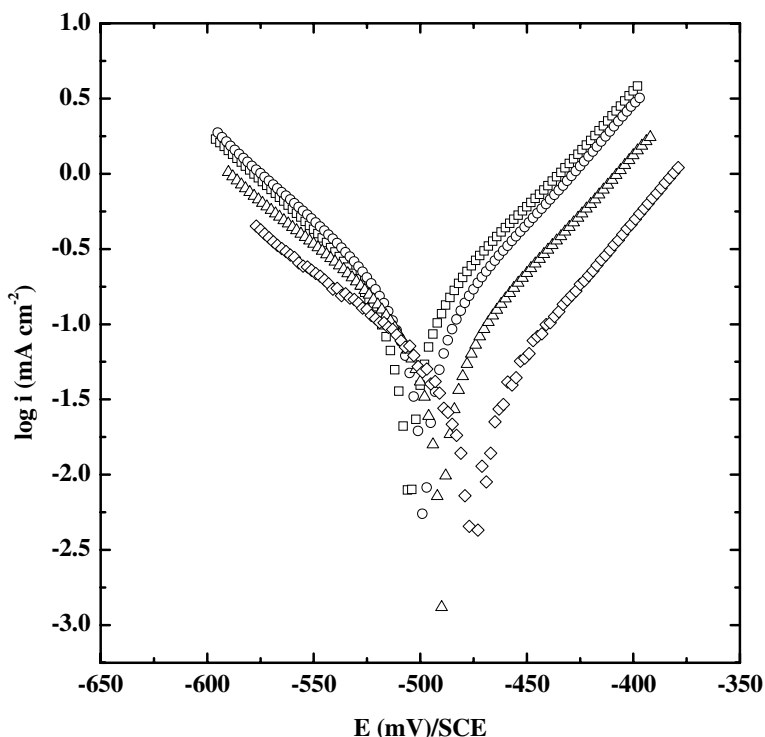


Fig. 11. Comparative anodic and cathodic polarization plot of 5×10^{-3} mol/dm³ salicylaldimine, R, *N*-(2-chlorophenyl)salicylaldimine, 2Cl-R, *N*-(3-chlorophenyl)salicylaldimine, 3Cl-R, and *N*-(4-chlorophenyl)salicylaldimine, 4Cl-R in 5% HCl. Key: (□) R, (○) 2Cl-R, (△) 3Cl-R, (◇) 4Cl-R.

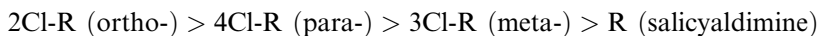
complex a didentate complex results and the main factor affecting the inhibition efficiency is the basicity of the complex alone.

The meta-position has no effect through resonance and shows the lowest inhibition although it too can form a didentate structure.

Further studies on this subject with other substituents like, I⁻, Br⁻, OH⁻ etc. are in progress.

5. Conclusions

1. All the Schiff bases investigated act as anodic and cathodic inhibitors.
2. The adsorption processes in all the Schiff bases obey the Langmuir (monolayer) adsorption isotherm.
3. The inhibiting efficiency follows the following pattern in terms of the substituted Cl position.



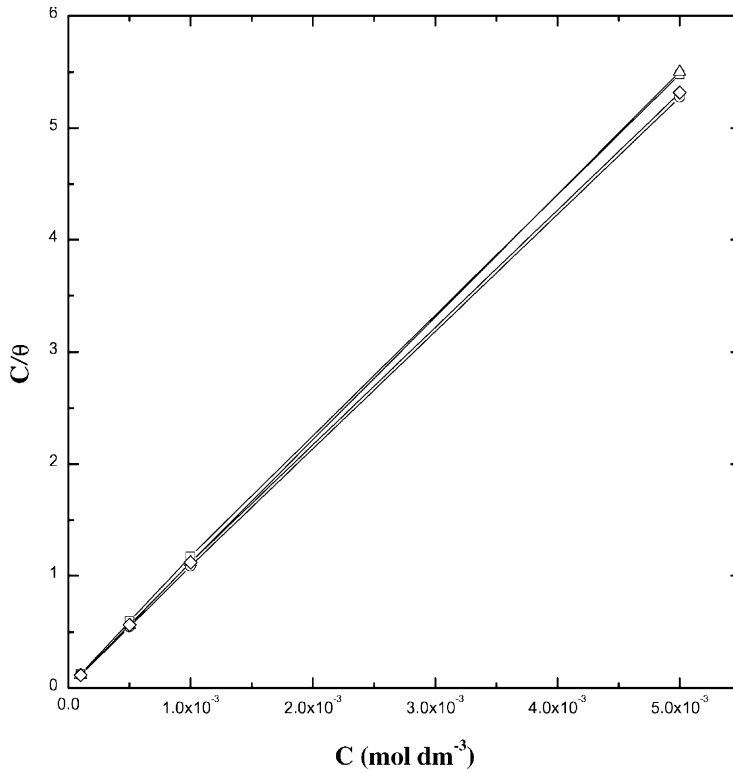


Fig. 12. Experimental results for salicylaldehyde, R, *N*-(2-chlorophenyl)salicylaldehyde, 2Cl-R, *N*-(3-chlorophenyl)salicylaldehyde, 3Cl-R, and *N*-(4-chlorophenyl)salicylaldehyde, 4Cl-R according to the Langmuir isotherm. Key: (□) R, (○) 2Cl-R, (△) 3Cl-R, (◇) 4Cl-R.

Acknowledgement

The authors wish to thank the Ankara University Research fund for their funding of this project. Project No: 2001/0705052.

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