THE INHIBITION MILD STEEL CORROSION IN PHOSPHORIC ACID SOLUTIONS BY 2- PHENYL-1-HYDRAZINE CARBOXAMIDE

A. DADGARINEZHAD*, F. BAGHAEI

Materials Engineering Department, Shahid Bahonar University, Kerman, Iran

(Received: July 15, 2008 - Accepted: April 24, 2009)

ABSTRACT

In this work the effect of 2-phenyl-1-hydrazine carboxamide on the corrosion of mild steel in solutions of phosphoric acid (H_3PO_4) has been investigated in relation to the concentration of the inhibitor and acid, by weight loss, potentiodynamic polarization, and AC impedance (EIS) measurements. Results obtained revealed that this compound is a good mixed -type inhibitor. Increasing the acid concentration increased the metal corrosion but did not affect on the inhibitor efficiency. The optimum inhibitor concentration remained 150 ppm for various concentration of H_3PO_4 . The surface morphologies of specimens after 1 hour of immersion in various solutions were studied by scanning electron microscopy (SEM). The Langmuir adsorption isotherm fitted well with the experimental data.

Keywords: Potentiodynamic; EIS; Inhibitor; SEM; Corrosion

INTRODUCTION

Phosphoric acid (H_3PO_4) has many important uses, especially in the production of fertilizers. Most of the acid is produced from phosphate rocks by the wet process based on the reaction between phosphate rocks and acid solutions¹. This acid (H_3PO_4) is a medium-strong acid, but it is still shows strong corrosiveness on ferrous or ferrous alloys². There is a great need to protect steel material used in the phosphoric acid industry from corrosion. Little work appears to have been done on the inhibition of steel in H_3PO_4 solutions³⁻⁷. Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms. Compounds with functional groups containing hetero-atoms which can donate lone pair electrons are found to be particularly useful as inhibitors for corrosion of metals². Some organic compounds have been synthesized and investigated as inhibitors for corrosion of metals in acidic solutions⁸⁻¹³. The goal of the present work was to study the inhibition characteristics of 2- phenyl-1-hydrazine carboxamide as corrosion inhibitor for mild steel in H_3PO_4 using different techniques such as weight loss, potentiodynamic polarization and AC impedance spectroscopy.

EXPERIMENTAL

Samples and solutions

Mild steel specimens having percent composition of 0.05C, 0.65Mn, 0.35Si, 0.01S, 0.01P and remaining Fe were used. Surface of specimens was mechanically polished on wet SiC abrasive paper (grade 300-1200), rinsed with distilled water, degreased with absolute ethanol and dried at room temperature before using. All used materials were extra pure and solutions were prepared by using distilled water.

Gravimetric studies

The specimens were used for gravimetric measurement had a rectangular form (1cm×1cm×0.1cm). The weight loss of specimens in various concentration of H_3PO_4 (1M, 2M, 3 M) with and without addition of different concentration of inhibitor after 1 hour of immersion period at 25° C was determined. The average three triplicate values was used according to the ASTM standard procedure described in literature¹⁴.

Electrochemical measurements

For electrochemical studies, the cell used was a conventional three electrodes Pyrex glass with a platinum counter electrode and a standard calomel electrode (SCE) as reference. The working electrode was embedded in Teflon so that its cross-sectional area (1 cm²) was in contact with the solution. The electrochemical impedance experiments were carried out using AC signals of amplitude 5mV peak to peak at the open circuit potential (OCP) in the frequency range 100 kHz to 100mHz after 30 min immersion in the electrolyte cell. The impedance experiments were carried out with a Potentiostat/Galvanostat 263A (EG&G) Princeton Applied Research HF response model 1025. Pseudo-Polarization curves were recorded with scanning rate of 1 mV/s, after 30 min immersion from -700 to 0 mV vs. SCE at room temperature.

Scanning electron microscopy

The surface microstructure of specimens after 1 hour of immersion in various

concentration of H_3PO_4 (1M, 2M, 3M) with and without addition of different concentration of inhibitor (150 ppm) was studied by using SEM Model LEO 1030.

RESULTS AND DISCUSSION

Weight loss

The inhibition efficiency of inhibitor ($\eta_w\%$) in various concentration of acid (H_3PO_4) was calculated as follows¹⁵.

$$\eta_w \% = \frac{\Delta W_0 - \Delta W}{\Delta W_0} \times 100 \quad (1)$$

Where ΔW_0 and ΔW are the weight losses per unit area per time in the absence and presence of the inhibitor, respectively. The obtained data are summarized in table 1.

Table 1. Inhibitor efficiencies obtained from weight loss measurement.

Inhibition efficiency (% η)			Inh.conc. (ppm)
3M H_3PO_4	2M H_3PO_4	1M H_3PO_4	
95.30	95.86	96.50	50
96.50	97.50	97.88	100
98.00	98.91	98.83	150
97.50	98.93	98.98	200

Table 1 shows the variation of inhibition efficiency percent (h%) with concentration of H_3PO_4 in presence and absence of various concentration of inhibitor. As seen , the inhibition efficiency increase with increasing inhibitor concentration to 150 ppm , in all

Concentration of acid and the maximum (h%) was approximately 98.9%.

Potentiodynamic polarization

fig 1 shows the polarization curves obtained for mild steel in various concentration of H_3PO_4 without inhibitor that indicated increasing mild steel corrosion by increasing acid concentration and fig2 shows polarization curves in 2M H_3PO_4 without and with different concentration of inhibitor. It is clearly seen that this inhibitor shifted both the anodic and cathodic branches of polarization curves of the pure acid solution to lower values of current density indicating the inhibition of the both hydrogen evolution (HER) and mild steel dissolution reactions.

Fig 1. polarization curves in different concentration of H_3PO_4 Fig 2. polarization curves in 2M H_3PO_4 in absence and presence of various concentration of inhibitor.

Table 2 gives the obtained parameters from polarization curves. The inhibition efficiency (h%) of inhibitor was calculated by the follow equation¹⁶.

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

Table 2. polarization parameter values.

% η	I_{corr} $\mu A/cm^2$	E_{corr} vs SCE/mv	Inh.conc/ ppm	H_3PO_4 conc.
-	430.500	-527.0	0	1M
99.20	3.439	-480.6	150	
-	567.900	-525.3	0	2M
96.1	22.140	-492.3	50	
98.0	11.358	-484.3	100	
99.3	3.975	-486.9	150	
99.0	5.679	-487.3	200	
-	1103.000	-517.0	0	3M
99.1	9.927	-474.5	150	

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

Electrochemical impedance spectroscopy

Fig 3a shows the Nyquist plots of mild steel in 2M H_3PO_4 without and with various concentration of inhibitor.

Fig 3. Nyquist plots.

a: in absence and presence of various concentration of inhibitor in 2M H_3PO_4 .

b: in various concentration of H_3PO_4 and optimum concentration of inhibitor.

The charge transfer resistance (R_{ct}) values are calculated from the difference in impedance at lower and higher frequencies¹⁵. The double layer capacitance (C_{dl}) was obtained from the follows equation¹⁷.

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

f is the frequency at the apex of the semicircle in the Nyquist plot. Fig.3b shows the Nyquist plots of mild steel in different concentration of H_3PO_4 with optimum concentration of inhibitor, it was found that by increasing the concentration of H_3PO_4 , the mild steel corrosion was constant. The inhibition efficiency percent (h%) of inhibitor is calculated by the follow equation¹⁸.

$$h\% = \frac{R_e - R_{0e}}{R_e} \times 100 \quad (3)$$

Where R_{ct} and R_{det} are the charge transfer resistance values with and without inhibitor, respectively. The impedance parameters derived from Nyquist plots are summarized in table 3.

Table 3. obtained parameters from the Nyquist plots.

% η	$C_{dl}/\mu Fcm^{-2}$	$R_{ct}/\Omega cm^2$	Inh.conc/ ppm	H ₃ PO ₄ conc.
-	365.80	12.9	0	2M
91.62	78.12	154.1	50	
97.75	61.40	575.6	100	
98.70	57.27	995.2	150	
98.40	73.25	811.0	200	
-	270.30	35.5	0	1M
97.67	55.91	1524.2	150	
-	388.90	8.6	0	3M
98.66	64.45	643.1	150	

From the Nyquist parameter values it was found, that increasing H₃PO₄ concentration increases the mild steel corrosion respectively, and by increasing the inhibitor concentration increase R_{ct} and decrease C_{dl} values. It is due to the adsorption of inhibitor on the metal surfaces and leads to protective film formation¹⁹.

So it was found, that increasing concentration of H₃PO₄ did not affect on the inhibition efficiency of inhibitor, however, the optimum inhibitor concentration remained 150 ppm for various concentration of H₃PO₄. This result was similar to the results observed from weight loss and potentiodynamic polarization methods.

Scanning electron microscopy

Micro structural studies of mild steel in various concentration of H₃PO₄ in absence and presence of optimum concentration of inhibitor were performed and were illustrated in fig.4.

Fig 4. Surface features of mild steel exposed to various concentration of H₃PO₄ in absence and presence of optimum conc. of inhibitor.

It is clear that the corrosion attack was more pronounced in absence of the studied inhibitor, while the film formed on the metal surface becomes more protective, where the specimen surface is nearly intact as even the original polishing scratches are seen exposure.

Adsorption isotherm

The performance of the studied inhibitor (2- phenyl-1-hydrazine carboxamide) as a corrosion inhibitor may be attributed to the presence of electron donor groups (N,O and aromatic ring) in the molecular structure of inhibitor, which favors the greater adsorption of it on the metal surface²⁰.

The unshared and **p** electrons interact with d-orbital of steel to provide a protective film²¹. To quantify the effect of inhibitor concentration on the corrosion rate, it is a common practice to fit the rate data to equilibrium adsorption expressions, such as the Langmuir equation²².

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (4)$$

Where θ is the fraction surfaces coverage by the inhibitor and K_{ads} is the equilibrium constant for the adsorption reaction:

$$\theta = \frac{\eta\%}{100} \quad (5)$$

The use of the Langmuir treatment is often justified with the argument that inhibition must involve adsorption. In this study, $C_{inh} \theta^{-1}$ is plotted against C_{inh} , a linear relationship is obtained for each media indicating the Langmuir behavior (fig.5).

Fig.5. Langmuir plots for inhibitor on mild steel in various concentration of H₃PO₄

CONCLUSIONS

2-phenyl-1-hydrazine carboxamide was a good inhibitor for mild steel in H₃PO₄ media.

This inhibitor acted as mixed inhibitor and maximum efficiency (98%) attains an optimum value at 150 ppm in H₃PO₄, and the acid concentration did not affect on the optimum efficiency of inhibitor.

The obtained results from different methods (EIS weight loss and polarization) were in good agreement.

The adsorption of inhibitor was consistent with a Langmuir isotherm model.

Micro structural studies elucidated a protective film on the metal surface in presence of inhibitor.

REFERENCES

- 1.- E. Khamis, M.A. Ameer, N.M. Alandis, and C. Al-Senai, Corrosion. Vol **56**, NO.2, 127, (2000).
- 2.- Lin. Wang, Corrosion Science. **48**, 608, (2006).
- 3.- Y. Jianguo, W. Lin, V. Oteno-Alego, D. P. Schweinsberg, Corrosion Sci. **37**, 6, 973, (1995).
- 4.- S. J. Zakavi, C. N. Mehta, J. Electrochem. Soc. India, **37**, 237, (1988).
- 5.- A. S. Fouda, H. A. Mostafa, Y. M. Darwish, M. N. Moussa, Bull. Soc. Chim, **2**, 261, (1987).
- 6.- S. Hettiarachchi, Y. M. Chan, R. B. Wilson, V. S. Agarwalu, Corrosion **45**, 30, (1989).
- 7.- B. Mernari, H. Elattari M. Traisnel, F. Bentis, M. Lagrence, Corros. Sci. **40**, 391, (1998).
- 8.- C. Varalakshmi, B. V. Appa Rao, Anti-Corros. Methods & Mater. **48**, 3, 171, (2001).
- 9.- M. A. Quraish, D. Jamal, Mater. Chem. Phys, **68**(1-3), 283, (2001).
- 10.- S. El Hajjaji, A. Lgamri, D. Aziane, A. Cuenbour, E. M. Essassi, M. Akssira, A. Ben Bachir, Prog. Org. Coat, **38**(3-4), 207, (2000).
- 11.- F. Bentiss, M. Lagrenee, M. Trasinel, B. Mernari, H. Elattari, J. Appl. Electrochem, **29**(9), 1073, (1999).
- 12.- M. Ei Achouri, S. Kertit, M. Salem, B. M. Essassi, M. Jellal, Bull. Electrochem, **14**(12), 462, (1998).
- 13.- A. M. S. Abdennabi, A.I. Abdulhadi, S.T. Abu-oradi, H. Saricimen, Corros. Sci, **38**, 1791, (1996).
- 14.- ASTM, Standard Practice for Laboratory Immersion Corrosion Testing of Metals, G31-72, 401, 1990.
- 15.- T. Tsuru, S. Hunuyama, C. Boshoku, J. Japan Soc. Corros. Engg, **27**, 573, (1987).
- 16.- M. Hosseini, S. F. L. Mertens, M. C. Chorbani, M. R. Arshadi, Materials Chemistry and Physics, **96**, 47, (2002).
- 17.- F. Bentiss, M. Traisnel, M. Lagrence, Corros. Sci, **42**, 127, (2000).
- 18.- Z-Quan, S. Chem, Y. Li, X. cui, Corros. Sci, **44**, 703, (2002).
- 19.- L. Elkadi, Me. Mari, B.M.F. Traisnel, Bentiss, M. Lagrence, Corros. Sci, **42**, 703, (2000).
- 20.- S. Kertit, B. Hummouti, Applied Surface Science, **93**, 59, (1996).
- 21.- S. Kertit, K. Bekkouch, B. Hamouti Metallurgie- Cit, **251**, (1998).
- 22.- M. Abdullah, Corrosion Science, **44**, 717, (2002).