Effect of *P*-Phenylediamine on the Corrosion of Austenitic Stainless Steel Type 304 in Hydrochloric Acid

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The effect of *P*-Phenylediamine on the corrosion behaviour of 304 stainless steel in 3M Hydrochloric acid solution contaminated with 3.5% sodium chloride was investigated using weight loss and potentiostatic polarization techniques. Corrosion parameters such as anodic and cathodic Tafel slope constants, corrosion potential, corrosion current, corrosion current densities, surface coverage and inhibition efficiency were calculated. The polarization measurements indicated that the inhibitors are of mixed type and inhibit corrosion by adsorption on the surface of steel due to the presence of more than one active centre in the inhibitor molecule. The inhibition effect ranged from 38.1% to 81.9% maximum at a concentration of between 0.125% to 1% before dropping sharply to between 9% and 4% at 1.25% to 1.5% concentration. The adsorption obeyed Langmuir adsorption isotherm up to 1% inhibitor concentration.

Keywords: p-phenylediamine, stainless steel, sodium chloride, hydrochloric acid

1. INTRODUCTION

Corrosion is the deterioration of a material (metallic alloy) due to interaction with its environment whereby the atoms leave the metal or form compounds in the presence of water and gases. Corrosion has been known to man since the earliest metallurgical times and has been a constant drain on his productive activities, as such, purposeful attention have been focused on the problem both by scientists and engineers [1]. It is a major industrial dilemma which results in millions of dollar lost each year [2]. Much of this loss is due to the corrosion of iron and steel. Stainless steel is a versatile material that is frequently utilized in various corrosive environments. The corrosion initiation process of stainless steel has aroused a great deal of attention in the last few decades because

the corrosion initiation is very complicated and it may cause various types of localized corrosions. Stainless steel derives their corrosion resistance by forming thin passive films on their surfaces that give protection to the base alloy. The formation of this film is instantaneous in an oxidizing atmosphere such as air, water, or other fluids that contain oxygen, but they do in fact suffer from certain types of corrosion in some environments such as pitting and uniform corrosion. Acidic solutions are aggressive to this film layer and results in severe pit formation [3, 4]. The highly corrosive nature of aqueous mineral acids on most metals requires degree of restraint to achieve economic maintenance and operation of equipment, minimum loss of chemical product and maximum safety conditions. In many industries, maintenance costs can be related directly to the cost of corrosion [5]. Mineral acid solutions such as hydrochloric acid are widely used for various treatments of materials in industry. The aqueous electrolyte phase in the overhead condenser, which comes from the brine water in the crude and steam stripping, contains mostly hydrochloric acid which is released by hydrolysis of $CaCl_2$ (calcium chloride) and $MgCl_2$ (magnesium chloride) and also contains H_2S (hydrogen sulfide) [5,6]. The corrosion in this unit is mostly due to the condensed HCl [6, 7].

Since steel could be attacked by the acidic media during its various application processes, the presence of corrosion inhibitors in the solutions is of utmost importance to keep the surface of steel intact [8]. Use of inhibitors is one of the most practical methods of metallic protection against corrosion [9]. The overhead system of the crude oil distillation columns are the single largest application for corrosion inhibitors [10]. The presence of inhibition compound in an environment, even in small concentrations, can lead to significant changes in the speed and form of corrosion of a metallic material in contact with the environment. The acceleration or inhibition of corrosion processes is specific and dependent on the metal-corrosive environment characteristics. Corrosion inhibitors are selected on the basis of solubility or dispersibility in the fluids which are to be inhibited [11]. Most of the efficient inhibitors used in industry are organic compounds. Organic compounds containing polar groups including nitrogen, sulfur, and oxygen [12–20] and heterocyclic compounds with polar functional groups and conjugated double bonds [21–25] have been reported to inhibit metallic corrosion. The dissolution rate of steel during cleaning, pickling, scaling and etching is quite high in acidic medium; the inhibition of such dissolution may be achieved with organic compounds containing π electrons and/or hetero atoms [26-40]. The inhibiting action of these organic compounds is usually attributed to their interactions with the metal surface via their adsorption. Polar functional groups are regarded as the reaction center that stabilizes the adsorption process [41]. In general, the adsorption of an inhibitor on a metal surface depends on the nature and the surface charge of the metal, the adsorption mode, its chemical structure, and the type of electrolyte solution [42].

Adsorption is generally over the metal surface forming an adsorption layer that functions as a barrier protecting the metal from corrosion [43, 44]. It has been commonly recognized that an organic inhibitor usually promotes formation of a chelate on a metal surface, by transferring electrons from the organic compounds to the metal and forming a coordinate covalent bond during the chemical adsorption [45]. In this way, the metal acts as an electrophile; and the nucleophile centers of inhibitor molecule are normally heteroatoms with free electron pairs that are readily available for sharing, to form a bond [46]. The power of the inhibition depends on the molecular structure of the inhibitor. Organic compounds, containing functional electronegative groups and π-electron in triple or

conjugated double bonds, are usually good inhibitors. The planarity and the lone electron pairs in the heteroatoms are important features that determine the adsorption of molecules on the metallic surface [47]. The inhibition efficiency of organic compounds is strongly dependent on the structure and chemical properties of the layer formed on the metal surface under particular experimental conditions. The efficiency of an organic inhibitor of metallic corrosion does not only depend on the structural characteristics of the inhibitor but also on the nature of the metal and environment. The selection of suitable inhibitor for a particular system is a difficult task because of the selectivity of the inhibitors and a wide variety of environments [48].

Different classes from organic compounds are used as corrosion inhibitors for iron alloys in various acid media [49-60]. Unfortunately, most of the organic inhibitors used are very expensive and health hazards. Their toxic properties limit the field of their application. Thus, it remains an important objective to find low-cost inhibitors of the non-hazardous type for the protection of metals against corrosion. This study aims to investigate the corrosion inhibition effect of *p*-Phenylenediamine (PPD) and its ability to provide protection against pitting and uniform corrosion at different concentrations in 3M HCl solution using linear polarization and weight loss technique. *P*-Phenylenediamine (PPD) is an organic compound, this derivative of aniline is a colorless solid, but typically samples can contain yellowish impurities arising from oxidation. It is primarily used as a dye intermediate, a photographic developing agent and a chemical intermediate. *P*-Phenylenediamine is also used as a vulcanization accelerator and as an antioxidant in rubber compounds [61-63].

2. EXPERIMENTAL PROCEDURE

2.1. Material

Commercially available Type 304 austenitic stainless steel was used for all experiments. The average nominal composition of the steel is 18.11%Cr, 8.32%Ni and 68.32%Fe. The material is cylindrical with a diameter of 1.80cm (18mm).

2.2. Inhibitor

P-Phenylenediamine (PPD) a colourless solid is the inhibitor used. The structural formula of PPD is shown in Fig. 2. The molecular formula is $C_6H_4(NH_2)_2$ while the molar mass is 108.1 g mol^{-1}.
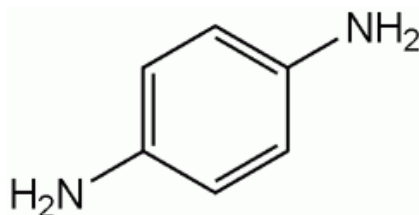

Figure 1. Chemical structure of *P*-Phenylenediamine (PPD)

P-phenylediamine was prepared in various concentrations of 0%, 0.125%, 0.25%, 0.5%, 0.75%, 1% 1.25% and 1.5% respectively.

2.3. Test Media

3M HCl acid with 3.5% recrystallised sodium chloride of Analar grade were used as the corrosive medium

2.4. Preparation of Test Specimens

The cylindrical stainless steel (1.80cm dia.) was mechanically cut into a number of test specimens of different dimensions in length ranging from 1.78 and 1.88cm 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 $6.0um$ to $1.0um$ diamond paste, washed with distilled water, rinsed with acetone, dried and stored in a dessicator for further weight-loss test and linear polarization.

2.5. Weight-loss Experiments

Weighed test species were fully and separately immersed in 200ml of the test media at varying concentrations of the inhibitor for 18days at ambient temperatures. Each of the test specimens was taken out every three days (72 hours), washed with distilled water, rinsed with acetone, dried and re-weighed. Plots of weight-loss (mg) and corrosion rate (mmpy) versus exposure time (hours) (Figs. 2 & 3) and those of percentage inhibition efficiency (%IE) (calculated) versus exposure time (hours) and percentage inhibitor concentration (Fig. 4 & 5) were made from table 1.

The corrosion rate (R) calculation is from this formula:

$$R = \left[\frac{87.6W}{DAT}\right] \quad \text{eqn. 1}$$

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 % inhibitor efficiency, (I.E), was calculated from the relationship.

$$\left[\frac{W1-W2}{W1}\right] \times 100 \quad \text{eqn. 2}$$

Where W_1 and W_2 are the corrosion rates in the absence and the presence respectively of a predetermined concentration of inhibitor. The %IE was calculated for all the inhibitors on the 18th day of the experiment (Table 1), while the surface coverage is calculated from the relationship:

$$\theta = \left[1 - \frac{W2}{W1}\right] \text{ eqn. 3}$$

Where θ is the substance amount of adsorbate adsorbed per gram (or kg) of the adsorbent, the unit of m is mol.g^{-1}. W_1 and W_2 are the weight loss of austenitic stainless steel coupon in free and inhibited acid solutions, respectively.

2.6. Linear polarization Resistance

Linear polarization measurements were carried out using, a cylindrical coupon embedded in resin plastic mounts with exposed surface of 2.54 cm^2. The electrode was polished with different grades of silicon carbide paper, polished to 6um, 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 200ml of electrolyte, with and without 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

$$R(mmpy) = \frac{0.00327 \ x \ icorr \ x \ eq.wt}{D} \quad \text{eqn.4}$$

Where i*corr* is the current density in uA/cm^2, D is the density in g/cm^3, eq. is the specimen equivalent weight in grams;

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

$$\% I.E = 1 - \left[\frac{c2}{c1}\right] 100 \quad \text{eqn.5}$$

where C1and C2 are the corrosion current densities in absence and presence of inhibitors, respectively.

3. RESULTS AND DISCUSSION

3.1. Weight-loss measurements

Weight-loss of austenitic stainless steel at various time intervals, in the absence and presence of different concentrations of (PPD) in 3M sulphuric acid at 25°C was studied.

Table 1. Data obtained from weight loss measurements for austenitic stainless steel in 3M HCL in presence of different concentrations of the PPD at 432hrs

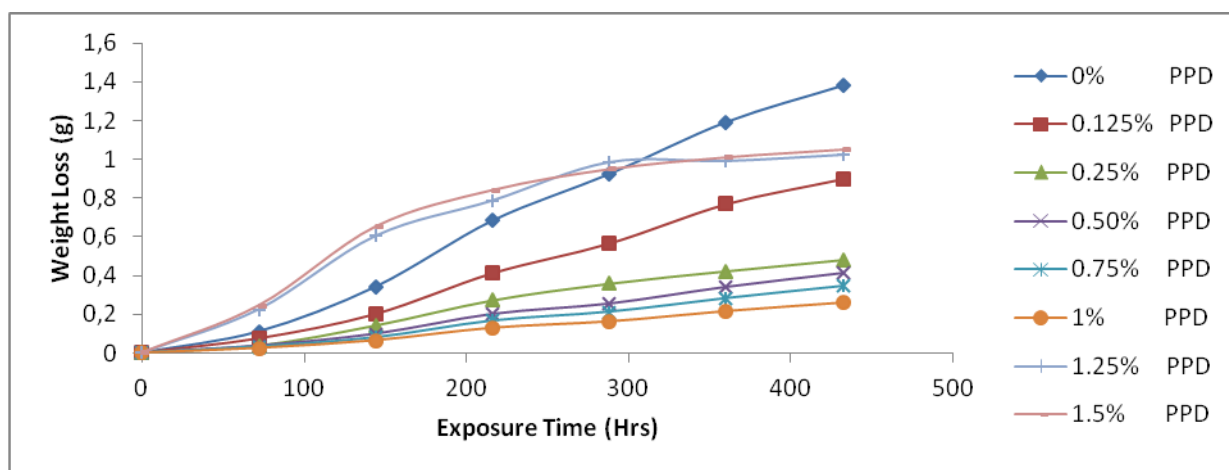| Samples	Corrosion Rate (mm/yr)	Weight Loss (g)	Inhibition Efficiency (%)	Inhibitor Concentration (%)
A	4.2719	1.382	0.00	0
B	2.6466	0.899	38.05	0.125
C	1.6408	0.591	61.59	0.25
D	1.2658	0.415	70.37	0.5
E	1.0005	0.345	76.58	0.75
F	0.7729	0.261	81.91	1
G	3.8876	1.023	9.00	1.25
H	4.0907	1.049	4.24	1.5

Figure 2. Variation of weight-loss with exposure time for samples (A − H) in (0% -1.5%) PPD concentrations.
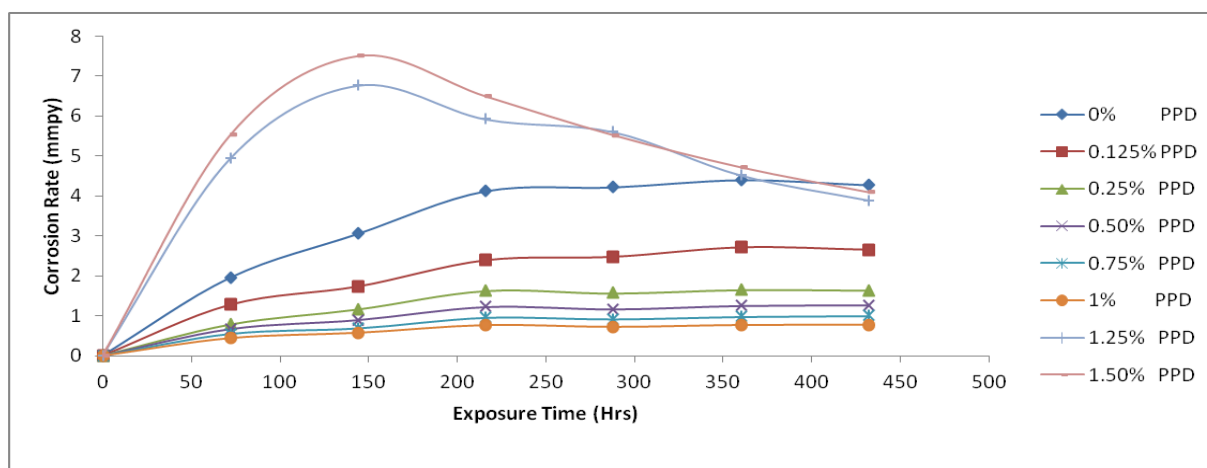

Figure 3. Effect of percentage concentration of PPD on the corrosion rate of austenitic stainless steel.

The values of weight-loss (wt), corrosion rate (CR) (mmpy) and the percentage inhibition efficiency (IE %) are presented in Table 1. It is clear that the decreasing corrosion rate is associated with increase in the inhibitor concentration which indicates that more inhibitor molecules are adsorbed on the metal surface, thereby providing wider surface coverage [64]. Figs. 2, 3 & 4 show the variation of weight-loss, corrosion rate and percentage inhibition efficiency with exposure time at different inhibitor concentration while fig. 5 shows the variation of %IE with inhibitor concentration. The curves obtained indicate progressive increase in %IE with increase in inhibitor concentration accompanied by a reduction in corrosion rate.
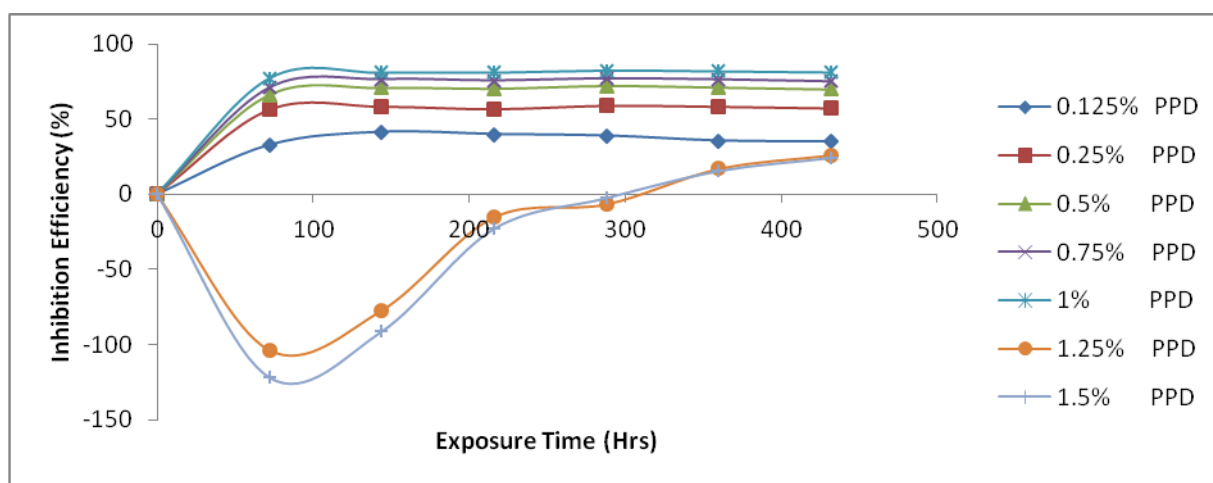

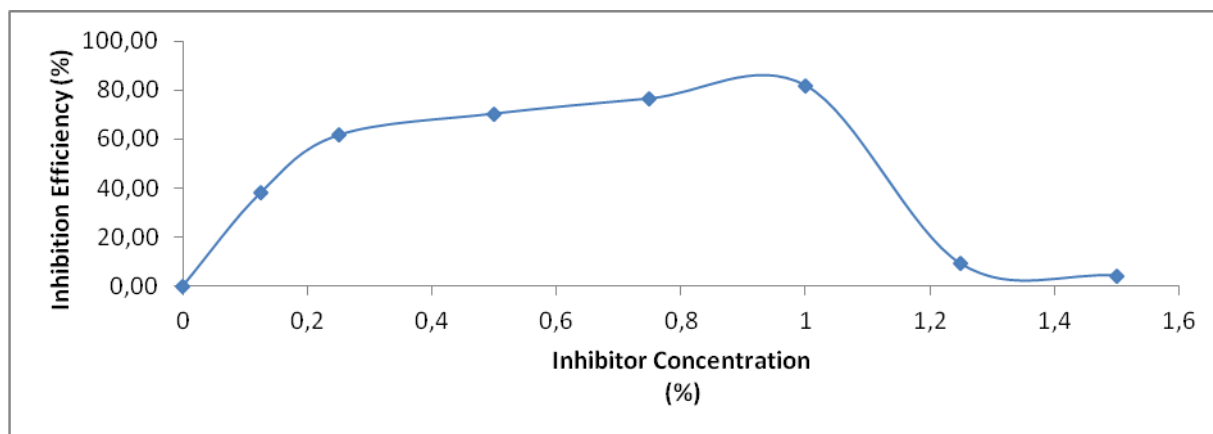**Figure 4.** Plot of inhibition efficiencies of sample (A-H) during the exposure period

Figure 5. Percentage inhibition efficiency of PPD at varying concentrations from weight loss at 432 hours.
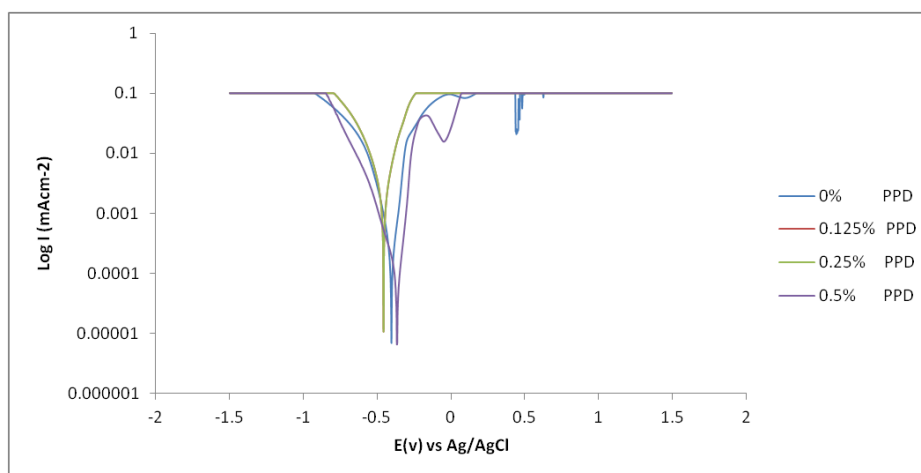
3.2. Polarization studies

The potential was scanned from −1.50 to 1.50 V vs. SCE at a rate of 0.0166 mV s^{-1}, which allows the quasi-stationary state measurements. The effect of the addition of PPD on the anodic and

cathodic polarization curves of austenitic stainless steel type 304 in 3 M HCl solutions at 25 °C was studied. Fig. 6 (a & b) shows the polarization curves of austenitic stainless steel in absence and presence of PPD at different concentrations. Anodic and cathodic currents were inhibited effectively with increasing concentrations of inhibitor. The inhibitor appeared to act as mixed type inhibitor since anodic (metal dissolution) and hydrogen evolution reactions were significantly influenced by the presence of the inhibiting compound in the corrosive medium. Generally, all scans exhibit slightly similar behavior over the potential domain examined, indicating similar electrochemical reactions took place on the metal. The electrochemical parameters such as, corrosion potential (E_{corr}), corrosion current (i_{corr})corrosion current density (I_{corr}), cathodic Tafel constant (bc), anodic Tafel slope (ba), surface coverage θ and percentage inhibition efficiency (%IE) were calculated and given in Table 2. These results show that the %IE increased while the corrosion current density generally decreased with the addition of PPD until 1% and 1.25% concentration where there was a slight increase in corrosion current density and a sharp increase in %IE and. The corrosion current density (I_{corr}) and corrosion potential (E_{corr}) were determined by the intersection of the extrapolating anodic and cathodic Tafel lines, % IE was calculated from Eq. 6

$$\% \ I.E= \qquad \% \qquad eqn. \ 6$$

Table 2. Data obtained from polarization resistance measurements for austenitic stainless steel in 3M HCl in presence of different concentrations of the PPD

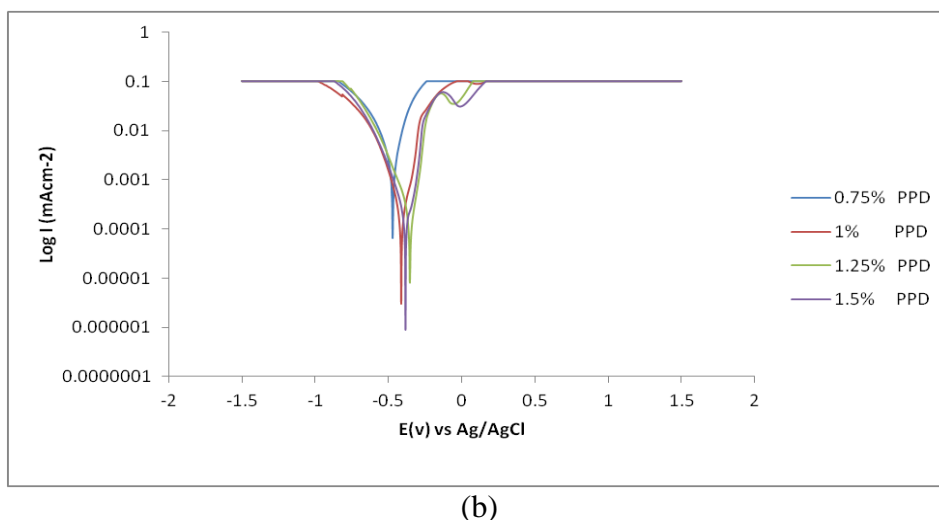| Samples	ba (V/dec)	bc (V/dec)	Ecorr, Obs (V)	jcorr (A/cm²)	icorr (A) (A)	Corrosion rate (mm/year)	Polarization resistance (Ω)	Molarity	Inhibitor Conc. (%)	Inhibition Efficiency (%)
A	0.041	0.190	-0.404	3.13E-04	7.94E-04	3.210	18.59	0.00E+00	0	
B	0.140	0.065	-0.394	1.87E-05	4.76E-04	1.925	40.32	1.16E-05	0.125	40.02
C	0.030	0.032	-0.457	9.73E-05	2.47E-04	1.000	27.45	2.31E-05	0.25	68.86
D	0.037	0.149	-0.366	4.11E-05	1.04E-04	0.422	123.13	4.62E-05	0.5	86.85
E	0.011	0.011	-0.471	5.21E-06	1.32E-05	0.053	178.65	6.94E-05	0.75	98.33
F	0.027	0.043	-0.413	7.73E-06	1.96E-05	0.079	363.63	9.25E-05	1	97.53
G	0.195	0.089	-0.354	2.85E-05	7.23E-05	2.930	36.68	1.16E-04	1.25	8.72
H	0.198	0.101	-0.384	3.01E-05	7.65E-05	3.093	38.1	1.39E-04	1.5	3.64

(a)

(b)

Figure 6. Comparison plot of cathodic and anodic polarization scans for austenitic stainless steel in 3M H_2SO_4 + 3.5% NaCl solution in the absence and presence of different concentrations of PPD at 25^oC. (a) 0% - 5% PPD (b) 7.5% - 15% PPD

Anodic and cathodic currents varied significantly with increasing concentrations of PPD. This compound appeared to act as a mixed type inhibitor since both cathodic (hydrogen evolution) and anodic (metal dissolution) reactions were influenced by the presence of PPD in the corrosive medium.

As shown in Table 2, the values of cathodic Tafel slope constants (bc) varied differentially in the presence of PPD concentrations, indicating changes in the mechanism of its inhibition. This suggests that inhibitor affects the mechanism of cathodic reaction (hydrogen evolution and oxygen reduction reaction) which is the main cathodic process under activation control, the addition of PPD modifies and suppresses the cathodic reactions. Results show that the inhibition mode of the tested PPD is by simple blockage of the surface via adsorption, accompanied by an increase in the number of adsorbed organic molecules on the steel with increase in inhibitor concentration, which impede more the diffusion of ions to or from the electrode surface as the degree of surface coverage (θ) increases [65].

There is a sharp increase in corrosion rate coupled with a sharp decrease in %IE after 1% inhibitor concentration. This shows that PPD is equally harmful at concentrations greater than 1% probably due to desorption at the metal electrolyte interface. The anodic Tafel lines (ba) are observed to change with addition of inhibitors suggesting that the inhibitor were first adsorbed onto the metal surface and impedes the passage of metal ions from the oxide-free metal surface into the solution, by merely blocking the reaction sites of the metal surface thus affecting the anodic reaction mechanism. Increasing the concentration of the inhibitor gives rise to an inconsistent change in anodic and cathodic current densities indicating that PPD acts as a mixed type inhibitor [66].

Corrosion potentials slightly shifted in both the positive and negative directions. A compound can be classified as an anodic or a cathodic-type inhibitor when the change in the Ecorr value is larger than 85mV [67, 68]. If displacement in Ecorr is <85, the inhibitor can be seen as mixed type. In this study the maximum displacement in Ecorr value between the uninhibited and inhibited sample was

67mV. Changes in potentials can be a result of competition of the anodic and the cathodic inhibiting reactions [69]. However, in the anodic range from the corrosion potential, the current density decreases due to decrease in active metal dissolution reaction, then stabilizes, indicating strong resistance to pitting corrosion before it starts to increase faster due to breakdown of the passive film and pit initiation.

The values of the anodic Tafel slope can be attributed to surface kinetic process rather than a diffusion-controlled one [70], where the inhibitor molecules are adsorbed via their polycentric adsorption sites on to the steel surface forming a protective layer. Furthermore, the results in Table 2 demonstrate clearly the inhibitory effect of PPD on the stainless steel corrosion between 0.125% - 1% concentration, whereby both icorr and CR decreases, after 1% both Icorr and CR increases The inhibition mechanism of these PPD compounds is a combination of surface blockage and electrostatic repulsion between adsorbed species and chloride ions. The adsorption of PPD depends on the inhibitors concentrations up 1% PPD. PPD act on both anodic and cathodic sites, reducing the corrosion rate without a significant change in the corrosion potential, generally by surface adsorption over the surface of the steel in contact with the inhibitor and consequently forming a thin protective layer. It is clear that the cathodic reaction (hydrogen evolution) is inhibited and the inhibition increases along with the inhibitor concentration. [71]. This controls corrosion by attacking cathodic activity, blocking sites where oxygen picks up electrons and is reduced to hydroxyl ion [72]. The variable constancy of this cathodic slope can indicate that the mechanism of proton discharge reaction changes by addition of the PPD to the acidic media.
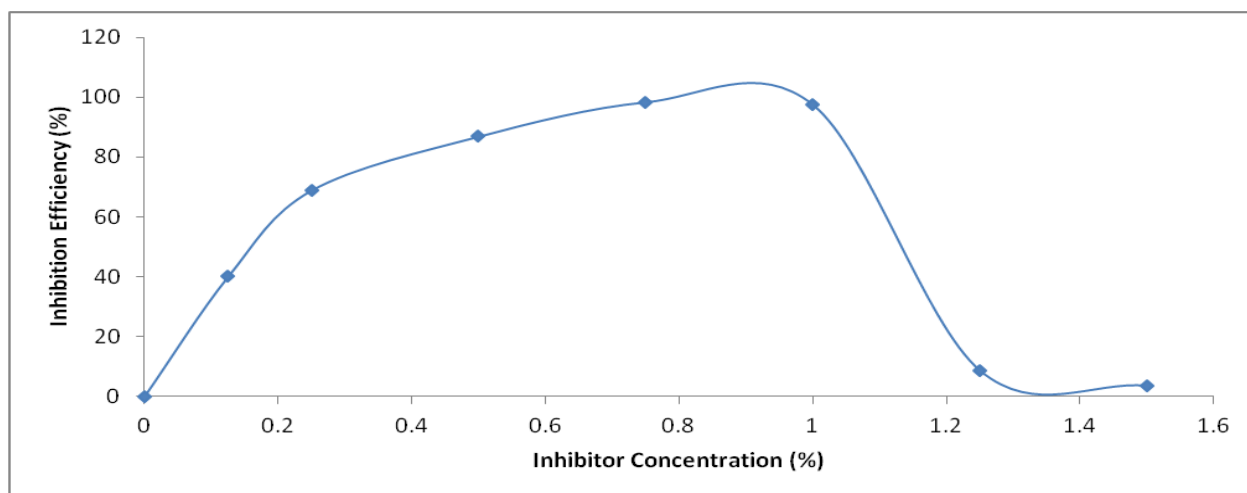

Figure 7. The relationship between % IE and inhibitor concentration for polarization test

3.3. Mechanism of inhibition

Adsorption of the inhibitor at the metal solution interface is the first step in the action mechanism of inhibitors in aggressive acid media. Adsorption depends on the nature and the state of the metal surface, type of corrosive medium and on the chemical structure of the inhibitor. The

efficiency of these inhibitors depends on the amine groups (NH_2) position on the benzene ring, the molecular structure effect, rigidity of π-delocalized system of PPD which may cause the increase or decrease of the electron density on the center of adsorption, leading to an easier electron transfer from the functional group to the metal, producing greater coordinate bonding and hence variable adsorption and inhibition efficiency depending on inhibitor concentration [73]. These functional groups have atoms of nitrogen, sulfur or oxygen. The polar function is frequently regarded as the reaction center for the adsorption process establishment, and the adsorption bond strength is determined by the electron density and polarizability of the functional group [74].

Amines in aqueous acidic solutions may exist as either neutral molecules or in the form of cations[75] depending on the concentration of H^+ ions in the solution. In acidic chloride solutions, the amines adsorb through electrostatic interaction between the positively charged anilinium cation and the negatively charged metal surface because of the specific adsorption of chloride on the metal [76]. Moreover, in aromatic amines, the interaction between the π electrons of the benzene ring and the positively charged metal surface also plays a role [77]. Murakawa and Hackerman[78] suggested that the stronger adsorption of organic molecules is not always a direct combination of organic molecules with the metal surface, but in some cases, it occurs through already adsorbed sulfate ions, which interfere with the adsorption of organic molecules. The adsorption of the inhibitor molecules can be visualized predominantly as RNH_3^+ ions lying flat on the electrode surface, with the principal adsorption forces arising from a π-bond orbital, as reported by Blomgren and Bockris(79). It is expected that compounds with a higher molecular weight and bulky structure may cover more area on an active electrode surface[80]. If such a bulky molecule can have chemisorptive properties, it is naturally expected to inhibit corrosion more effectively.

The adsorption of amine molecules on the metal surface takes place in the form of (1) a neutral molecule through chemisorption, involving the sharing of electrons between nitrogen and iron atoms; (2) π electron interaction with the metal surface; or (3) the adsorption of the cationic form of the inhibitor on the chloride-adsorbed iron surface. Of these, the adsorption through the cationic form was more probable because amines exist in a protonated cationic form in acid media [81, 82].

Studies report that the adsorption of the organic inhibitors mainly depends on some physicochemical properties of the molecule related to its functional groups, to the possible steric effects and electronic density of donor atoms; adsorption is suppose also to depend on the possible interaction of p-orbitals of the inhibitor with d-orbitals of the surface atoms, which induce greater adsorption of the inhibitor molecules onto the surface of carbon steel, leading to the formation of a corrosion protecting film [83].

The type of adsorption involving organic molecules at the metal solution interface are (i) electrostatic attraction between charged molecules and the charged metal, (ii) interaction of *n* electrons with the metal, (iii) interaction of uncharged electron pairs in the molecule with the metal and (iv) a combination of the above [44]. It is apparent that the adsorption of PPD on the steel surface could occur directly on the basis of donor acceptor between the lone pairs of the heteroatoms, the extensively delocalized π electrons over the C6 ring of benzene, the PPD molecule and the vacant d-orbitals of iron surface atoms [55]. The functional group responsible for PPD adsorption on metal surface is the

lone pair of the nitrogen atom: iron ions on metal surface which act as a Lewis acid because they accept electrons from a donor group [84].

In acidic solution, these compounds can exist as protonated species; these protonated species may adsorb on the cathodic sites of the stainless steel and decrease the evolution of hydrogen. These compounds are able to adsorb on anodic sites through N atoms, which is an electron donating groups. The adsorption of these compounds on anodic sites decreases anodic dissolution of stainless steel by the electron-rich heteroatoms in PPD which adsorbs on the anodic site through their lone pairs of electrons of nitrogen thus reduces the anodic dissolution of metal.

Inhibition of the stainless steel corrosion PPD was also found to depend on its stability in acidic solutions up to 1% concentration. Transfer of lone pairs of electrons on the nitrogen to the surface to form coordinate type linkage is favored by the presence of vacant orbital in iron atom of low energy. Polar character of substituent in the changing part of the inhibitor molecule seems to have a prominent effect on the electron charge density of the molecule. The presence of one active adsorption centers (one N-atoms) do not necessarily impact on the electron charge density on the molecule but increase in the inhibition efficiency as this occurs with increasing concentration of the compound between 0.125% and 1%. The presence of chloride ion increases this migration; the passive barrier becomes less effective at holding iron ions inside. Finally, at some point, the film ceases to exist and is replaced by an anodic site. The mechanism by which chloride ion accelerates corrosion of steel is complex, as stated below [85].

(1) Penetration of oxide film by chloride ion.
(2) Adsorption of chloride ion rather than a passivating species.
(3) Field effect of chloride ion pulling ferrous ions out of the metal.
(4) Catalysis of corrosion reaction by a bridging structure.
(5) Complex formation between chloride ion and some form of iron [86].

Some of the inhibition mechanisms identified by a previous study in aqueous solutions [87], suggests that PPD was able to displace chloride ions from the steel surface and to protect the surface passive film. This differed from the finding from the study in aqueous solutions [87], where the PPD-to-chloride concentration ratio was much higher and a durable passivating film was formed by PPD on the steel surface. PPD effectively delayed the onset of steel corrosion and inhibited the steel corrosion even when the passive film was compromised. According to Moretti et al [88] the strong absorption of PPD onto the steel surface inhibited the cathodic reaction of steel corrosion by limiting the access of oxygen to the steel.

Generally, the adsorption of organic compounds can be described by two main modes of interaction: physisorption and chemisorption. The former requires the presence of electrically charged metal surface and charged species in the bulk of solution, while the latter involves charge-sharing or charge-transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of a bond [89-91].

3.4. Adsorption isotherm

The mechanism of corrosion protection may be explained on the basis of adsorption behavior [92]. Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions. The adsorptive behavior of a corrosion inhibitor is an important part of this study, as it provides important clues to the nature of the metal-inhibitor interaction [64].Interaction information between the inhibitor molecule and metal surface can be provided by adsorption isotherm [93]. For an inhibitor to have a high surface coverage on the surface, a chemical bond between the inhibitor and the metal atom stronger than the one for water molecules 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 adsorbates and the metal surface atoms. Langmuir adsorption isotherm was applied to describe the adsorption mechanism for PPD compounds as it fits the experimental results at 25 $^{\circ}$C.

The conventional form of the Langmuir isotherm is,

$$\frac{\theta}{1-\theta} = Kc \quad \text{eqn.7}$$

and rearranging gives

$$\frac{c}{\theta} = \frac{1}{\theta} + c \quad \text{eqn.8}$$

where θ is the degree of coverage on the metal surface, C is the inhibitor concentration in the electrolyte, and K_{ads} is the equilibrium constant of the adsorption process. The plots of C/θ versus the inhibitor concentration were linear (Fig. 8) indicating Langmuir adsorption isotherm.
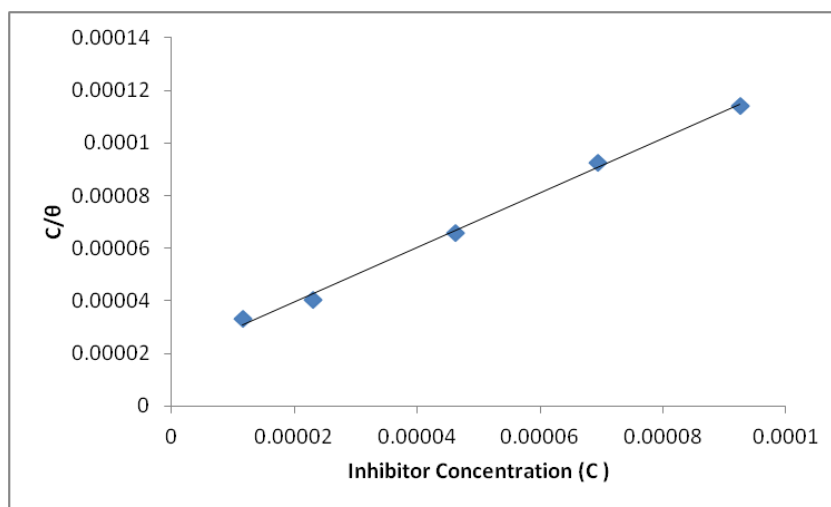

Figure 8. Relationship between $\frac{c}{\theta}$ and inhibitor concentration (C) for austenitic stainless steel at 0.125% - 1% PPD.

The deviation of the slopes from unity is attributed to the molecular interaction among the adsorbed inhibitor species, a factor which was not taken into consideration during the derivation of the Langmuir equation. Langmuir isotherm assumes that:

(i) The metal surface contains a fixed number of adsorption sites and each site holds one adsorbate.

(ii) ΔG_{ads} is the same for all sites and it is independent of θ.

(iii)The adsorbates do not interact with one another, i.e. there is no effect of lateral interaction of the adsorbates on ΔG_{ads} [94].

Table 3. Data obtained for the values of Gibbs free energy, Surface coverage and equilibrium constant of adsorption at varying concentrations of PPD

Samples	Free Energy of Adsorbtion (Δgads)	Equilibrium Constant of adsorption (K)	Molarity (C)	Surface Coverage (θ)
B	36.58	46315.7	0.0000116	0.3494935
C	37.15	57939.83	0.0000231	0.5723589
D	36.80	50435.61	0.0000462	0.6997106
E	36.40	43311.94	0.0000694	0.7503618
F	36.58	46432.56	0.0000925	0.8111433
G	29.84	3025.24	0.000116	0.2597685
H	29.10	2283.78	0.000139	0.2409551

The free energies of adsorption, ΔGads, were calculated from the equilibrium constant of adsorption using the following equation as shown in Table 3

$$\Delta G_{ads} = -2.303RT\log(55.5K)$$

Where 55.5 is the molar concentration of water in the solution, R is the universal gas constant and T is the absolute temperature. Generally, values of ΔG_{ads} around -20 kJ/mol or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption); those around -40 kJ/mol or higher involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of bond [95]. The value of ΔGads reflects the strong adsorption capability. The negative values of ΔGads showed that the adsorption of inhibitor molecules on the metal surface is spontaneous [96]. The values of ΔG_{ads} calculated ranges between −29.10 and −37.15 kJ mol^{-1} for PPD. Accordingly, the values of ΔG_{ads} obtained in the present study indicate that the adsorption mechanism of PPD on austenitic stainless steel involves two types of interaction, chemisorption and physisorption. Indeed, due to the strong adsorption of water molecules on the surface of stainless steel, one may assume that adsorption occurs first due to the physical forces [97]. 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 [97]. The intermolecular bonding to the adsorption sites is both chemical and physical physical, but is sufficiently strong to prevent displacement of adsorbed molecules along the surface The nitrogen and oxygen atoms of the inhibitor molecules are readily adsorbed onto the metal surface, forming insoluble stable films on the metal surface, thus decreasing metal dissolution

4. CONCLUSIONS

P-Phenylediamine is a good inhibitor for austenitic stainless steel in acidic chloride environment with maximum inhibition efficiency of 89.1% at an inhibitor concentration of 1%. The inhibition efficiency increases with inhibitor concentration before decreasing sharply at 1.25%. Polarization curves demonstrate that PPD behave as mixed type inhibitor. Potentiodynamic polarization measurements indicate that the presence of PPD significantly decreases corrosion currents and the effect was enhanced upon increasing its concentration. Weight-loss measurements indicated that the dissolution rate decreased to a significant extent due to the presence of PPD especially at high concentrations. PPD inhibits corrosion by adsorption of the inhibitor on the steel surface blocking the active sites and inhibition of the hydrogen evolution reactions. The adsorption of the compound on the stainless steel surface was found to obey Langmuir adsorption isotherm between 0.125% to 1% PPD concentration. The order of the inhibition efficiency of inhibitor at varying concentration as given by linear polarization measurements is in good agreement with that obtained from weight loss measurements. The free energy of adsorption indicates that the process was spontaneous and inhibition was due to physiochemical reactions on the steel surface.

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