Electrochemical and thermodynamic investigation of benzenamine as corrosion inhibitor of austenitic stainless steel (type 304) in hydrochloric acid solution

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ABSTRACT

The inhibiting action of benzenamine (BEZ) on the corrosion of type 304 stainless steel in 3M hydrochloric acid was investigated through electrochemical tests. Results show BEZ to be an excellent inhibitor. The compound was observed to be of mixed type in action. Inhibition efficiency increased with increase in BEZ concentration giving an optimal value of 96.14% at 6.25% BEZ concentration from weight loss and 88.7% at 5% BEZ concentration from polarization tests. X-Ray diffractometry revealed the absence of corrosion products. Statistical analysis using ANOVA showed the statistical significance of BEZ concentration on its inhibition efficiency performance. The compound obeyed Langmuir adsorption isotherm.

Keywords: corrosion; benzenamine; inhibition; pitting; austenitic stainless steel; hydrochloric acid
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INTRODUCTION

Acid solutions are commonly employed in industry for cleaning, acid decaling and pickling of steel, which often lead to corrosion of the alloy. Hydrochloric acid is frequently applied in industrial operations such as chemical cleaning and pickling to abstract oxide scales and rusts from the metal surfaces. A cost effective technique for corrosion control in harsh conditions is the augmentation of chemical additive known as inhibitors to the acidic solution in contact with the metal surface. Effective inhibitors perform excellently even in aggressive environments and high temperatures between 60 to 95 °C. The most efficient corrosion inhibitors used in hydrochloric acid solutions consists of heteroatoms such as sulphur, nitrogen and oxygen [1 - 6].Organic compounds [7 - 13]have been reported for their corrosion inhibition performance for steel in acidic environments. They typically function via adsorption of the molecules on the metal surface, forming a protective film to corrosion attack. This research is to further establish the usefulness and economic viability of organic derivatives as for corrosion prevention. Therefore, the present study aims to investigate the inhibition effect and adsorption properties of benzenamine on Type 304 stainless steel corrosion in hydrochloric acid. Benzenamine is an aromatic amine compound comprising of a phenyl group connected to an amino group. Benzenamine is the prototypical aromatic amine. Being an antecedent to multifarious industrial chemicals, its major application is in the production of precursors to polyurethane.

155

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MATERIALS AND METHODS

Material
Commercially available Type 304 austenitic stainless steel was used for all experiments of average nominal composition; 18.11%Cr, 8.32%Ni and 68.32%Fe. The material is cylindrical with a diameter of 18mm.

Inhibitor
Benzenamine(BEZ) a brownish, translucent liquid, obtained from SMM Instruments, South Africa is the inhibitor used. The structural formula of BEZis shown in Fig. 1. The molecular formula is $C_6H_5NH_2$while the molar mass is 93.13gmol^{-1}.
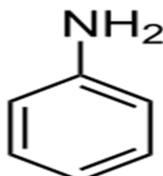
Figure1 Chemical structure of Benzenamine(BEZ)

BEZ was prepared involume concentrations of 1.25%, 2.5%, 3.75%, 5%, 6.25% and 7.5% per 200 ml of the acid solution.

Test Media
3M hydrochloric acid with 3.5% recrystallised sodium chloride of Analar grade were used as the corrosion test media.

Preparation of Test Specimens
The cylindrical stainless steel (18mm dia.) was mechanically cut into a number of test specimens of dimensions in length ranging from 17.8mm and 18.8mm coupons. The two surface ends of each of the specimen were ground with Silicon carbide abrasive papers of 80, 120, 220,800 and1000 grits. They were then polished with 6 μm to 1 μm diamond paste, washed with distilled water, rinsed with acetone, dried and stored in a dessicator for further weight-loss test and linear polarization.

Weight-loss Experiments
Weighted test species were fully and separately immersed in 200ml of the test mediaat specific concentrations of the BEZ for 360h at ambient temperature of 25°C. Each of the test specimens was taken out every 72 h, washed with distilled water, rinsed with acetone, dried and re-weighed. Plots of weight-loss (mg)and corrosion rate (mm/y)versus exposure time (h)(Fig.2&3)for the test media and those of percentage inhibition efficiency(%*IE*)(calculated) versusexposure time (h) and percentage BEZ concentration(Fig.4 & 5) were made from table 1.

The corrosion rate (*R*) calculation is from this equation 1:

$$R= \left[\frac{87.6W}{DAT}\right] (1)$$

Where*W* is the weight loss in milligrams, *D* is the density in g/cm^2, *A* is the area in cm^2, and *T* is the time of exposure in hours. The %*IE* was calculated from the relationship in equation 2.

$$\%IE = \left[\frac{W1-W2}{W1}\right] \times 100 \qquad (2)$$

The %*IE* was calculated for all BEZ concentration every 72 h during the course of the experiment, while the surface coverage is calculated from the relationship:

$$\theta = \left[1 - \frac{W2}{W1}\right] (3)$$

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Whereθ is the substance amount of adsorbate adsorbed per gram (or kg) of the adsorbent. $W_1$and W_2 are the weight loss of austenitic stainless steel coupon in free and inhibited acid solutions respectively.

Open Circuit Potential Measurement
A two-electrode electrochemical cell with a silver/silver chloride was used as reference electrode. The measurements of OCP were obtained with Autolab PGSTAT 30 ECO CHIMIE potentiostat. Resin mounted test electrodes/specimenswith exposed surface of 254 mm^2 were fully and separately immersed in 200ml of the test media (acid chloride) at specific concentrations of BEZ for a total of 288 h. The potential of each of the test electrodes was measured every 48 h. Plots of potential (mV) versus immersion time (h) (Fig. 6) for the two test media were made from the tabulated values in Table 2.

Linear Polarization Resistance
Linear polarization measurements were carried out using, a cylindrical coupon embedded in resin plastic mounts with exposed surface of 254 mm^2. The electrode was polished with different grades of silicon carbide paper, polished to 6μm, rinsed by distilled water and dried with acetone. The studies were performed at ambient temperature with Autolab PGSTAT 30 ECO CHIMIE potentiostat and electrode cell containing 200 ml of electrolyte, with and without BEZ inhibitor. A graphite rod was used as the auxiliary electrode and silver chloride electrode (SCE) was used as the reference electrode. The steady state open circuit potential (OCP) was noted. The potentiodynamic studies were then made from -1.5V*versus* OCP to +1.5 mV *versus* OCP at a scan rate of 0.00166V/s and the corrosion currents were registered. The corrosion current density (j_{corr}) and corrosion potential (E_{corr}) were determined from the Tafel plots of potential *versus* log *I*. The corrosion rate (*R*),the degree of surface coverage (θ) and the percentage inhibition efficiency (%*IE*) were calculated as follows

$$R = \frac{0.00327 * J_{corr} * E_q}{D} \quad (4)$$

Where J_{corr} is the current density in uA/cm^2, *D* is the density in g/cm^3;*E*q is the specimen equivalent weight in grams;

The percentage inhibition efficiency (%*IE*) was calculated from corrosion rate values using the equation.

$$\%IE = 1 - \left[\frac{C_2}{C_1}\right] \times 100 \quad (5)$$

where $C_1$and C_2 are the corrosion rates in absence and presence of BEZ inhibitors, respectively.

X-Ray Diffraction Analysis
X-ray diffraction (XRD) patterns of the film formed on the metal surface without BEZ addition was analyzed using a Bruker AXS D2 phaser desktop powder diffractometer with monochromatic Cu Kα radiation produced at 30kV and 10mA, with a step size of 0.03^o 2θ. The Measurement program is the general scan xcelerator. Analysis of the steel sample inhibited with BEZ was done with PANalyticalX'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and receiving slits with Fe filtered Co-Kα radiation. The phases were identified using X'PertHighscore plus software.

Statistical Analysis
Two-factor single level statistical analysis using ANOVA test (F-test) was performed so as to investigate the significant effect of BEZ inhibitor concentration and exposure time on the inhibition efficiency values of BEZ in the acid media.

RESULTS AND DISCUSSION

Weight-loss measurements
Weight-loss of austenitic stainless steel at various time intervals, in the absence and presence of BEZ concentrations in 3M HCl acid at 25°C was studied. The values of weight-loss (*W*), corrosion rate (*R*) and the percentage inhibition efficiency (%*IE*) are presented in Table 1. It is clear that the decreasing corrosion rate is associated with increase inBEZ concentration which indicates that more BEZ molecules are adsorbed on the metal surface, thereby providing a wider surface coverage on the steel surface. Fig.2, 3 & 4shows the variation of weight-loss, corrosion rate and

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percentage inhibition efficiency versus exposure time at specific BEZ concentration while Fig. 5show the variation of BEZ %*IE* with BEZ concentration. The curves obtained indicate progressive increase in %*IE* with increase in BEZ concentration accompanied by a significant decrease in corrosion rate.

The high %*IE* is most probablydue to the blocking effect of the surface by adsorption and film formation.This decreases the active sitesnecessary corrosion. Adsorption is influenced by the molecularproperties of BEZ, surface charge of the metal and the ionization effect of theBEZ molecule. In the electrolyte, the BEZ exists either as noble and protonated molecules[14].The protective film prevents the diffusion of Fe^{2+} to the liquid/metal interface while at the same time inhibits the diffusion of $Cl^-$to the metal/liquid interface. The results confirm that BEZ reduces corrosion rates to a significant extent, especially after 1.25% BEZ concentration achieving a maximum inhibition efficiency of 96.1% in HCl.The excellent performance exhibited by the compound may be due to the presence of the protonated form of N atoms of the compound which enables it to adsorb quickly on the metal surface, thus forming an insoluble stable film on the surface of the stainless steel.

Table 1Data obtained from weight loss measurements for austenitic stainless steel in 3M HCl in presence of specific concentrations of the BEZ at 360h

Sample	Weight Loss (g)	Corrosion Rate (mm/y)	BEZ Concentration (Molarity)	BEZ Concentration (%)	BEZ Inhibition Efficiency (%)	Surface Coverage (θ)
A	4.842	26.73	0	0.00	0	0
B	1.472	6.31	0.000268	1.25	69.60	0.6960
C	0.583	2.93	0.000537	2.50	87.96	0.8796
D	0.346	1.65	0.000805	3.75	92.85	0.9285
E	0.198	0.84	0.001074	5.00	95.91	0.9591
F	0.187	0.66	0.001342	6.25	96.14	0.9614
G	0.458	1.68	0.001611	7.50	90.54	0.9054
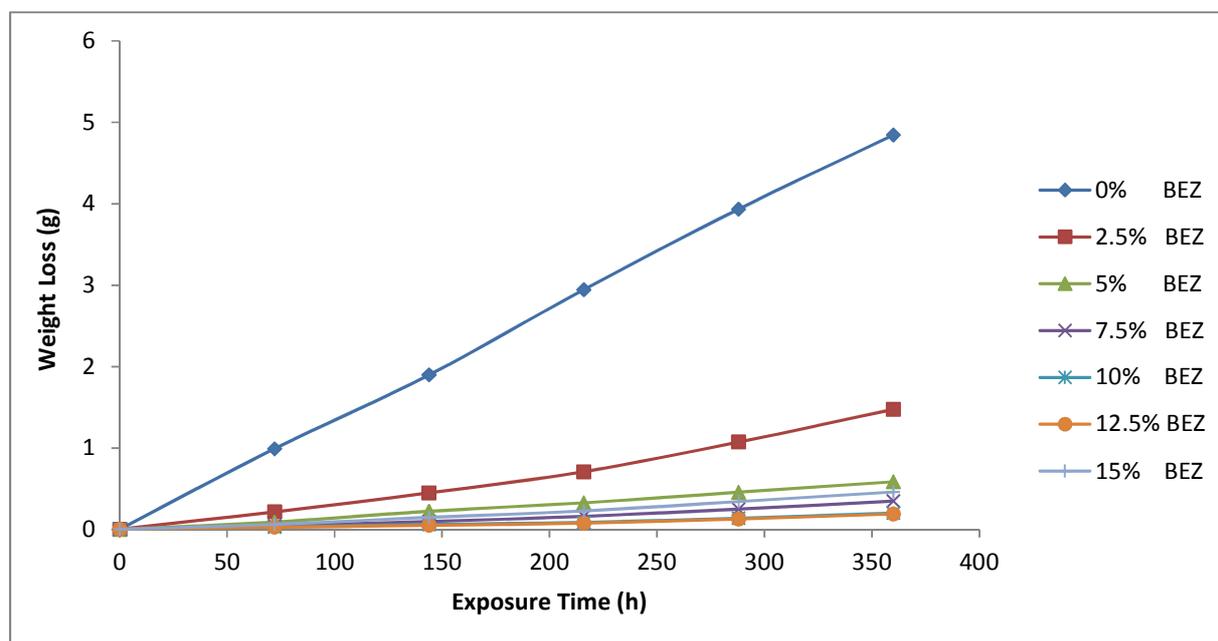
Figure 2 Variation of weight-loss with exposure time for samples (A – G) in (0% -15%) BEZ concentrations in 3M HCl

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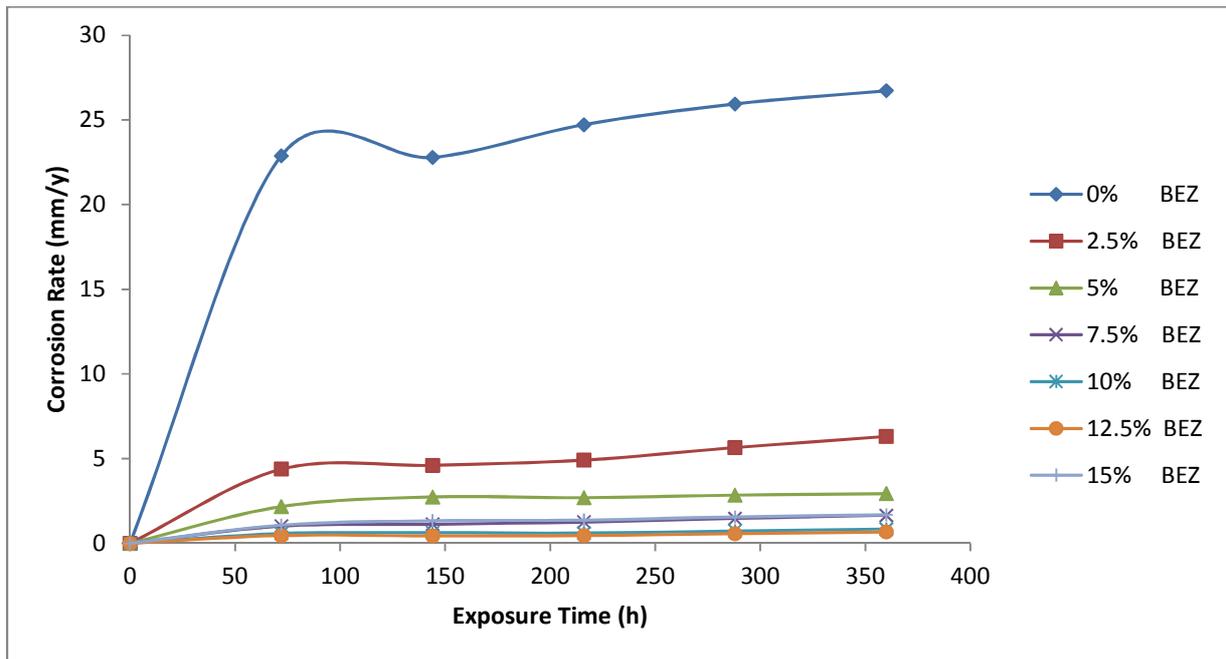
Figure3 Effect of percentage concentration of BEZ on the corrosion rate of austenitic stainless steel in 3M HCl
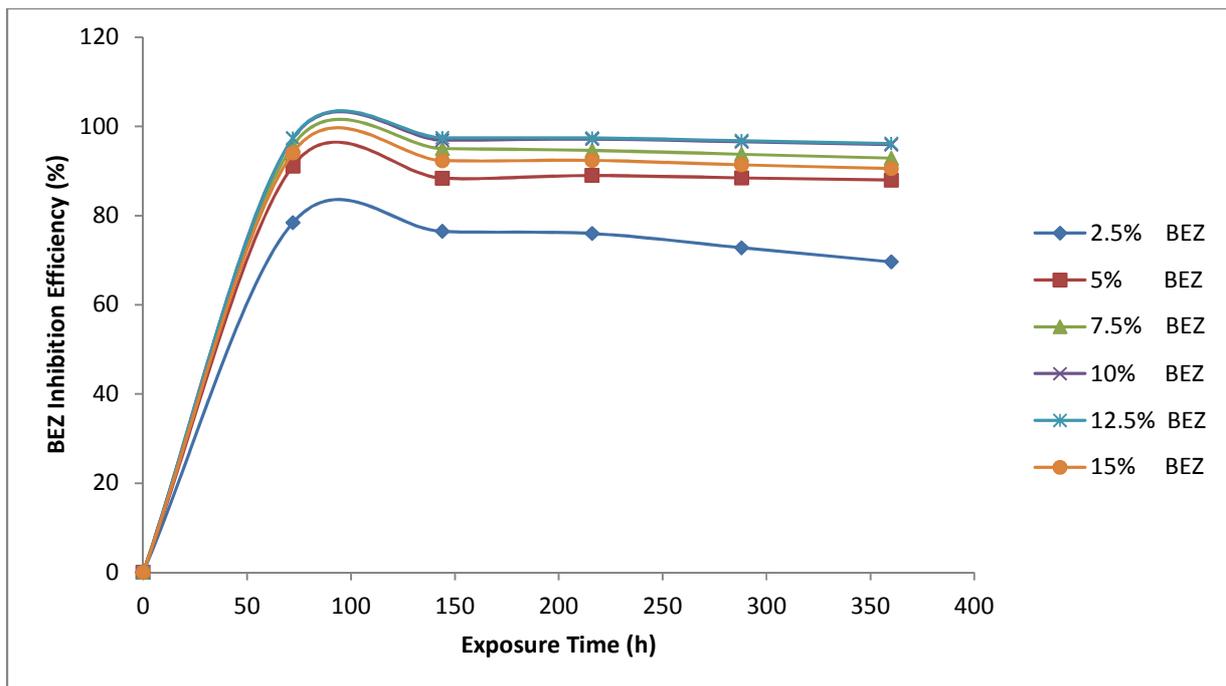
Figure 4 Plot of inhibition efficiencies of sample (A-G) versus exposure time in 3M HCl during the exposure period

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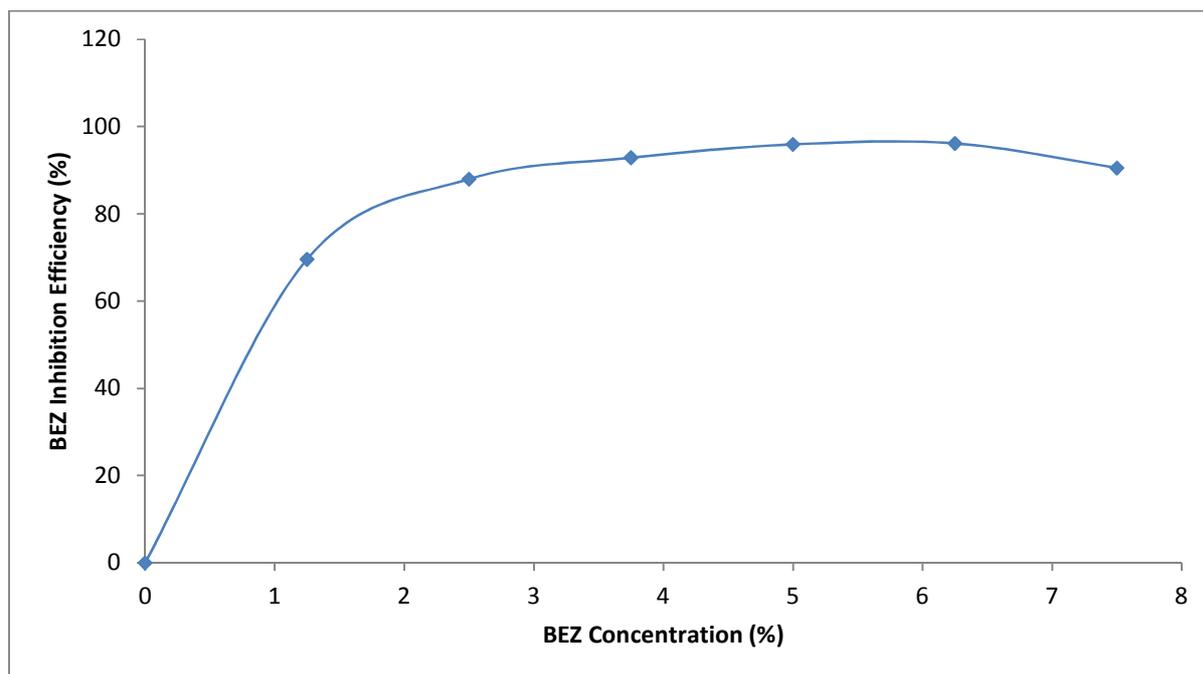
Figure 5Variation of Inhibition efficiency of BEZ versus BEZ concentrations from weight loss analysis in 3M HCl

Open Circuit Potential Measurement

The open-circuit potential value of the specimen electrodes was observed for a total of 288 h in the acid chloride solutions as shown in Table 2.Fig.6depicts the variation of open-circuit potentials with time in 3M HCl chloride solutions respectively in the absence and presence of specific concentrations of BEZ inhibitor. In the test solutions a progressive potential displacement towardsnegative values was noticed in 0% BEZ concentrations during the immersion hours. This corresponds with anodic dissolution of the steel specimen in the absence of BEZ.

At 1.25% BEZ concentration there is a gradual positive shift in corrosion potential to the noble direction due to the inhibitive action of BEZ at this concentration. The influence of BEZ on the electrochemical process is minimal as the corrosion potential after 288 h of exposure remains in the domain of intermediate corrosion, i.e. the corrosion protection is slightly effective. After 1.25% BEZ concentration, the increase in the number of BEZ molecules at higher concentrations has a profound influence on the electrochemical corrosion behaviour of the steel and the electrolytic action of the corrosion species. The marked decrease in potential values is due to the instantaneous action of the cationic species of BEZ which are strongly adsorbed through electrostatic attraction unto the steel surface wherewith it chemisorbs through charge transfer. The heterocyclic atom (nitrogen) and the amine functional group are responsible for the film forming characteristics of BEZ.

The protective film is responsible for the potential values after 1.25%BEZ concentration (2.5% -7.5% BEZ). The film prevents the diffusion of chlorides responsible for anodic degradation of the steel in 0% BEZ as observed in the corresponding potential values. The average potential at 288 h after 1.25% BEZ concentration ranges between ~300 and 302mV which is well within the zone of passivation potentials for stainless steel. This is further confirmed from the corrosion rates and inhibition efficiency values. The intermolecular interaction resulting in the potential values obtained is explained under mechanism of inhibition.

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Table 4 Data obtained from potential measurements for austenitic stainless steel in 3M HCl in presence of specific concentrations of the BEZ

BEZ Concentration (%) Exposure Time (h)	0	1.25	2.5	3.75	5	6.25	7.5
0	-385	-433	-321	-311	-316	-327	-323
48	-391	-426	-305	-316	-317	-319	-325
96	-401	-421	-311	-318	-311	-311	-314
144	-406	-387	-302	-324	-304	-305	-313
192	-425	-361	-297	-309	-298	-312	-302
240	-432	-352	-301	-306	-302	-308	-291
288	-446	-344	-299	-301	-301	-311	-287
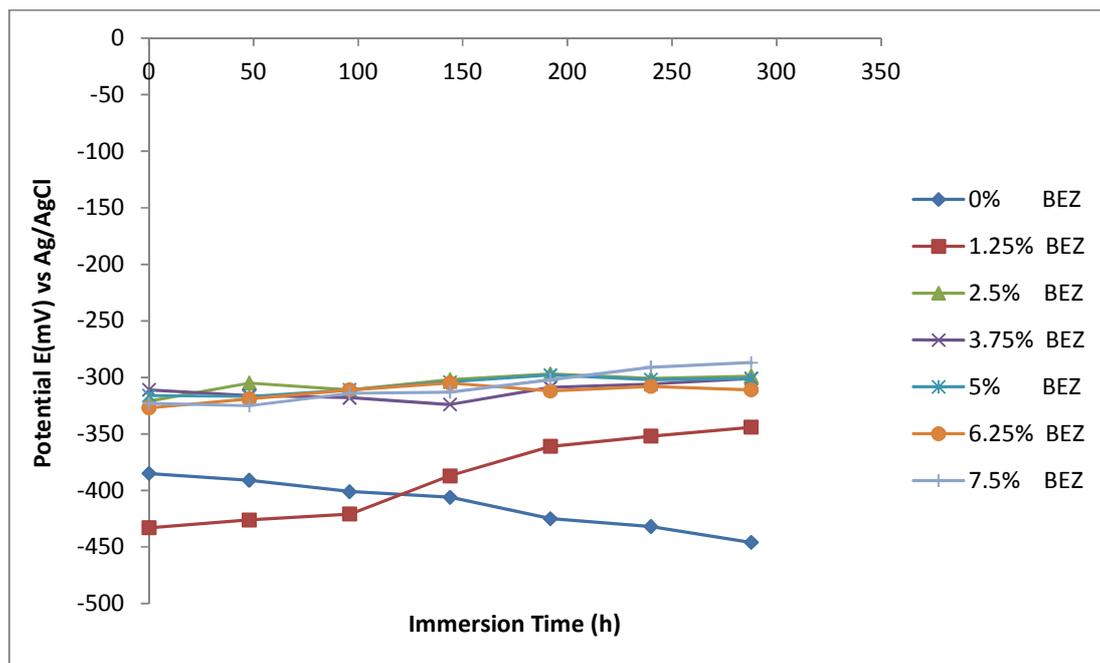
Figure 6 Variation of potential with immersion time for potential measurements in 3M HCl

Polarization studies

Potentiostatic potential was cursorily examined from –1.5 V to +1.5 V vs. Ag/AgCl at a scan rate of 0.0166 mV s^{-1}.The effect of the addition of BEZ on the anodic and cathodic polarization curves of austenitic stainless steel type 304 in 3M HClsolutions at 25 °C was studied at ambient temperature. Fig.7 shows the polarization curves of BEZ in 3M HCl. Results obtained using Tafel and linear polarization methods indicate that BEZ inhibited the electrochemical process of corrosion. Anodic and cathodic currents were significantly influenced in the presence of BEZ. The adsorption of BEZ is slightly independent of the value of its concentrations in the acid solutions as shown in Fig.7. Increase in %BEZ concentration results in a progressive increase in inhibition efficiency in HCldue to the availability of more BEZmolecules to counteract the actions of the corrosive species, block the active sites and form a compact protective barrier on the alloy surface in the solution.

The corrosion potential shifts towards more positive potentials as BEZconcentration increases, thus passivating iron through adsorption. This also can be attributed to deposition of BEZ molecules on the alloy as a result of interaction between BEZ and the oxidized metal surface which effectively seals the surface against further reaction; however the cathodic process predominates over the anodic. The polarization scans are generally similar at all concentrations.The results shows increase in %IE with decrease in corrosion rates.Electrochemical variables such as, corrosion potential (E_{corr}), corrosion current (i_{corr}), corrosion current density (J_{corr}), cathodic Tafel constant (bc), anodic Tafel slope (ba) , surface coverage θ and percentage inhibition efficiency (%IE) were calculated and given in Table 3. The corrosion current density (J_{corr}) and corrosion potential (E_{corr}) were determined by the intersection of the extrapolatinganodic and cathodic Tafel lines, %IE was calculated from equation 6.

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$$\%IE = \frac{c_1 - c_2}{c_1}\% \quad (6)$$

Table 3Data obtained from polarization resistance measurements for austenitic stainless steel in 3M HCl in presence of different concentrations of the BEZ

Sample	BEZ Concentration (%)	*ba* (V/dec)	*bc* (V/dec)	E_{corr} (V)	j_{corr} (A/cm²)	i_{corr} (A)	Corrosion Rate (mm/yr)	Rp (Ωcm²)	BEZ Inhibition Efficiency (%)
A	0	1.16	0.995	-0.41	9.11E-02	2.32E-01	9.361	2.16E+00	0
B	1.25	0.096	0.29	-0.34	3.30E-03	8.40E-03	3.395	1.44E+00	63.7
C	2.5	0.461	0.52	-0.339	3.22E-02	8.19E-02	3.308	5.37E+00	64.7
D	3.75	0.255	0.307	-0.349	2.17E-03	5.52E-03	2.229	6.16E+00	76.2
E	5	0.127	0.198	-0.43	1.03E-03	2.62E-03	1.059	4.17E+00	88.7
F	6.25	0.234	0.145	-0.341	1.10E-03	2.79E-03	1.126	5.28E+00	88.0
G	7.5	0.1	0.208	-0.345	1.09E-03	2.76E-03	1.116	3.27E+00	88.1
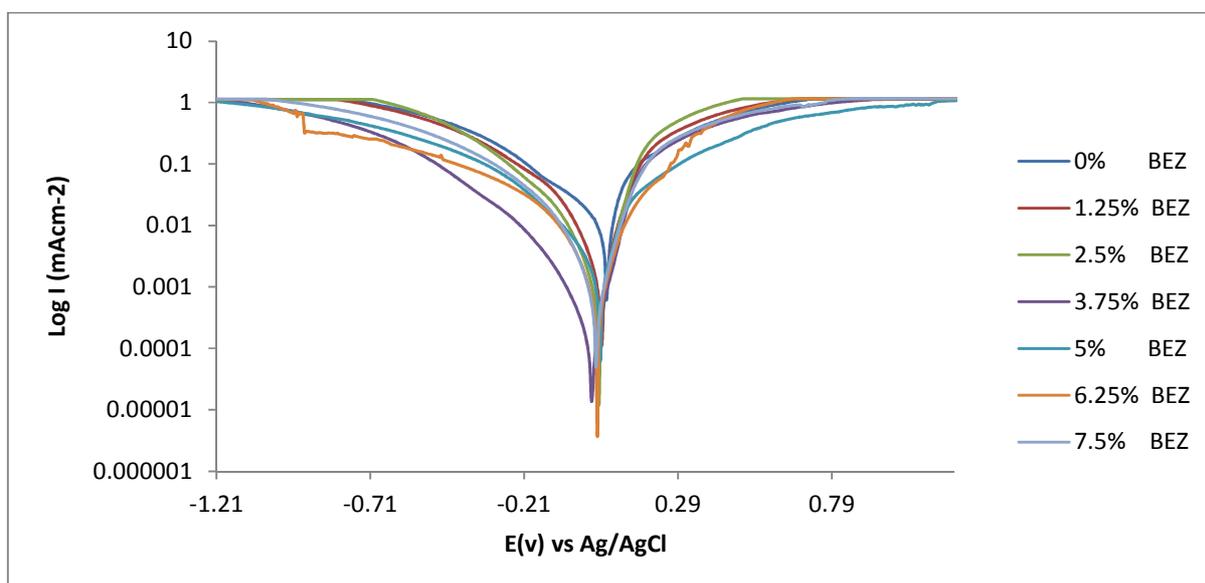
Figure 7 Comparison plot of cathodic and anodic polarization scans for austenitic stainless steel in 3M HCl + 3.5% NaCl solution in the absence and presence of (0% - 7.5%) at 25°C

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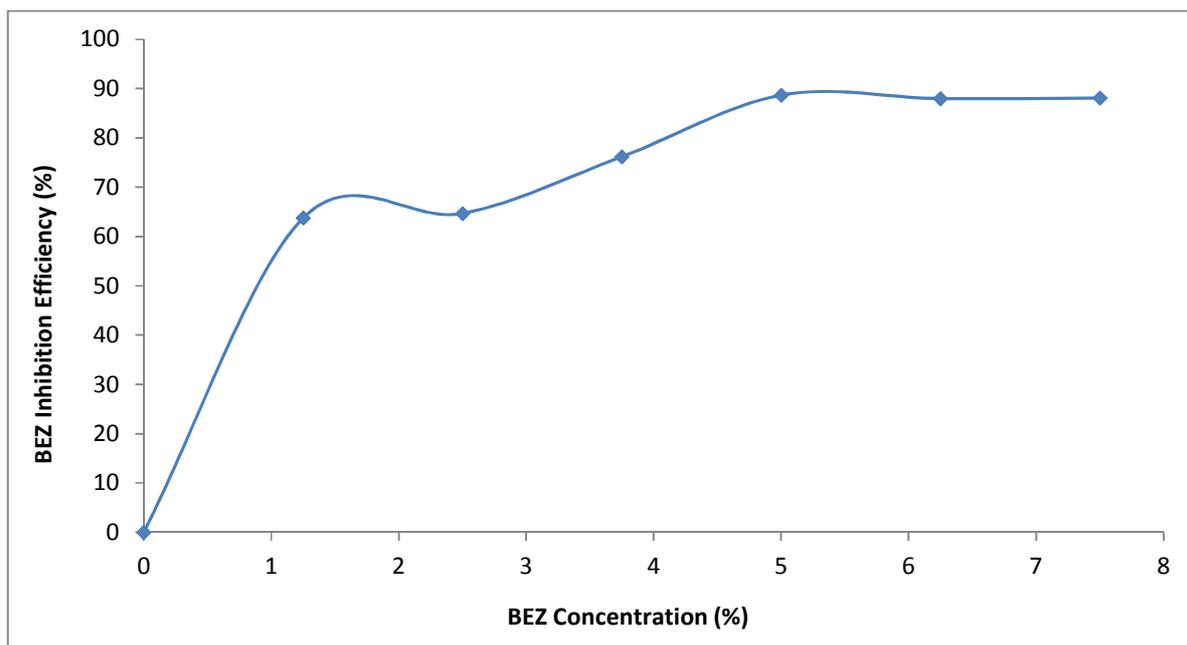
Figure8Relationship between BEZ %*IE* and BEZ inhibitor concentration for polarization test in 3M HCl

Table 3 showedthe results where BEZdisplayed greater tendency for cathodic inhibition as observed in the displacement direction of the E_{corr} values.This suggests that BEZ affects the mechanism of cathodic reaction (hydrogen evolution and oxygen reduction reaction) which is the main cathodic process under activation control and the addition of BEZ modifies and suppresses the reaction.

In the tested solutions results show that inhibition is by the blockage of sites responsible for anodic dissolution via adsorption through charge transfer with nitrogen atoms in addition to the accumulation of adsorbed BEZ cations on the steel as BEZconcentration increases[15]. This hampers the electrolytic transport of corrosiveanions to the metal surface as the surface coverage increases.Corrosion potentials slightly shifted in the negative direction in HCl. The maximum displacement in E_{corr} value was -7.1mV in HCl, thus in HCl, BEZ is a mixed type inhibitor[16].Changes in corrosion potentials in HCl is due to electrochemical interaction between anodic and the cathodic inhibiting reactions. BEZ shifts the equilibrium of corrosion process to the passive direction causing a formation of thin passivation oxide film over the anodic sites, which may increase the anodic potential and depressed the oxidation process.

The values of the anodic Tafel slope can be attributed to diffusion controland surface kinetics through film formation, where BEZ molecules are adsorbed via their functional groups on to the steel surface forming a protective layer, while simultaneously precipitating on the cathodic sites thereby inhibiting reduction reactions through increase of surface impedance. The high %*IE*s exhibited by BEZ may be attributed to its adsorption on the metal surface through polar groups as well as through *pi-* electrons of the double bond[17]. This leads to greater coverage of the metal surface by BEZ, thereby resulting in higher %*IE*. The inhibiting effect of BEZ can be attributed to its parallel adsorption at the metal solution interface. The parallel adsorption takes place owing to the presence of one or more active centers for adsorption.

XRD Analysis
X-ray diffraction (XRD) patterns of stainless steel surfaces from and 3M HCl solutions are shown in Fig.9 & 10 respectively. The identified patterns lists for the XRD analysis of austenitic stainless steel in the acid solution without BEZ are shown in Table4. The peak values at 2θ for the steel in thesolutions without BEZ (Fig.10) showed the presence of iron oxides due to the redox corrosion process that took place on the steel surface. The electrochemical reaction resulted in the formation of the oxides as a result of the action of chloride ion, responsible for the anodic dissolution process. The peaks at $2\theta = 39.5°$ and $50.5°$ can be assigned to iron (iii) oxide (Fe_2O_3). Observation of the diffraction peaks for the inhibited steel surfaces showed the absence of iron oxides and chemical

163

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compounds associated with corrosion. The compounds present especially chromium oxide at peak $2\theta = 51°$ is responsible for the passivation of the steel in addition to the effective inhibiting action of BEZ.
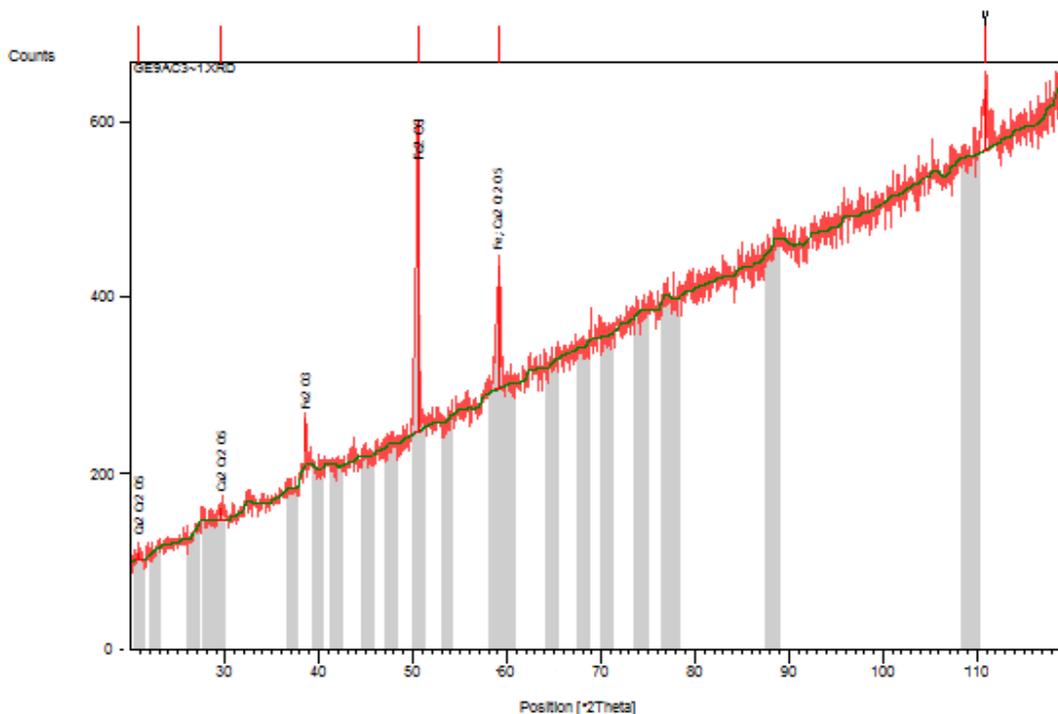
Figure 9XRD pattern of the surface film formed on austenitic stainless steel before immersion in the absence of BEZin 3M HCl
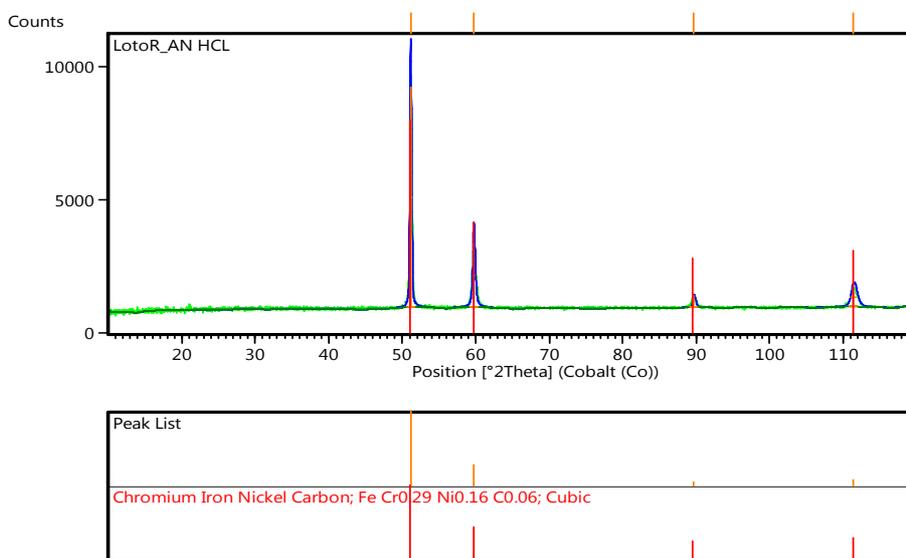
Figure 10 XRD pattern of the surface film formed on austenitic stainless steel after immersion in the presence of BEZ in 3M HCl

Table 4 Identified Patterns List for XRD analysis of austenitic stainless steel in 3M HCl withBEZ

164

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Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-089-4185	51	Iron	0.312	0.497	Fe
*	00-048-0791	28	Calcium Chromium Oxide	0.7	0.058	$Ca_2 Cr_2 O_5$
*	01-073-0603	41	Hematite, syn	-0.187	0.032	$Fe_2 O_3$

Adsorption isotherm

The mechanism of corrosion inhibition can be explained on the basis of adsorption behavior of the BEZadsorbate on the metal surface[18]. Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions. The adsorptive behavior of BEZ is an important part of this study, as it provides important clues to the nature of the metal-BEZ interaction. For an inhibitor to have a high surface coverage on the metal, a chemical bond between the inhibitor molecule and the metal atom stronger than the one for water molecules/corrosive anions should be formed. The adsorption of corrosion inhibitors at the metal/solution interface is due to the formation of either electrostatic or covalent bonding between the adsorbate and the metal surface atoms. Langmuir adsorption isotherm was applied to describe the adsorption mechanism for BEZ compounds in 3MHCl solutions, as it best fits the experimental results at 25 $^{\circ}$C.

The conventional form of the Langmuir isotherm is,

$$\left[\frac{\theta}{1-\theta}\right] = KC \quad (7)$$

and rearranging gives

$$\left[\frac{c}{\theta} = \frac{1}{\theta}\right] + C \quad (8)$$

where$\theta$is the degree of coverage on the metal surface, C is BEZ concentration in the electrolyte, and K_{ads} is the equilibrium constant of the adsorption process. The plots of$\frac{c}{\theta}$versus the BEZ concentration$C$ were linear (Fig.11) indicating Langmuir adsorption.
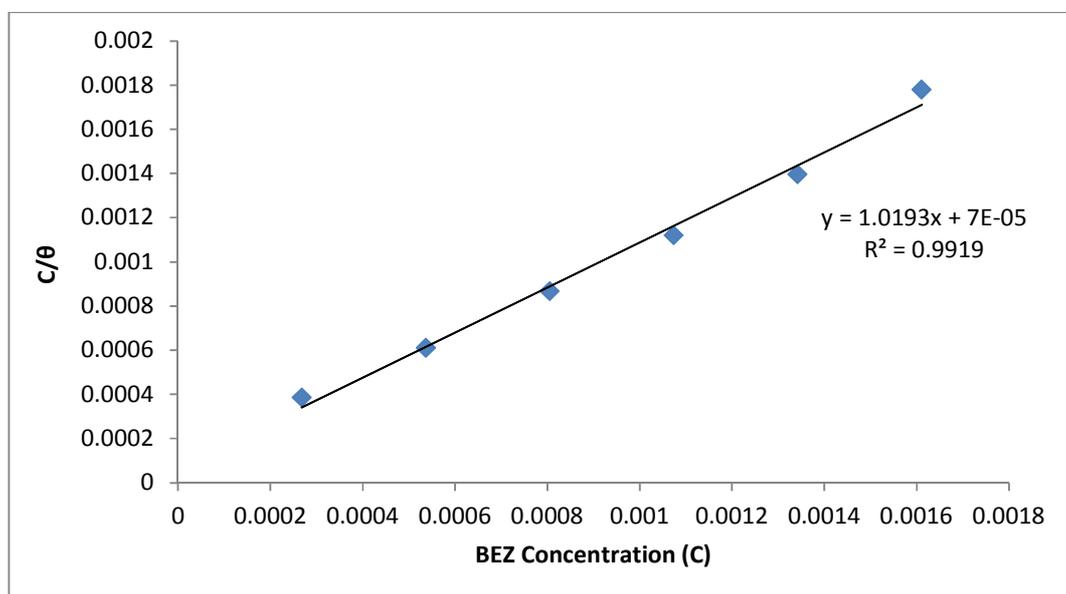
Figure11 Relationship between $\frac{c}{\theta}$ **and BEZ concentration (***C***) in 3M HCl**

The deviation of the slopes from unity in Fig. 11is attributed to the molecular interaction among the adsorbed BEZ specieson the metal surface and changes in the values of Gibbs free energy of adsorption with increasing surface coverage[19]. This was not taken into consideration during the derivation of the Langmuir equation. Langmuir

165

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isotherm predicts unity as the value of the slope. However,the fitted line gave a value less than unity for the slopes. This suggests a slightdeviation from ideal conditions assumed in Langmuir model.

Thermodynamics of the corrosion process

The values of the apparent freeenergy change i.e. Gibbs free energy (ΔG_{ads}) for the adsorption process can be evaluated from the equilibrium constant of adsorption using the following equation as shown in Table 5.

$$\Delta G_{ads} = -2.303RT\log[55.5K_{ads}] \quad (9)$$

Where 55.5 is the molar concentration of water in the solution, R is the universal gas constant, T is the absolute temperature and K_{ads} is the equilibrium constant of adsorption. $K_{ads}$is related to surface coverage (θ) by the following equation.

$$K_{ads}C = \left[\frac{\theta}{1-\theta}\right] \quad (10)$$

Table 5 Data obtained for the values of Gibbs free energy, Surface coverage and equilibrium constant of adsorption at varying concentrations of BEZ in 3M HCl

BEZ Concentration (*C*)	Free energy of Adsorption (ΔGads) (kJ/mol)	Surface Coverage (*θ*)	Equilibrium Constant of Adsorption (*K*ads)
0	0	0	0
0.268	-32.41	0.6960	8542.5
0.537	-33.55	0.8796	13603.9
0.805	-33.95	0.9285	16141.9
1.074	-34.69	0.9591	21838.5
1.342	-34.29	0.9614	18549.2
1.611	-31.50	0.9054	5941.7

The resultspresented in Table 5 provide additional evidence of slight deviation from ideal condition ofLangmuir model as observed in the differential values of Free energy of Adsorption (ΔG_{ads}) with increase in surface coverage (θ) values. The dependence of free energy of adsorption (ΔG_{ads})of BEZ on surface coverage isascribed to the inhomogeneous attributes of the stainless steel. Onaustenitic stainless steel not all sites can be equivalent on the surface due to heterogeneity, thus the differential adsorption energies as observed in the experimental data (Table5).The free surface energy depends on the orientation of metal crystals and concentration of flaws (such as dislocations, vacancies, micro-distortions of crystal lattice, etc) at the interface.

Values of ΔG_{ads} around -20 kJ/molare consistent with physisorption; those around -40 kJ/mol or higher involve charge sharing to form a coordinate type of bond chemisorption. The value of ΔG_{ads}in HClreflectsstrong adsorption capability. The negative values of ΔG_{ads} showed that the adsorption of BEZ molecules on the metal surface is spontaneous [20 – 21]. The values of ΔG_{ads} calculated ranged between -31.50 kJ mol^{-1} to -34.69kJ mol^{-1}.Accordingly, the value of ΔG_{ads} obtained in the present study indicates that the adsorption mechanism of BEZ on austenitic stainless steel is physiochemical but more of chemisorption. The removal of water molecules from the surface is accompanied by chemical interaction between the metal surface and the adsorbate, and that turns to chemisorptions.   The intermolecular bonding is sufficiently strong to prevent displacement of adsorbed BEZmolecules along the surface. The nitrogen and oxygen atoms of BEZ molecules are readily adsorbed onto the metal surface, forming stable precipitates on the metal surface, thus decreasing metal dissolution.

Statistical Analysis

Two-factor single level experimental ANOVA test (F-test) was used to analyse the separate and combined effects of the percentage concentrations of BEZ and exposure time on the inhibition efficiency of BEZ in the corrosion of inhibition of austenitic stainless steels in 3M HCl solutions and to investigate the statistical significance of the effects.The F-test was used to examine the amount of variation within each of the samples relative to the amount of variation between the samples.

The Sum of squares among columns (exposure time) was obtained with the following equation.

$$SS_c = \frac{\sum T_c^2}{nr} - \frac{T^2}{N} \quad (11)$$

166

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Sum of Squares among rows (BEZ concentration)

$$SS_r = \frac{\sum T_r^2}{nc} - \frac{T^2}{N} \tag{12}$$

Total Sum of Squares

$$SS_{Total} = \sum x^2 - \frac{T^2}{N} \tag{13}$$

The results using the ANOVA test is tabulated in Table 6 as shown below.

Table 6Analysis of variance (ANOVA) for inhibition efficiency of BEZ inhibitor in 3M HCl (at 95% confidence level)

Source of Variation	Sum of Squares	Degree of Freedom	Mean Square	Mean Square Ratio	Min. MSR at 95% confidence Significance F	F%
BEZ concentration	1766.37	5	353.27	34.88	2.71	94.45
Exposure Time	41.37	4	10.34	1.02	2.87	0
Residual	202.56	20	10.13			
Total	2010.29	29				

The analysis in 3M HClwas evaluated for a confidence level of 95% i.e. a significance level of α=0.05.The ANOVA results in test solutions reveal only one of the experimental sources of variation (BEZ concentration) to be statistically significant on BEZ inhibition efficiency with F-values of 34.88 in HCl. These are greater than significance factor at α=0.05 (level of significance or probability). The F-values of exposure time in the solutions are less than the significant value factor hence they are statistically irrelevant. The statistical influence of BEZ concentration in HClis 94.45%. The influence of the exposure time is less than 0% thus practically negligible. BEZconcentration is the only significant model terms influencing inhibition efficiency of BEZ on the corrosion of the steel specimen in the acid solutions. On this basis only percentage concentration of BEZ significantly affects the inhibition efficiency of BEZ in the acid media irrespective of the exposure time.
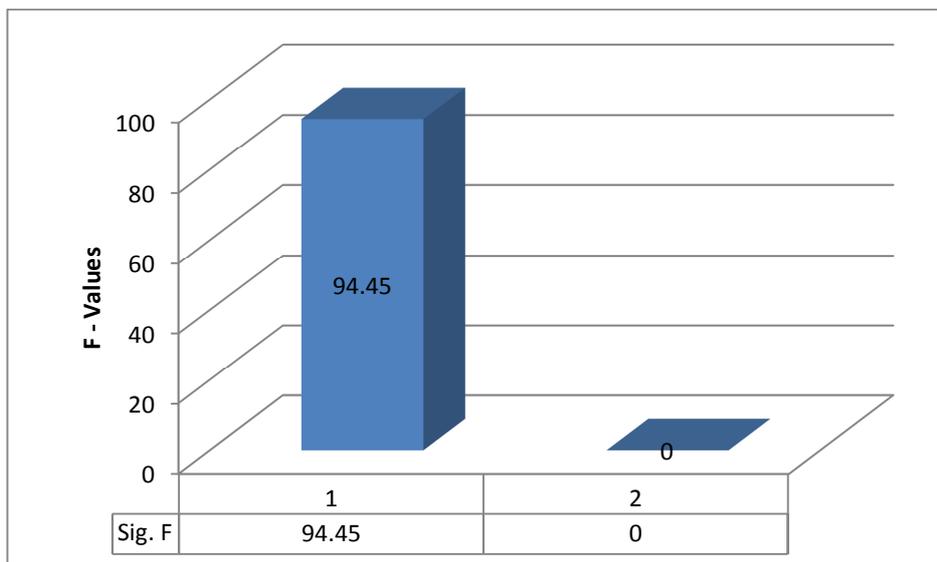
Figure12: Influence of BEZ concentration and exposure time on BEZ inhibition efficiency in 3M HCl

CONCLUSION

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Benzenamine (BEZ) showed excellent corrosion inhibition characteristics on type 304 austenitic stainless steel in 3 M hydrochloric acid due to the blocking effect of the surface by adsorption and film formation. This decreases the active sites necessary corrosion. Increases in BEZ concentration resulted in a proportionate increase in BEZ inhibition efficiencyThe protective film formed prevents the diffusion of Fe^{2+} to the liquid/metal interface while at the same time inhibits the diffusion of Cl^- to the metal/liquid interface. The average corrosion potential observed is well within the zone of passivation potentials for stainless steel. The diffraction peaks for the inhibited steel surfaces showed the absence of iron oxides and chemical compounds associated with corrosion. BEZ was observed to obey Langmuir adsorption isotherm as a result of the molecular interaction among the adsorbed BEZ species on the metal surface and changes in the values of Gibbs free energy of adsorption with increasing surface coverage. Thermodynamic calculations showed the mechanism of adsorption is through chemical interaction. Statistical analysis using ANOVA showed the overwhelming influence and statistical significance of BEZ concentration on the inhibition efficiency performance of BEZ.

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