G.U. Journal of Science
23(3):287-293 (2010)

www.gujs.org

Effect of a New Schiff Base on the Corrosion and Dezincification of Brass in 1 M HCl

Athare DADGARINEZHAD[1♠], Fatemeh.BAGHAEI[1]

[1]*Shahid-Bahonar University of Kerman, Material Science and Engineering Department, Kerman, Iran*

Received: 23.09.2009 Revised: 25.03.2010 Accepted: 16.04.2010

ABSTRACT

In this study the effect of a new synthetic Schiff base namely bis -(2-hydroxy-3-methoxy)-1,6-diaminohexane salicylaldimine on the corrosion and dezincification of a 70/30 brass in 1M HCl has been studied using weight loss , electrochemical (polarization & impedance) and solution analysis techniques. Results obtained revealed that this compound is very good inhibitor and behaves as mixed type of inhibitor for brass 70/30 in this acid medium. Solution analysis and surface composition (weight%) of the alloy in the presence and absence of inhibitor by atomic absorption spectroscopy (AAS) and energy dispersive X-Ray analysis (EDAX) revealed the decrease in dissolution of both Cu and Zn in the presence of this inhibitor. The dezincification factor (Z) was calculated by using analysis solution.

Key Words: *Inhibitor, polarization, impedance, dezincification, corrosion.*

1. INTRODUCTION

One of the applications of brasses is for the casting of decorative item. Brasses are widely used for outdoor applications and sanitary fittings, which are exposed to corrosive environments, also they are widely used in industries ,particularly as condensers and heat exchangers in power plants [1].These equipments should be regularly cleaned, because their heating transmission are diminished due to precipitate the oxides and carbonates. Acid solution are widely used in industry the most important areas of application being acid pickling , industrial acid cleaning, acid descaling and oil well acidizing [2]. Inhibitors are usually used in these processes to control the corrosion of the metal. The choice of the inhibitor is based on two considerations. First, it can be synthesized conveniently from relatively cheap raw materials. Second, the presence of an electron cloud on the aromatic ring, the electronegative sulphur, nitrogen, oxygen atoms and the relatively long chain compounds to induce greater adsorption on the metal surface promoting effective inhibition [3].Generally , a strong coordination bond causes higher inhibition efficiency, the inhibition increases in the sequence $O<N<S<P$ [4-13]. The inhibition of corrosion by schiff bases can be attributed to its molecules with π-electrons of –C=N-groups and π-electrons of aromatic ring. Conjugating large π bond through which its molecules are likely to be adsorbed strongly on the metal surface[14].The aim of the present work was to study the inhibition efficiency of a new synthetic schiff base namely bis -(2-hydroxy-3-methoxy)-1,6-diaminohexane salicylaldimine(Figure 1) on the corrosion and dezincification of a 70/30 brass in1M HCl. Electrochemical methods such as Tafel polarization , impedance spectroscopy ,weight loss and solution analysis were used. Dezincification of brass was analyzed using atomic absorption spectroscopy. The composition

♠Corresponding author, e-mail: a.dadgar@mail.uk.ac.ir

of brass surface was analyzed using dispersive x-ray analysis (EDAX).

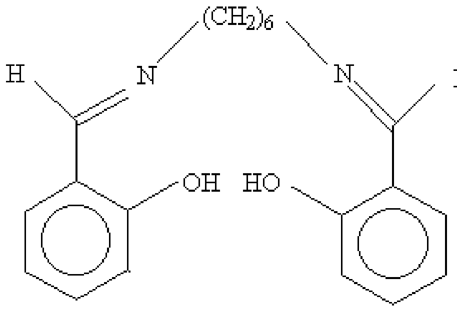

Figure 1.The structure of schiff base.

2. EXPERIMENTAL DETAILS

2.1. Materials

For polarization studies, the thick brass sheet with a composition of Cu 70% and Zn 30% ,was embedded in epoxy resin, to expose geometrical surface area of $1cm^2$ to electrolyte. The electrode was polished to mirror finish, using fine grain emery paper of (120-1200) grade under water flow, washed with double distilled water and acetone and dried prior to the experiments. The solutions were prepared with analytical grade and chemically pure reagents (Merck).Schiff base compound with structure shown in fig.1 was dissolved in absolute ethanol to obtain 1000ppm concentration, then from this concentration by adding to corrosive electrolyte were prepared designated concentration of Schiff base.

2.2. Weight-loss Studies

Weight-loss experiments were carried out with rectangular brass coupons ($1\times1\times0.1$ cm^2). The coupons were immersed in 100 mL of 1M HCl solution with and without inhibitor and allowed to stand at room temperature according to the ASTM standard procedure described in literature [15].

2.3. Electrochemical Studies

The anodic and cathodic polarization behavior of 70/30 brass in 1M HCl solution with and without of various concentration of inhibitor was determined using a Potentiostat/Galvanostat 263A (EG&G) Princeton Applied Research HF response model 1025, in a conventional three-electrode cell assembly with a Pt-counter electrode (CE) , a standard calomel electrode (SCE) and working electrode(WE). The polarization curves were obtained using a sweep rate of 1 mV s^{-1} from -500 to -100 mV after 30 min. immersion in electrolyte at room temperature. The electrochemical impedance experiments were carried out using AC signals of amplitude 5 mV peak to peak at the open circuit potential(E_{ocp}) in the frequency range 100 kHz to 10 mHz after 30 min immersion in the electrolyte cell.

2.4. Solution Analysis

During the anodic polarization, the metal dissolution takes place releasing considerable amount of metal ions from the material. The solutions left after polarization measurements were analyzed by atomic adsorption spectrometer (model Spectra A-20) to measure the amount of Cu and Zn leached out from the alloys. The solution containing the maximum concentration of the inhibitors and a blank solution containing no inhibitors for comparison were chosen.

2.5. Surface Analysis

The comparison of the brass surface after polarization measurements was analyzed using energy dispersive X-Ray analysis (EDAX) using SEM (model CamScan MV2300).

3. RESULT AND DISCUSSION

3.1. Weight-loss Measurements

The percentage of inhibition efficiency (η_w%) over the period was calculated using the following equation [16].

$$\eta_w \% = \frac{w_0 - w}{w_0} \times 100 \quad (1$$

Where w_0 and w are the mean values of three plicate weight loss of samples after immersion in solution without and with inhibitor respectively. The results of weight-loss measurements are shown in table1.

Table1. Obtained parameters from weight-loss measurement.

Inhibitor conc. (ppm)	25	50	75	100
(η_w%)	40.33	78.42	83.93	89.99

3.2. Potentiodynamic Polarization Studies

Figure 2. represents the polarization curves of 70/30 brass in 1M HCl in the presence and absence of various concentration of Schiff base. It is observed that, both of the cathodic and anodic curves show lower current density in the presence of the Schiff base than those recorded in the solution without the Schiff base. This behavior indicated that used Schiff base have effect on both cathodic and anodic reactions of corrosion process. Therefore, this compound could be classified as mixed type inhibitor.

The parameters and corrosion inhibition efficiencies (η %) derived from these curves are given in table 2. The inhibition efficiency percent (η %) of inhibitor is calculated by the follow equation (17).

$$\eta\% = \frac{I_0 - I}{I_0} \times 100 \qquad (2)$$

Where I_0 and I are the uninhibited and inhibited corrosion current densities determined by extrapolation of catholic and anodic Tafel lines at 150 mV more positive and negative than E_{corr}.

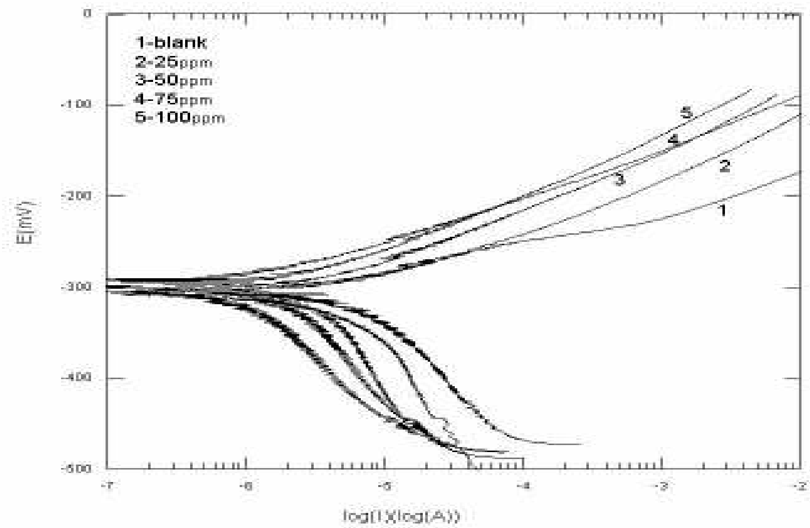

Figure 2. Polarization curves in absence and presence of various concentration of inhibitor.

Table 2.Electrochemical parameters obtained from polarization curves.

Inhibitor Conc / ppm	E_{Corr} /mV Vs.SCE	I_{Corr} μA /cm^2	η%
0	-296.1	3.210	——
25	-296.8	1.974	38.50
50	-295.7	0.793	75.30
75	-294.3	0.555	82.71
100	-293.4	0.359	88.82

3.3. Impedance Measurements

Electrochemical impedance spectroscopic (EIS) measurements have been carried out for brass in 1M HCl in the absence and presence of various concentration of inhibitor .The Nyquist plots are shown in Figure 3.

The charge transfer resistance, R_{ct} values were calculated from the difference in the resistance measurements obtained at lower and higher frequencies. The double layer capacitance (C_{dl}) was obtained from the follow equation (18).

$$f(-Z''_{max}) = \frac{1}{2\pi C_{dl} R_t} \qquad (3)$$

Where f is the frequency at the apex of the semicircle in the Nyquist plot.

The inhibition efficiency percent (η %) of inhibitor was calculated by the follow equation (19).

$$\eta\% = \frac{R_{ct} - R_{0ct}}{R_{ct}} \times 100 \qquad (4)$$

Where R_{ct} and R_{0ct} are the charge transfer resistance value with and without inhibitor, respectively .The impedance parameters derived from EIS experiments were listed in Table3. According to results of table 3 the inhibition efficiency increases with inhibitor concentration increasing and is in good agreement with weight loss and polarization results.

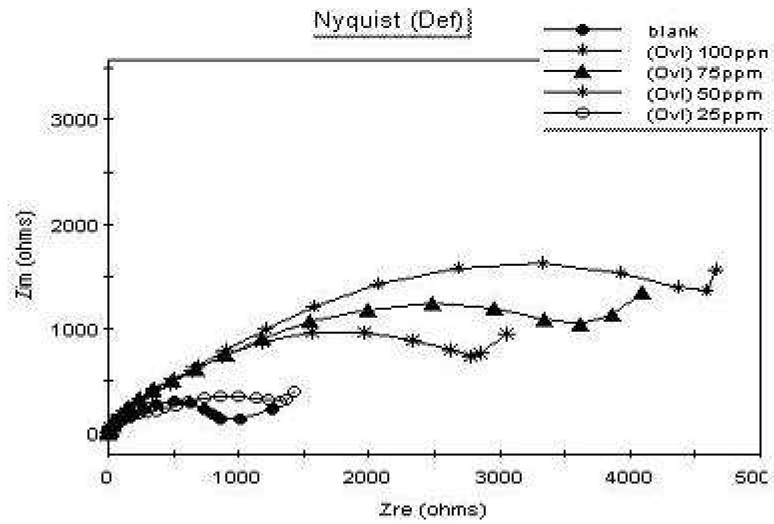

Figure 3. Nyquist plots for brass in 1M HCl + different concentration of inhibitor.

Table 3. Impedance parameter values for 1M HCl + different conc. of inhibitor.

Inh Conc.(ppm)	R_{ct} (Ω cm^2)	C_{dl} (μF/cm^2)	η%
0	1188	1049.00	——
25	1863	924.30	36.62
50	4421	900.21	73.13
75	6279	800.40	81.08
100	7960	720.40	85.08

3.4. Solution Analysis

The results of solution analysis and the corresponding dezincification factor (z) in the presence and absence of inhibitor at their maximum concentration level for brass were summarized in table 4.

Table 4. Effect of maximum concentration of inhibitors on the dezincification of brass.

Inhibitor conc./ppm	**Solution Analysis**		**Dezincification Factor (z)**	**IE%**	
	Cu /ppm	**Zn /ppm**		**Zn**	**Cu**
0	0.23	4.75	46.15	——	——
100	0.05	0.56	26.10	78.26	88.21

The dezincificion factor (z) was calculated using the following equation [20]

$$Z = \frac{(Zn / Cu)_{sol}}{(Zn / Cu)_{alloy}} \tag{5}$$

Where the ratio $(Zn/Cu)_{sol}$ is determined from solution analysis and $(Zn/Cu)_{alloy}$ is the ratio of weight percent in the alloy.

The copper/zinc ratio in solution was found smaller than that of the bulk alloy. This indicates that the growth of surface film and dissolution of the alloy controlled by diffusion [21], which is related to the difference between the ionic radii of $Zn^{+2}$and Cu^{+1}ions. The results indicated that the inhibitor is able to minimize the dissolution of both copper and zinc. The percent inhibition efficiency (IE%) against the dissolution of zinc was correspondingly higher as compared to the dissolution of copper which is also reflected in the values of dezincification factor. This suggests that the schiff base efficiently prevent the dezincification of 70/30 brass in 1M HCl solution.

3.5. Surface Composition Analysis

The surface composition (weight %) of the alloy in the presence and absence of inhibitor was given in table 5.

Table 5.Surface composition (wt %) of brass in 1M HCl solution after polarization without and with maximum concentration of inhibitor.

Inhibitor conc.(ppm)	Cu/wt.%	Zn/wt.%	Cl/wt.%
Alloy	70	30	——
0	68.35	26.53	5.12
100	69.23	29.18	1.59

In the absence of inhibitor, the metal ions were leached in HCl solution and the (wt%) of Cu and Zn are present in the surface layer were reduced. more over, the higher concentration of chloride ions on the surface shows the penetration of Cl^- ions into the alloy. However, in the presence of inhibitor the (wt %) of Cu and Zn is smaller and closer to that of the bulk composition of alloy. Based on the surface analysis, this inhibitor exhibited good inhibition efficiency in 1M HCl solution.

3.6. Mechanism of Corrosion Inhibition

It is well known that the inhibitive action of organic compound containing S, N and/or O is due to the formation of a co-ordinate type of bond between the metal and the pair of electrons present in the additive. The tendency to form co-ordinate bond and hence the extent of inhibition can be enhanced by increasing the effective electron density at the functional group of the additive. In aromatic or heterocyclic ring compounds, the effective electron density at the functional group can be varied by introducing different substituents in the ring leading to variations of the molecular structure. The higher inhibition efficiency of the Schiff base compound studied is due to the basis of donor-acceptor interaction between the π electrons of the inhibitor and the vacant d-orbital of copper surface or interaction of inhibitor with already absorbed chloride ions [22].

3.7. Adsorption Isotherm

In order to get a better understanding of the electrochemical process on the metal surface, adsorption characteristics was also studied. Of course, it is well known that adsorption of inhibitor molecule strongly depends on its chemical structure. 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,

$$f(\theta, \mathrm{X})\exp(-2\alpha\theta) = \mathrm{K}C \quad (6)$$

Where $f(\theta, \mathrm{X})$ is the configurationally 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 surface coverage θ can readily be calculated from any of the Eq. (1), (2) or (4), as in that case it is numerically identical to the value of the inhibition efficiency:

$$\theta = \eta = \frac{\eta\%}{100} \quad (7)$$

In the following, impedance data (Eq. (4)) were used for θ calculation.

Figure 4 represented the data obtained from Langmuir isotherm for brass electrode in 1M HCl with various cons. of Schiff base .This isotherm is:

$$\frac{\theta}{1-\theta} = KC \quad (8)$$

Where θ is the surface coverage, C is the concentration and K is the constant of the adsorption process. According to Eq. (8) the plot of $\theta / (1-\theta)$ vs. C_{inh} yield a straight line, clearly proving that the adsorption of the Schiff base in 1M HCl on brass obeys the Langmuir isotherm [23].

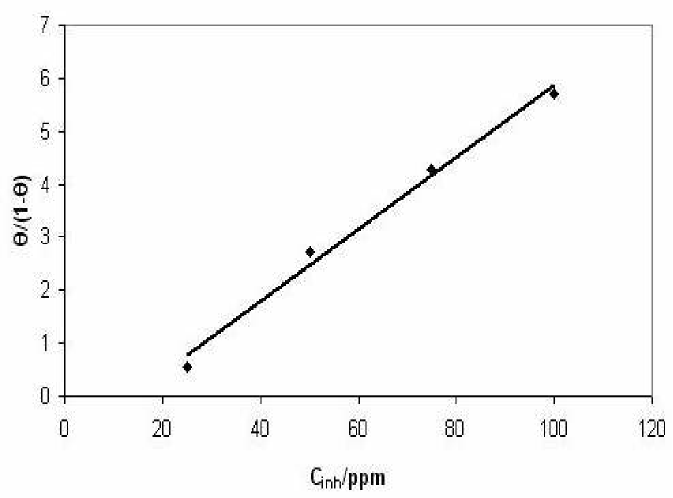

Figure 4. Langmuir adsorption plot for inhibited brass in 1M HCl.

4. CONCLUSION

1-This new synthetic schiff base, was effective corrosion inhibitor in 1M HCl solution for brass.

2-Polarization studies showed that schiff base behaved as a mixed (anodic-cathodic) inhibitor.

3-Impedance studies indicated that with increasing inhibitor concentration R_{ct} values increased, while C_{dl} values decreased.

4-Solution analysis showed that this inhibitor is able to minimize the dissolution of both copper and zinc.

5-The obtained inhibition efficiencies (η%) from different techniques were in good agreement.

6-The inhibition was due to the adsorption of the schiff base on the brass surface and blocking of active sites, and adsorption of the Schiff base on the surface obeyed the Langmuir,s isotherm.

REFERENCES

[1] Karpagavalli, R., Balasubramaniam, R., “Development of novel brasses to resist dezincification”, ***Corrosion Science***, 49: 963-979 (2007).

[2] Larabi, L., Harek, Y., Traisnel, M., Mansri, A., “Synergistic influence of poly(4-vinylpyridine) and potassium iodide on inhibition of corrosion mild steel in 1M HCl”, ***J. of Applied Electrochemistry***, 34: 833-839 (2004)

[3] Agmal, M., Mideen, A.S., Qurasihi, M.A., “2-hydrazino-6-methyl-benzothiazole as an effective inhibitor for the corrosion of mild steel in acidic solutions”, ***Corrosion Science***, 36: 79 (1994).

[4] Ei-Taib Heakal, F., Haruyama, S., “Impedance studies of the inhibitive effect of benzotriazole on the corrosion of copper in sodium chloride medium”, ***Corros. Sci.***, 20: 887 (1980).

[5] Meticos-Hukovic, M., Grubac, Z., Stupnisk-Lisac, E., “Organic corrosion inhibitors for aluminum in perchloric acid”, ***Corros.***, 50: 2 (1994).

[6] Upec, U., Iboc, U., Ita, B., Offiong, O., Ebenso, E., “Inhibitory action of methyl and phenyl thiosemicarbazone derivatives on the corrosion of mild steel in hydrochloric acid”, ***Mater.Chem. Phys.***, 40: 87 (1995).

[7] Tadros, A.B., Abd-El-Nabey, A.B., “Inhibition of the acid corrosion of steel by 4-amino-3-hydrazino-5-thio-1, 2, 4-triazoles ”, ***J. Electroanal.Chem.***, 24: 433 (1988).

[8] Aouniti, A., Hammouti, B., Brighli, M., Kertit, S., Berhili, F., El Kadiri, S., Ramdani, A., “Inhibition of the acid corrosion of iron with new pyrazole derivatives”, ***J. Chim. Phys.***, 93: 1262 (1996).

[9] Kertit, S., Hammouti, B., “Corrosion inhibition of iron in 1M HCl by 1-phenyl-5-mercapto-1, 2, 3, 4-tetrazole”, ***Appl. Surf.. Sci.***, 93: 59 (1996).

[10] Bouayed, M., Rabaa, H., Srhiri, A., Saillard, J.Y., Ben Bachir, A., Le Beuze, A., “Experimental and theoretical study of organic corrosion inhibitors on iron in acidic medium”, ***Corros. Sci.***, 41:501 (1999).

[11] Cheng, X.L., Ma, H.Y., Chen, S.H., Yu, R., Chen, X., Yao, Z.M.,“Corrosion of stainless steels in acid solutions with organic sulfur-containing compounds”, ***Corros. Sci.***, 41: 321 (1999).

[12] Raicheva, S.N., Aleksiev, B.V., Sokolova, E.I., “The effect of the chemical structure of some nitrogen- and sulphur-containing organic compounds on their corrosion inhibiting action”, ***Corros. Sci.***, 34: 343 (1993).

[13] Schweinsberg, D.P., Ashworth,V., “The inhibition of the corrosion of pure iron in 0.5 M sulphuric acid

by *n*-alkyl quaternary ammonium iodides", ***Corros. Sci.***, 28: 539 (1988).

[14] Agrawal, Y.K., Talati, J.D., Shah, M.D., Desai, M. N., Shah, N.K., "Schiff bases of ethylenediamine as corrosion inhibitors of zinc in sulphuric acid", ***Corros. Sci.***, 46: 633 (2004).

[15] ASTM, "Standard practice for laboratory immersion corrosion testing of metals", G31-72, ASTM, 401 (1990).

[16] Bentiss, F., Traisnel, M., Lagrenee, M., "The substituted 1,3,4-oxadiazoles: a new class of corrosion inhibitors of mild steel in acidic media", ***Corros .Sci.***, 42: 127 (2000).

[17] Hosseini, M., Mertens, S.F.L., Chorbani, M.C., Arshadi, M.R., "Asymmetrical schiff bases as inhibitors of mild steel corrosion in sulphuric acid media", ***Materials Chemistry and Physics.***, 9647:1-9 (2002).

[18] Bentiss, F., Traisnel, M., Lagrene. M., "The substituted 1,3,4-oxadiazoles: a new class of corrosion inhibitors of mild steel in acidic media", ***Corros .Sci .***, 42: 127 (2000).

[19] Quan, Z., Chen, S., Li, Y., Cui, X.,"Adsorption behaviour of Schiff base and corrosion protection of resulting films to copper substrate", ***Corrs.Sci.***,44: 703 (2002).

[20] Ravichandran, R., Nanjundan, S., Rajendran, N., "Effect of benzotriazole on the corrosion of brass in NaCl solutions", ***Applied Surface Science***, 236: 241-250 (2004).

[21] Van Ooij, W.J., " Surface composition, oxidation and sulfidation of cold-worked brass and brass-coated steel wire as studied by x-ray photoelectron spectroscopy I. Surface composition of commercial cold-worked brass", ***Surface Technology***, 6(1):1-18 (1977).

[22] Ravichandran, R., Rajendran, N., "Influence of benzotriazole derivatives on the dezicification of 65-35 brass in sodium chloride", ***Applied Surface Science***, 239: 182-192 (2005).

[23] Emregul, K.C., Kurtaran, R., Atakol, O., "An investigation of chloride-substituted Schiff bases as corrosion inhibitors for steel", ***Corrosion Science***, 45: 2803-2817 (2003).