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Performance Of Benzotriazole As Corrosion Inhibitors Of Carbon Steel In Chloride Solution Containing Hydrogen Sulfide

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ABSTRACT: *Corrosion and inhibition studies on API 5LX65 carbon steel in chloride solution containing various concentrations of benzotriazole has been conducted at temperature of 70°C using Electrochemical Impedance Spectroscopy (EIS). Corroded carbon steel surface with and without inhibitor have been observed using X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Energy Dispersive Spectroscopy (EDS). The objectives of this research are to study the performance of benzotriazole as corrosion inhibitors. The experimental results of carbon steel corrosion in 3.5% NaCl solution containing 500 mg/l H_2S at different BTAH concentrations showed that corrosion rate of carbon steel decreases with increasing of BTAH concentrations from 0 to 10 mmol/l. The inhibition efficiency of BTAH was found to be affected by its concentration. The optimum efficiency obtained of BTAH is 93% at concentration of 5 mmol/l. The result of XRD and EDS analysis reveal the iron sulfide (FeS) formation on corroded carbon steel surface without inhibitor. The EDS spectrum show the Nitrogen (N) bond on carbon steel surface inhibited by BTAH.*

Key words: *corrosion rate, hydrogen sulfide, carbon steel API 5LX65, benzotriazoIe, Electrochemical Impedance Spectroscopy.*

I INTRODUCTION

The damages by corrosion generate not only high costs for inspection, repairing and replacement, but in addition these constitute a public risk, thus the necessity of developing novel substances that behave like corrosion inhibitors [1]. In general, the organic compounds have demonstrated a great effectiveness in inhibiting the aqueous corrosion of many metals and alloys [2,3]. At the present time, these compounds are the frequently used inhibitors and they are generally considered because of their good effectiveness. The effect of inhibitors adsorbed on metallic surfaces in acid solutions, is to slow down the cathodic reaction as well as the anodic process of dissolution of the metal. Such effect is obtained by forming a barrier of diffusion or by means of the blockage of the reaction sites [4].The molecules that, at the same time, contain nitrogen and sulfur in their structures are of particular importance, since these provide an excellent inhibition compared with the compounds that contain only sulfur or nitrogen [5].The property of inhibition of the corrosion of these compounds is attributed to their molecular structure.

The aim of this work is to investigate the performance of benzotriazole as corrosion inhibitors of carbon steel in cloride solution containing hydrogen sulfide. The chemical compound tested was benzotriazole (BTAH) such as figure 1, a well known inhibitor for copper and stainless steels [6]. Although BTAH has been largely studied as a corrosion inhibitor for stainless steels or steels in acid environments [7] its effect on the corrosion resistance of carbon steels in cloride solution containing hydrogen sulfide has not been investigated. Interacting the corrosion of steel in NaCl 3,5% + 500 mg/l H_2S medium at temperature of 70°C employed Electrochemical Impedance Spectroscopy (EIS) and weight loss methods. The thermodynamic parameters for both dissolution and adsorption processes were calculated using Nyquist curve and analyzed by Software Echem Analyst and discussed.

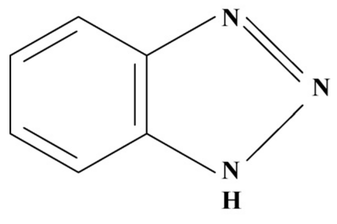

Figure 1. Chemical structure of benzotriazole (BTAH)

II EXPERIMENTAL

Test specimen are made of API 5LX65 carbon steel plate (composition is depicted on Table 1) and used as working electrode. All the specimens are cold mounted with epoxy resin, leaving one face (1.2 cm^2 area) exposed to the electrolyte. The exposed surface of each specimen is ground using silicon carbide paper up to 1000 grit, then washed in distilled water and finally rinsed by alcohol before application. The electrolyte solution is composed of 3.5% NaCl + 500 ppm H_2S and acetic acid as pH 4 buffer. To study the effect of benzotriazole concentration on carbon steel corrosion rate, various concentration of benzotriazole (BTAH) is added into the electrolyte solution.

Experiments are conducted in potentiostatic mode at various concentration of BTAH (0, 0,1, 1,0 and 5,0 mmol/liter) using a three-electrode electrochemical cell. The counter electrode is a large piece of silver (surface area more than 4 cm^2) and reference electrode is an Ag/AgCl. All potentials in this work are referred to Ag/AgCl. The EIS tests are carried out in triplicate to evaluate the tests reproducibility.

Table 1. Chemical Composition of API5LX65 carbon steel

Component	Weight %
C	0.09
Mn	1.6
P	0.015
S	0.005
Si	0.4
Nb	0.055
Ti	0.02
V	0.05
Ni	0.25
Cr	0.4
Fe	balance

EIS characterizations are conducted under these following conditions: 10 mV in amplitude, 100 kHz to 10 mHz in frequency range, 50 rpm in rotation rate, after 3 hours immersion of the carbon steel electrode in the test solutions. All experiments were performed using a potentiostatic EIS 600 frequency response analyzer and Reference-600 potentiostat model (Gamry). All data were analyzed using Gamry Echem Analyst software. The corrosion morphology of API 5LX65 carbon steel after EIS measurement in 3.5% NaCl + 500 ppm H_2S solution with and without BTAH using a rotating speed of 250 rpm at pH 4 and temperature of 70^oC was characterized by scanning electron microscope (SEM). Chemical composition of API 5LX65 carbon steel corrosion product is analyzed by energy dispersive spectroscopy (EDS) and X-ray diffraction spectrometry (XRD).

III RESULTS AND DISCUSSION

Effect of BTAH concentration

The corrosion behavior of API 5LX65 carbon steel, in 3.5% NaCl + 500 ppm H_2S and acetic acid as pH 4 buffer in the absence and the presence of various concentrations of BTAH were investigated by the EIS method at 70^oC after immersion period for 3 hours. The locus of the Nyquist plots was regarded as one part of a semicircle. The Nyquist plots of carbon steel in inhibited and uninhibited 3.5% NaCl + 500 ppm H_2S and acetic acid solutions containing various concentrations of BTAH are shown in figure 2. The figure 2 shows the curve widening semicircle imaginary impedance against the real impedance BTAH due to higher concentration in the solution. In addition BTAH concentrations 1.0 and 5.0 mmol/l appears to be happening widening spectrum Nyquist curve and there are inductive loop. It shows no adsorption of organic molecules BTAH as early formation of protective film [8].

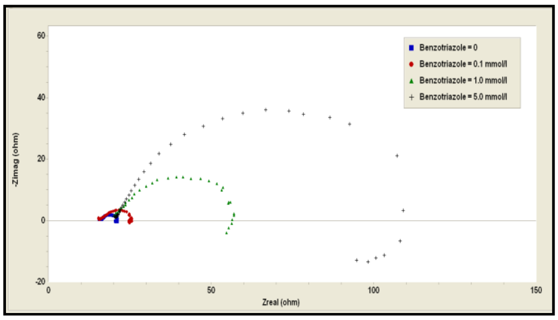

Figure 2. Nyquist curves for API 5LX65 carbon steel in 3.5% NaCl + 500 ppm H_2S and acetic acid containing various concentrations of BTAH

The electrochemical parameters determined from the Nyquist curve are given in Table 1. It appears that the value of polarization resistance (Rp) increases with increasing concentration of BTAH, while the relative value of Rs look no major changes. Increased value of Rp indicates that the steel surface protective layer is formed due to the

addition of BTAH the solution. It is powered by the C_{dl} value decreases with increasing concentrations of BTAH. As a result, the corrosion current density (i_{cor}) and the corrosion rate (CR) decreased with increasing concentrations of BTAH.

The effect of BTAH concentration to inhibit corrosion of carbon steel in chloride containing dissolved H_2S has also been studied using the open-circuit potential (OCP). Figure 3 shows the curve of corrosion potential versus time for API 5LX65 carbon steel were immersed in a solution of 3.5% NaCl + 500 mg/l for 3 hours with various concentrations of BTAH at pH 4, rotating rate 250 rpm and temperaur 70 ^{o}C. It is seen that the corrosion potential of carbon steel in solution without addition of BTAH stable at -516 mV vs Ag/AgCl). While the addition of BTAH 0.1 mmol/l, corrosion potential stabilized at -520 mV vs Ag/AgCl; addition of 1.0 mmol/l BTAH, corrosion potential stabilized at -503 mV vs Ag / AgCl, and the addition of 5,0 mmol/l BTAH, corrosion potential stabilized at -478 mV vs Ag / AgCl. The changes in corrosion potential with time can provide information on the interaction between BTAH which is an organic compound with the electrode surface after the addition. On the addition of 1.0 and 5.0 mmol/l BTAH seem corrosion potential change toward a more positive direction. This suggests that the addition of 5.0 mmol/l BTAH can increase the BTAH adsorption on the electrode surface[9]

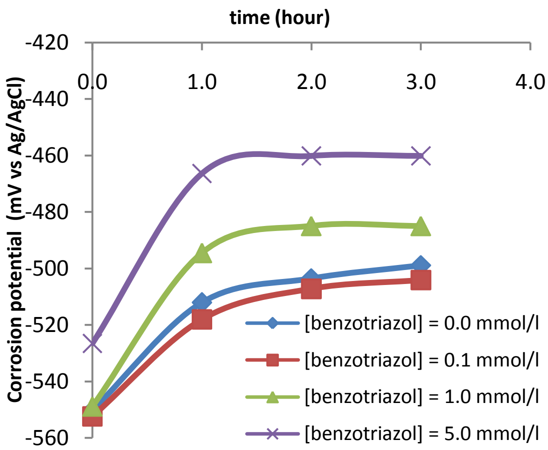

Figure 3. Open-circuit potential vs time of API 5LX65 carbon steel in 3.5% NaCl + 500 ppm H_2S and acetic acid containing various concentrations of BTAH

Table 1. Electrochemical parameters of EIS measurements on API 5LX65 carbon steel in 3.5% NaCl + 500 mg /l H_2S with variations BTAH concentration at pH 4, temperature 70 ° C, and rotation rate of 250 rpm

[Benzotriazol] (mmol/l)	R_s (ohm)	R_p (ohm)	C_{dl} (Farad) x 10^{-6}	i_{cor} (µA/cm^2)	CR (mm/th)	IE (%)
0	21,15	6,12	945,30	136,52	1,58	-
0,1	19,44	10,26	769,40	86,41	1,00	41
1	23,48	41,39	292,30	21,42	0,25	84
5	24,99	98,28	156,20	9,02	0,10	93

Inhibition efficiency of BTAH

The inhibition efficiency of BTAH for API 5LX65 carbon steel was calculated by using the following equation [10] :

$$IE\ (\%) = \frac{R_p - R_p^o}{R_p}\ x\ 100$$

Where R_p and R_p^o is polarization resistance value without and with inhibitor, respectively. The value of inhibition efficiency of BTAH for API 5LX65 carbon steel from this investigation are given in Table 1. It is clear that inhibition efficiency increased with increasing inhibitor concentrations. The corrosion inhibition was caused by the adsorption of inhibitor on the metal surface in 3.5% NaCl + 500 mg /l H_2S. The optimum efficiency obtained of BTAH is 93% at concentration of 5 mmol/l. The effectiveness of a compound as corrosion inhibitor mainly depends on the structure of the organic compounds. Inhibition efficiency is observed to increase with BTAH concentration, whereas at lower BTAH concentration activation effect is noticed. This may be attributed to the observation that at lower concentrations inhibitor is chemically adsorbed on the electrode surface, while at higher concentrations multilayer film is formed [11].

IV Analysis of Corrosion Product and Surface Morphology

Phase analysis by X-ray diffraction is shown in Figure 4a. It indicates that the compound formed on the surface of carbon steel after 3 hours immersed in NaCl solution containing H_2S under condition of pH 4, temperature 70°C and rotating speed of 250 rpm without inhibitors, especially iron sulfide (FeS). In addition, from the XRD results in Figure 4b for the addition of 5.0 mmol / l BTAH, FeS was formed on the surface of carbon steel specimens although the intensity is lower compared with the condition without inhibitor. XRD results of the determination of this seems consistent with the results obtained by EDS spectra show that the surface of the specimen plus 5 mmol / l BTAH formed oxides and little nitrogen bonds are formed as shown in the results of EDS in Figure 5b. The content of nitrogen (N) on the surface of carbon steel diambah 5.0 mmol / l for BTAH at 4.56 to 6.33%. This means that there BTAH performance as corrosion inhibitor of carbon steel in chloride solution containing hydrogen sulfide.To determine the morphology of carbon steel corrosion products after experiencing corrosion surface with SEM observations. The results of SEM image in Figure 5b shows that the results of the corrosion of iron sulfide layers (FeS) is formed on the surface of carbon steel specimens, whereas in Figure 5c with the addition of 5.0 mmol / l seems there is a cobweb structure on the surface of carbon steel which indicates that there bond between BTAH with the steel surface.

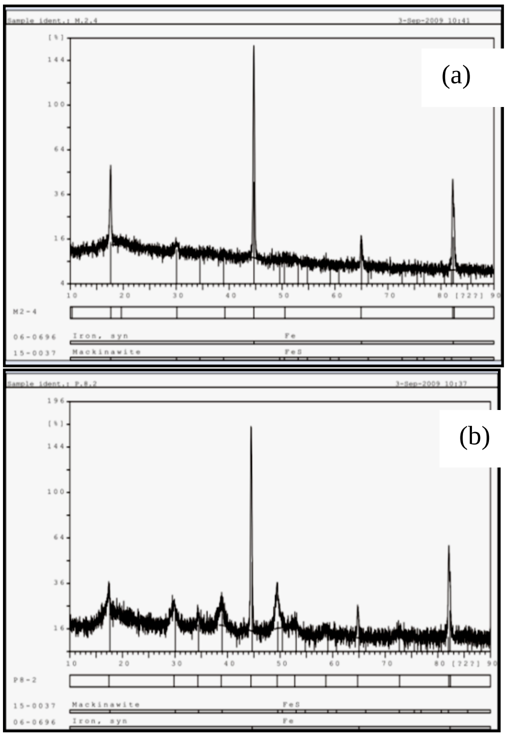

Figure 4. X-Ray diffraction for : (a) polished API 5LX65 carbon steel, (b) API 5LX65 carbon steel in 3.5% NaCl + 500 mg/l H_2S + 5,0 mmol/l BTAH at pH 4, temperature 70 ^oC

V CONCLUSION

The experimental results of carbon steel corrosion in 3.5% NaCl solution containing 500 mg/l H_2S at different BTAH concentrations showed that corrosion rate of carbon steel decreases with increasing of BTAH concentrations from 0 to 10 mmol/l. The inhibition efficiency of BTAH was found to be affected by its concentration. The optimum efficiency obtained of BTAH is 93% at concentration of 5 mmol/l. The result of XRD and EDS analysis reveal the iron sulfide (FeS) formation on corroded carbon steel surface without inhibitor. The EDS spectrum show the Nitrogen (N) bond on carbon steel surface inhibited by BTAH.

VI ACKNOWLEDGMENTS

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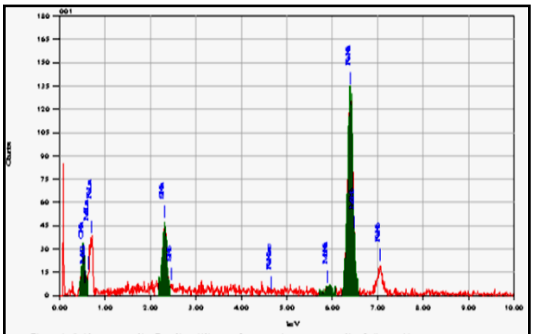
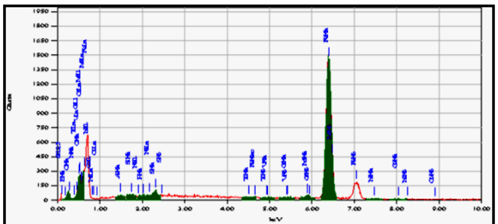


Element	(keV)	mass%	Error%	At%	Compound		mass%	Cation	K
O		26.57							
S K	2.307	4.56	0.32	10.34	SO3	11.39	2.06	6.0448	
Mn K	5.894	1.44	0.56	1.91	MnO	1.86	0.38	1.9274	
Fe K	6.398	67.43	0.58	87.75	FeO	86.74	17.45	92.0279	
Total		100.00		100.00		100.00	19.89		

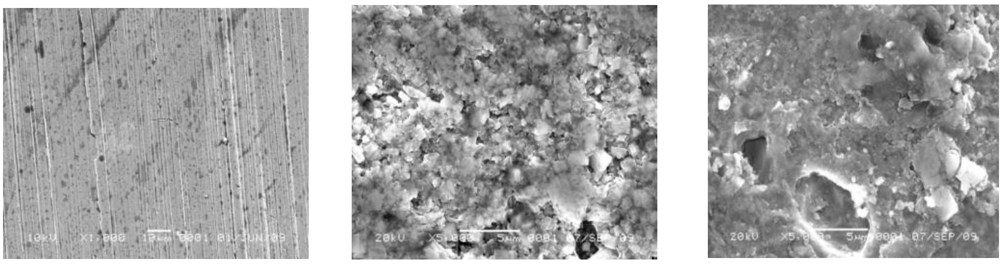
(a)



Element		(keV)	mass%	Error%	At%	Compound		mass%	Cation	K
B K	*									
C K	*	0.277	1.20	0.05	5.80	C	1.20	0.00	0.3402	
N K	*	0.392	4.55	0.10	18.76	N	4.55	0.00	11.0491	
O			21.72							
Al K	*	1.486	0.19	0.11	0.21	Al2O3	0.37	0.13	0.1082	
Si K	*	1.739	0.09	0.09	0.18	SiO2	0.19	0.06	0.0668	
P K	*	2.013	0.07	0.10	0.07	P2O5	0.16	0.04	0.0766	
S K	*	2.307	0.53	0.09	0.95	SO3	1.32	0.29	0.6179	
Ti K	*									
V K	*	4.949	0.09	0.14	0.05	V2O5	0.16	0.03	0.1203	
Cr K	*	5.411	0.06	0.12	0.04	Cr2O3	0.09	0.02	0.0933	
Mn K		5.894	0.86	0.15	0.90	MnO	1.11	0.28	1.0286	
Fe K		6.398	69.87	0.16	72.32	FeO	89.88	22.12	85.6505	
Ni K	*	7.471	0.31	0.27	0.30	NiO	0.39	0.09	0.3423	
Cu K	*	8.040	0.47	0.34	0.42	CuO	0.58	0.13	0.5062	
Nb L	*									
Total			100.00		100.00		100.00	23.18		

(b)

Figure 5. Energy-Dispersive X-Ray Spectroscopy (EDS) for : (a) polished API 5LX65 carbon steel, (b) API 5LX65 carbon steel in 3.5% NaCl + 500 mg/l H_2S + 5,0 mmol/l BTAH at pH 4, temperature 70 ^oC



(a) (b) (c)

Figure 6. Scanning electron microscope micrograph (X5000) for : (a) polished API 5LX65 carbon steel, (b) API 5LX65 carbon steel in 3.5% NaCl + 500 mg/l H_2S at pH 4, temperature 70^oC, (c) API 5LX65 carbon steel in 3.5% NaCl + 500 mg/l H_2S + 5,0 mmol/l BTAH at pH 4, temperature 70 ^oC