http://www.e-journals.net

ISSN: 0973-4945; CODEN ECJHAO
E-Journal of Chemistry
2010, **7(2),** 331-340

Synthesis, Characterization and Corrosion Protective Efficiency of 2[2-Oxo-phenyl hydrazinyl ethyl] benzamide on Mild Steel in Sulphuric Acid Medium

RINKI GOEL[§*], WEQAR A. SIDDIQI[§],
V.M. CHAUBEY[§] and BAHAR AHMED

[§]Department of Applied Science & Humanities,
Faculty of Engineering and Technology,
Jamia Millia Islamia, New Delhi – 110025, India.

Department of Pharmaceutical Chemistry,
Faculty of Pharmacy, Jamia Hamdard, New Delhi – 110025, India.

rinkigoel_jmi@yahoo.com

Received 25 May 2009; Accepted 15 July 2009

Abstract: 2[2-Oxo-phenyl hydrazinyl ether] benzamide (2BA) was synthesized, characterized and tested effective for corrosion inhibition of mild steel in 1 N H_2SO_4 solution using galvanodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. Polarization resistances calculated from the EIS measurements are in good agreement with those obtained from alternating current (AC) polarization measurements. The mild steel samples were also analyzed by Scanning Electron Microscopy (SEM). The result showed that 2BA is an excellent inhibitor for mild steel in acid medium. The inhibition was assumed to occur *via* adsorption of the inhibitor molecule on the metal surface. In the 303-323K temperature range, the 2BA adsorption follows Langmuir isotherm model. The protection efficiency increases with increasing the inhibitor concentration in the range of 250-1000 ppm but slightly decreases with increasing temperature.

Keywords: Mild steel, Corrosion inhibitors, Acid medium, Electrochemical impedance spectroscopy.

Introduction

It is generally assumed that corrosion inhibition performed by chemical compound added to the electrolyte is to be attributed almost as a first stage, to the adsorption of the additives (ions or neutral polar molecules) to the metal/solution interface. The nature and the surface charge of the metal, the type of corrosion media and molecular structure of the inhibitor

influence its adsorption in acid corrosion. The inhibitor adsorption may determine a structural change of the double layer, thus it reduces the rate of the electrochemical partial reaction, the anodic metal dissolution and the cathodic hydrogen ions reduction. The theoretical consideration of a correlation between the molecules structure of organic compounds and their ability to adsorb on the metal surface and hence to inhibit the corrosion process is aimed at in a series of the studies[1-3].

The action of such inhibitors is a specific interaction between certain functionalities and the metal surface. Hetero atoms such as nitrogen, oxygen and sulphur, play a crucial role therein owing to their free electron pairs[4-5]. Compounds with π bonds also generally exhibit good inhibitive properties, the electrons for the surface interaction being provided by the π-orbital. Both features obviously can be combined within the same molecule, which may then give rise to particularly potent inhibitors. Schiff bases-the condensation product of an amine and a ketone or aldehyde and with $R_2C=NR'$ as general formula are known example of this category and have been investigated for the inhibition of acid corrosion of mild steel[6-7] aluminum[8] and copper[9] and of neutral halide corrosion of copper[10-12]. The explanation lies in the presence of unoccupied π^*-orbital in the Schiff base molecule, which enable electron back donation from the transition metal *d*-orbitals and stabilize the existing metal inhibitor bond[6-7]. The aim of this work is to investigate the role played by newly synthesized 2[2-oxo-2phenyl hydrazinyl ethyl] benzamide on the corrosion behavior on mild steel in 1 N H_2SO_4. In view of this, 2[2-oxo-2phenyl hydrazinyl ethyl] benzamide (2BA) was synthesized and characterized using IR and NMR analysis techniques. The inhibitive action of 2BA on the corrosion behavior of mild steel in 1 N H_2SO_4 solution at three levels of concentration and at three different temperatures was measured. Corrosion inhibition was investigated using electrochemical technique (Polarization and EIS) and weight loss measurements.

Experimental

2[2-Oxo-2-phenyl hydrazinyl ethyl] benzamide was synthesized in the laboratory using well established methods and characterized by spectral analysis method. The IR spectra (in KBr pellets) were recorded on a Nicolet-Protege 460 spectrometer. ^{1}H NMR spectra were recorded on a 300 MHzDPX300 spectrometer.

Synthesis

In the laboratory, 2[2-oxo-phenyl hyrazinyl ethyl] benzamide (2BA) was synthesized from ester of hippuric acid using the following procedure:

A mixture of 0.01(mol) ester of hippuric acid, 0.01 (mol) of phenyl hydrazine, 0.2 mL of glacial acetic acid and 25 mL of absolute ethanol was refluxed for 24 h. The crystalline product thus obtained was filtered, washed, dried and recrystalized in methanol. The yield of crystals was 83% and their melting point was 178-179 °C. The required intermediates were prepared using reported procedures[13]. Their purity was monitored by TLC and its structure was established by spectral measurements.

Specimens

Mild steel specimens (1 cm^3) having the chemical composition (wt) of C (0.21%), Si (0.36%), Mn (1.25%), P(0.025%), S (0.046%), Cr (0.16%), Ni (0.16%), Cu (0.41%), Mo (0.017%), Sn (0.017%), Al (0.003%) and Fe (Bal), were used.

Weight loss measurements

Weight loss measurements were carried out by weighing the mild steel specimens before and after immersion in 100 cm^3 acid solution for different time intervals in the absence and

presence of various concentrations of compound at different temperatures. The inhibition efficiency (%) of the inhibitor was calculated by Equation 1:

$$\%IE = \frac{W_o - W}{W_o} \times 100 \quad (1)$$

Where, W_o and W are weight losses without and with inhibitor.
The corrosion rate of mild steel was calculated using[10] Equation 2

$$\mu = \frac{3.45 \times 10^6 \, W}{ADT} \quad (2)$$

Where, W = weight loss (g), D = Density of mild steel specimen (g cm^{-3}), A = Area of the coupon (cm^2), T = exposure time (h).

Polarization measurements

A conventional three-electrode system consisting of mild steel as working electrode, platinum foil as counter electrode and saturated calomel as reference electrode, was used for the polarization measurement. The anodic and cathodic polarization values were measured under galvanostatic condition in the range of 0 to ± 200 μA.

The percentage inhibition efficiency (% IE) was calculated using the equation 3:

$$\%IE = \frac{I_{corr} - I°_{corr}}{I_{corr}} \times 100 \quad (3)$$

Where, $I°_{coor}$ and I_{corr} are the corrosion current densities in the absence and presence of inhibitor.

Electrochemical impedance spectroscopy studies (EIS)

Impedance spectroscopy measurements were carried out in the frequency, ranging from 42 Hz to 5 MHz using LCR HI- Tester (H10K1 3532-50).

SEM and FT-IR studies

The surface morphology of the steel samples was investigated after anodic polarization using SEM technique (JSM 840 Jeol). FT-IR spectra (in KBr pellets) were recorded on a nicolet protege 460 spectrophotometer.

Results and Discussion

Characterization of 2[2-Oxo phenyl hydrazinyl ether] benzamide

Ester of hippuric acid (4) on treatment with phenyl-hydrazine in ethanol containing trace of glacial acetic acid as catalyst, yielded 2[2-Oxo phenyl hydrazinyl ether] benzamide (**1**) **a** is glycin, NaOH, H_2O, 23 °C, **b** is ethanol, H_2SO_4, reflex 8 h and **c** is phenyl hydrazine reflex 24 h.

The characterization data of (1) are given below

IR KBr (cm^{-1}) γ max-3231(NH), 3005 (C=C, Ar), 2950(CH3, CH2), 1745(C=O), 1584, 1537(C=C), 1496(C-N), 1242, 1196(C-N), 763(C=C) $cm^{-1.}$ **^{1}H NMR** (300MHz,D_2O): δ 3.99 (2H, d, J=6.8H_2, CH_2), 4.40 (2H, d, J=6.8Hz, >CH_2), 6.90 (2H, d, J=9.0Hz Ar-H), 7.51 (5H, m, Ar-H), 7.92 (2H, d, J=9.0Hz, Ar-H), 8.44 (1H,s,>NH), 8.70(1H,s,>NH), 8.92 (1H,s, >NH).

Weight loss measurements

The values of percentage inhibition (%IE) and corrosion rate (μ_{corr}) obtained from weight loss method at different concentrations of inhibitor and at different temperatures are summarized in Table 1. It has been found that 2BA compound inhibits the corrosion of mild steel in 1 N H_2SO_4 solution at different concentrations used in this study *i.e.* 250, 500, 1000 ppm.

Table 1. Corrosion parameters obtained from weight loss measurements for various inhibitor concentrations at different temperatures in 1 N H_2SO_4.

Temp. K	Concentration, ppm	Weight loss, g	μ_{corr}, cm, h	IE, %
303	1.0 N H_2SO_4	0.2316	6.544	---
	250	0.0549	1.539	76.31
	500	0.0340	0.948	85.3
	1000	0.0180	0.506	92.2
313	1.0 N H_2SO_4	0.4798	16.62	---
	250	0.2245	7.831	53.22
	500	0.0844	2.933	82.41
	1000	0.0596	2.071	87.5
323	1.0 N H_2SO_4	0.6657	20.5	---
	250	0.4201	12.9	36.9
	500	0.1278	3.9	80.8
	1000	0.1051	3.2	84.21

It has also been observed from Figure 1 that the inhibition efficiency of the mild steel increases with the increase in concentration of 2BA compound. The variation of inhibition efficiency with solution temperatures for various inhibitor concentrations are shown in Figure 2.

It can be seen that inhibition efficiency obtained at different concentrations of inhibitor causes a significant decrease with an increase in temperature from 303 K to 323 K while inhibition efficiency of the inhibitor increases with increase in the concentration. This behavior could be attributed due to strong interaction of compound with the metal surface that results in the adsorption of inhibitor molecules[15-17]. The lone pair of electron on the nitrogen will coordinate with the metal atoms of active sites. The presence of higher electron density of carbonyl group in 2BA causes stronger interaction with metal surface. Functional graphs such as -NH-, -N=N- and -C=N-, having π bonds, are found in inhibitor which inhibit corrosion of metal by interaction with the electrode surface through electron sharing to increase adsorption and hence higher inhibition of corrosion[18-20].

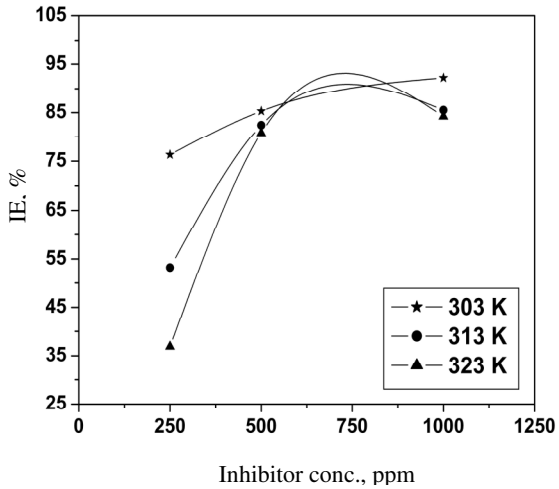

Figure 1. Variation of inhibition efficiency as a function of inhibitor concentration at different temperatures in 1 N H_2SO_4.

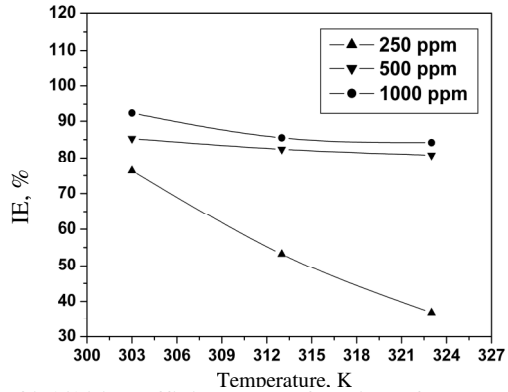

Figure 2. Variation of inhibition efficiency as a function of temperature for various inhibitor concentrations in 1 N H_2SO_4.

Polarization measurement

Anodic and cathodic potentiodyamic polarization curve of mild steel in 1 N H_2SO_4 at 303 K in the absence and presence of 2BA compound of various concentrations associated with electrochemical parameters and % inhibition efficiency (%IE) is shown in Figure 3.

Corrosion current density (I_{corr}), Corrosion potential (E_{corr}), Tafel slopes (β_a and β_c), surface coverage and %IE are given in Table 2. The result shows that I_{corr} values decrease with increase in the concentrations of inhibitors and least I_{corr} was obtained at 1000 ppm of the inhibitors. The value of tafel slope shows that the corrosion inhibition efficiency may be due to the control of hydrogen evolution reaction. From the polarization curves of 2BA, there is a simpler shift of both the anodic and cathodic curves towards lower current density region. The degree of surface coverage (θ) was determined using[21] the Equation 4:

$$\theta = 1 - \frac{I°_{corr}}{I_{corr}} \quad (4)$$

Where, $I°_{corr}$ and I_{corr} are the corrosion current densities in the absence and presence of inhibitor respectively.

The degree of coverage 'θ' was found to increase with increase in the concentration of additive and decrease with the increase in the temperature.

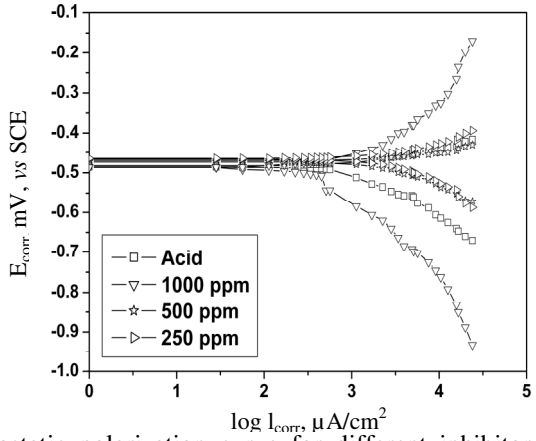

Figure 3. Galvanostatic polarization curve for different inhibitor concentrations in 1 N H_2SO_4 at 303 K.

Table 2. Corrosion parameters obtained from polarization measurements for various inhibitor concentrations at different temperatures in 1 N H_2SO_4.

Temp. K	Conc. ppm	E_{corr} mV	Log I_{corr} μA cm^{-2}	θ	β_a mV/dec	β_c mV/dec	IE, %
303	Blank	512	3.24	---	141	99	---
	250	482	2.75	0.763	160	92	76.31
	500	495	2.32	0.853	167	103	86.3
	1000	543	1.67	0.922	325	234	92.2
313	Blank	522	3.38	---	151	111	---
	250	482	2.93	0.5322	133	91	53.22
	500	495	2.48	0.824	100	85	82.4
	1000	525	2.03	0.895	457	163	89.5
323	Blank	500	3.45	---	73	75	---
	250	485	3.15	0.369	98	40	36.9
	500	482	2.73	0.808	159	81	80.8
	1000	480	2.1	0.864	432	168	86.4

Electrochemical impedance measurements

The experimental results of EIS measurements obtained for the corrosion of mild steel without and with inhibitor are summarized in Table 3. Figure 4 shows the complex impedance plots for mild steel in 1 N H_2SO_4 with and without various concentration of 2BA at 303 K.

Table 3. Impedance parameters obtained using electrochemical impedance method in 1 N H_2SO_4 at 303 K

Concentration, ppm	R_p Ω cm^2	Capacitance, C_{dl} μF cm^2	IE, %
1.0 N H_2SO_4	52.84	602.3	---
250	235	249	77.5
500	386	151.5	86.4
1000	788	74.2	93.3

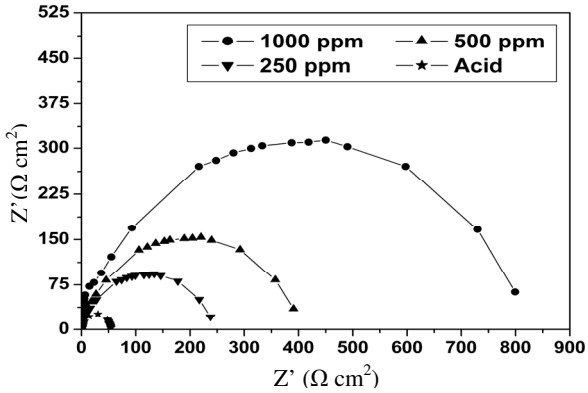

Figure 4. Nyquist plot for different inhibitor concentrations in 1 N H_2SO_4.

Thermodynamic parameters

In order to understand the mechanism of corrosion inhibition, the adsorption behavior of the organic adsorbate on the steel surface must be known. The degree of surface coverage (θ) for

different concentration of inhibitor has been evaluated from galvanodynamic polarization measurements. The data were tested graphically by fitting to various isotherms. A straight line was obtained on plotting log (θ/1-θ) against log C, suggesting that the adsorption of the compound on mild steel surface follows Langmuir adsorption isotherm model[22] (Figure 5).

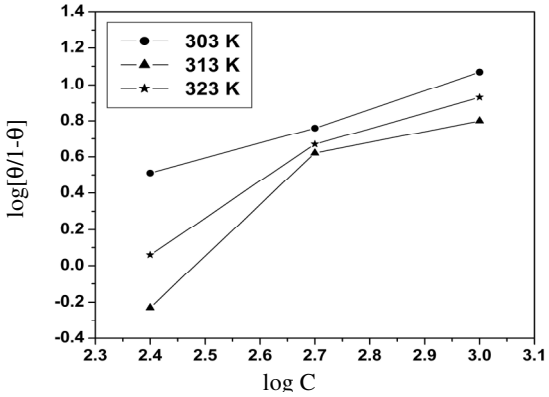

Figure 5. Langmuir adsorption isotherm at different temperatures in 1 N H_2SO_4.

Adsorption isotherm

The inhibition efficiency of 2BA compound is determined by their adorability on the surface of the corroding metal. Where mono layer adsorption occurs on the steel surface, the Langmuir adsorption isotherm[22] may be expressed by equation 5:

$$\frac{\theta}{1-\theta} = AC\exp\left(-\frac{\Delta H}{RT}\right) \quad (5)$$

Where T is temperature, A is independent constant, C is inhibitor concentration, R is gas constant, ΔH is heat of adsorption and θ is surface coverage by the inhibitor molecule. Figure 6 shows the Plot of log θ/(1- θ) *versus* (1/T) at different additive concentrations. The slope of the linear parts of curves is equal to - ΔH/2.303R from which the average heat of adsorption, ΔH were calculated at different concentration of inhibitor and are given in Table 4. The negative valves of ΔH reflect the exothermic behavior of 2BA compound on the metal surface.

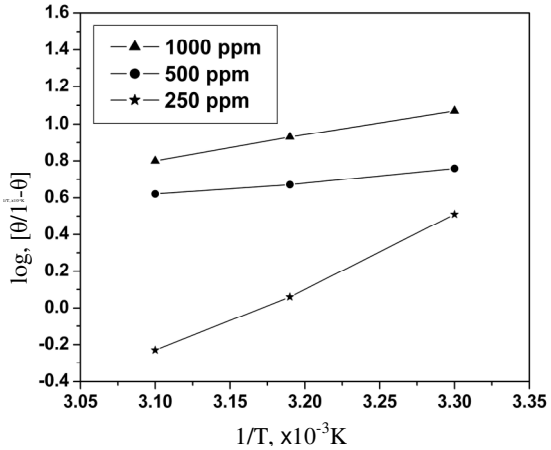

Figure 6. Arrehenius plots log (θ/ 1-θ) *vs.* 1/T in 1 N H_2SO_4 at various inhibitor concentrations.

Table 4. Activation parameters at various inhibitor concentrations in 1 N H_2SO_4.

Concentration, ppm	E_a kJ mol^{-1}	ΔH kJ mol^{-1}
1.0 N H_2SO_4	20.19	---
250	37.96	-71.1
500	38.72	-13.44
1000	41.86	-25.73

Activation energy

The activation energy of the corrosion process can be calculated using the Equation 7:

$$K = A\exp\left(-\frac{E_a}{RT}\right) \tag{7}$$

Where E_a is the activation energy, A is the frequency factor, T is the absolute temperature, R is the gas constant and K is the rate of metal dissolution reaction[16].

The values for the compound studied are listed in Table 4. This result agrees with the order of IE. The activation energy is higher in the presence of additives than in its absence. During the corrosion reaction mechanism, the charge transfer is blocked with adsorption of 2BA molecules to the metal surface, causing the increase in the activation energy[23-24]. The higher values of E_a are good evidence for the chemisorption mechanism of 2BA compound on the steel surface.

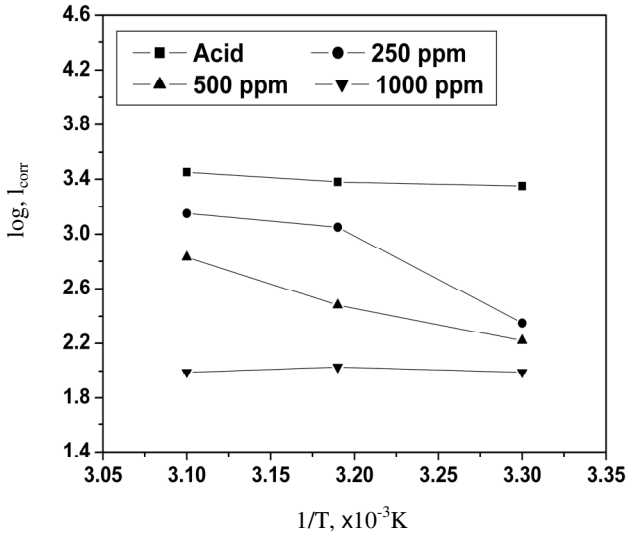

Figure 7. Variation of corrosion current with temperature in 1 N H_2SO_4.

Morphological investigation

Microstructural studies of mild steel in 1 N H_2SO_4 in absence and presence of a certain concentration of compound at 303K were performed and illustrated in the Figures. It is clear that the corrosion attack was more pronounced in the absence and presence of low inhibitor concentration (500 ppm) of the studied inhibitors at 303 K temperature (Figure 8a, 8b), while the film formed on the metal surface becomes more protective with increase of inhibitor concentration (1000 ppm) at 303K (Figure 8c).

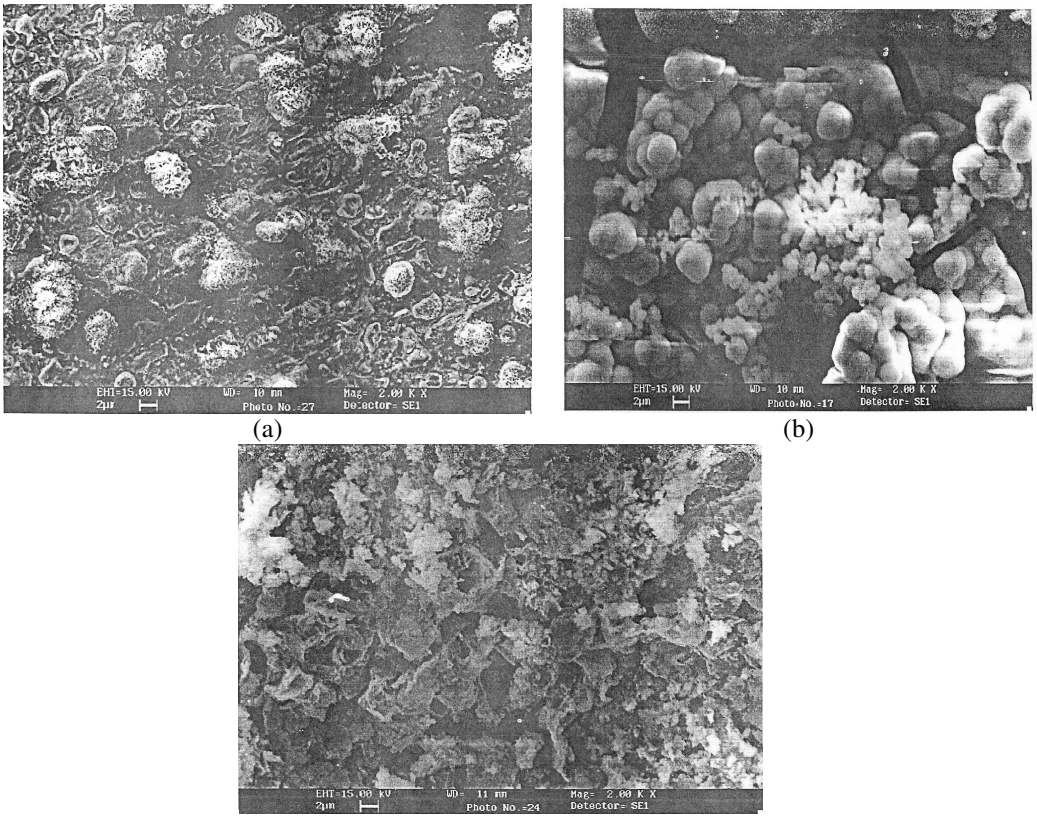

Figure 8 (a, b, c). SEM images (2000x) at different concentration of inhibitor in 1 N H_2SO_4.

This is attributed to the involvement of compounds in the interaction with the active sites of metal surface. This results in enhanced surface coverage of the metal so that there is a contact between metal and the aggressive medium.

IR Studies

The compound formed on the corroded steel specimens after polarization were scrapped, collected and subjected to FT-IR spectral studies. The involvement of NH group, C=C and C=O in interaction reaction with metal surface atom could be proved by the respective IR spectra. The shift in the adsorption peaks from NH (3231-3229) C=CAr (3005-3002) C=O (1745-1741) C=C (763-760) further the intensity of the peaks stretching frequency is decreased which implies that the shift peaks in this compound is coordinated to Fe^{+2} resulting in the formation of a Fe^{+2} inhibitor complex on the metal surface.

Conclusion

2BA compound inhibits the corrosion of mild steel in 1 N H_2SO_4. The inhibition efficiency increases by increasing the inhibitor concentration. Polarization measurement shows that the 2BA studied act as mixed type inhibitors. AC impedance plots of mild steel show that polarization resistance increases with increase in inhibitor concentration. The adsorption of 2BA molecules on the metal surface from 1 N H_2SO_4 solution obeys Langmuir adsorption

isotherm. The negative sign of ΔH_{ads} indicates that the adsorption process is spontaneous and exothermic. SEM examination of the electrode surface confirmed the existence of such adsorbed film.

Acknowledgment

One of the authors (Rinki Goel) is thankful to the Prof. Alimuddin and Mr. Khalid Mujasam Batoo Department of Applied Physics, A.M.U. Aligarh, India for providing necessary laboratory facilities to perform Impedance measurements.

References

1. Grigoriev B P and Ekilik B B Chemical Structure and Protective Action of Corrosion inhibitors, Rost Gos, Univ., Rostow, 1987.
2. Popova A, Christor M, Railheva S and Sokolova E, *Corros Sci*., 2004, **46**, 1333.
3. Abdennabi A M, Abdulhadi A I and Abu-orabi S, *Anti-Corros Method Mater*., 1998, **2**, 103.
4. Raichera S N, Aleksier V B and Sokolova I E, *Corros Sci.,* 1993, **34,** 343.
5. Hluchan V, Wheeler B L and Hackerman N, *Werkst,* K*orros*., 1998, **39**, 512.
6. Emregul K C and Atakol O, *Mater Chem Phys.,* 2003, **82**, 188.
7. Shokry H, Yuasa M, Sekine I, Issa R M, EI-Baradie H Y and Gomma G K, *Corros Sci.,* 1998, **40**, 2173.
8. Gomma G K and Wahdan M H, *Mater Chem Phys*., 1995, **39**, 209.
9. Li S, Chen S, Lei S, Ma H, Yu R and Liu D, *Corros Sci*., 1999, **41**, 1273.
10. Li S L, Wang Y G, Chen S H, Yu R, Lei S B, Ma H Y and Liu D X, *Corros Sci.,* 1999, **41**, 1769.
11. Ma H, Chen S, Niu L, Shang S, Li S, Zhao S and Qvan Z, *J Electrochem Soc.,* 2001, **148 B,** 208.
12. Quan Z, Chen S, Li Y and Cui X, *Corros Sci*., 2002, **44**, 703.
13. Gilbert A M, Kirisits M, Toy P, Nunn D S, Failli A, Dushin E G, Novikova E, Peterson P J, Mccarthy D J, Mcfadyen I and Fritz C C, *Bioorg Med Chem Lett.,* 2004, **14,** 37.
14. Olivares O, Likhanova N V, Gomez B, Navarrete J, Llanos Serrano M E, Arce E and Hallen J M, *Appl Surf Sci*., 2006, **252**, 2894
15. Chaudhary R S and Sharma S, *Indian J Chem Technol.,* 1999, **6**, 202.
16. Abdallah M, *Corros Sci*., 2002, **44,** 717.
17. Fan H B, Wang H L, Guo X P and Zheng F S, *Anti-Corros Method Mater*., 2002, **49**, 270.
18. Achary G, Sachin H P, Naik Y and Venkatesha T V, *Mater Chem Phys.,* 2008, **107**, 44.
19. Ozen M, Dehri J and Erbil M, *Appl Surf Sci*., 2004, **236**, 155.
20. Xuehui P, Baorong H, Weihua L, Faqian L and Zhigang Y, *Chin J Chem Eng.,* 2007, **15**, 909.
21. Larabi L, Harek Y, Benali O and Ghalem S, *Prog Org Coat.*, 2005, **54,** 256.
22. Saliyan V R and Adhikari A V, *Corros Sci.,* 2008, **50**, 51.
23. Osman M M, El-Ghazawy R A and Al. Sabagh A M, *Mater Chem Phys.,* 2003, **80**, 55.
24. Ameer M A, Khamis E and Al-Senani G, *J Appl Electrochem.,* 2002, **32,** 149.