4-Aminobenzenesulfonic Acid as Effective Corrosion Inhibitor for Carbon Steel in Hydrochloric Acid

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Abstract

The inhibitive activity of 4-aminobenzenesulfonic acid (SA) on the corrosion of carbon steel in 1 M HCl medium has been studied by weight loss, potentiodynamic, and impedance spectroscopy measurements. Experimental results reveal that sulphanilic acid goes about as an inhibitor in the corrosive condition. The inhibition efficiency increases with an increase in the SA concentration. The greatest inhibition efficiency is 92.14% at SA concentration 1000 ppm. Thermodynamic and kinetic parameters have been got from temperature studies. Electrochemical estimation reveals that sulphanilic acid acts as a mixed inhibitor and the adsorption isotherm follows Langmuir. The surface examination by SEM and surface composition was evaluated using EDX that shows the presence of a protective layer of SA molecules on the surface.

Keywords: Corrosion; Sulphanilic acid; Carbon steel; Electrochemical measurements; and Adsorption isotherm

1. Introduction

Corrosion of metals is a huge issue that must be gone up against for wellbeing, condition, and monetary contemplations. Corrosion is the decay of the basic properties of the objects with its environment; Millions of dollars are gone every year due to consumption [1-3]. The insurance of metals because of the consumption process has gotten a lot of consideration by and large because of huge harm to characteristic assets and funds because of corrosion. Carbon steel is the most widely recognized type of steel as a result of its generally minimal effort and material properties that are adequate for some applications, especially in nourishment, oil, concoction, and electrochemical enterprises, and force creation [4-7]. Carbon steel is known to be a flexible ferrous compound used for a wide scope of utilization because of its blend of mechanical properties, simplicity of creation, and low buy cost.

Be that as it may, it has low corrosion opposition [7-12]. The corrosion can be decreased by appropriate systems that hinder or stop the anodic or cathodic reactions or both [13-17]. Among the few techniques for consumption control and anticipation, the utilization of corrosion inhibitors is common. Most inhibitors are organic compounds contain \( \pi \)-bonds and the heteroatom (N, S or O) that exhibit excellent inhibitive properties [18-23]. One of the organic compounds exacerbates that can be utilized as the consumption inhibitor is Sulphanilic acid. The decision of Sulphanilic acid as consumption inhibitors depends on following contemplations: (a) SA is low poisonous and cheap, (b) presence of –NH2 and -SO3H groups as dynamic focuses encourages its adsorption on the metal surface (c) soluble in the test solution. In the present work, the corrosion restraint properties of SA against carbon steel in acidic solutions have been examined.

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estimation of the inhibition behavior was studied using weight loss, potentiodynamic polarization measurement, and electrochemical impedance spectroscopy (EIS). The apparent energy of activation of the corrosion process in absence and presence of sulphanilic acid was calculated by changing temperature. The other purpose of the current work is calculating the standard free energies and also determined the mode of adsorption. The nature and the morphology analysis using SEM & EDX were also studied.

Experimental:

2.1. Materials

Commercially obtainable Sulphanilic acid with molecular formula C₆H₇O₃NS is used. The SA was affirmed by FT-IR spectroscopic examination utilizing Nicolet iS10 FT-IR spectrometer, Thermo Fisher Scientific (USA). Stock solutions of SA were made by dissolving it in 1 M HCl (AR grade). The corrosive medium, 1M HCl solution are prepared from analytical grade 37% HCl by diluting with double-distilled water.

Molecular structure of Sulphanilic acid (SA)

Carbon steel (CS) having composition of 0.38% C, 0.83% Mn, 0.22% Si, 0.059% Ni, 0.087% Cr, 0.12% Cu, 0.023% P, 0.057% S and the remains Fe. In the weight loss experiments, CS mechanically cut from commercially available steel into coupons of 4.0×1.5× 0.0457 cm dimensions, polished with silicon carbide paper from 600 to 1200 grades to a metallic shine, rinsed with acetone and distilled water. The steel specimens for the electrochemical study are cut from steel sample of dimensions, 8.0×1.0×0.0457 cm, and coated with epoxy resin leaving a surface area of 1 cm².

2.2. Weight Loss Method

CS specimens in triplicate are immersed in 100 mL of 1 M HCl solutions without and with different concentration of SA inhibitor (200, 400, 600, 800 and 1000 ppm). After specified periods, the Carbon steel specimen was removed, washed by double distill water and acetone, then dried and weighed. The weight was determined by using a digital balance before and after immersion. Corrosion rates CR, inhibition efficiency IE % and surface coverage θ are calculated using the following equations:

\[ CR = \frac{W - W_o}{AT} \]  

Where, W and W₀ are the weight before and after immersion, A surface area and T is immersion time in hours.

\[ IE\% = \frac{C_R - C_{R(i)}}{C_R} \times 100 \]  

Where, Cᵣ and Cᵣᵢ are the corrosion rate of the carbon steel in the absence and presence of different concentration of SA.

2.3. Electrochemical measurements

Electrochemical estimations were performed with a usual three- electrode cell using Auto lab Potentiostat / Galvanostat ‘PGSTAT302N’. The potential of the working electrode carbon steel was measured against Ag/ AgCl as reference electrode and a platinum wire as counter electrode.

2.3.1. Potentiodynamic polarization

Open circuit potential (OCP) was measured to allow stabilization of the steady state potential. Polarization measurements were acquired by changing the potential from the open circuit potential values obtained -250 to + 250 mV with the scan rate of 1 mV s⁻¹. The corrosion parameters as, corrosion potential Eᵣᵣᵣᵣᵣ, corrosion current density iᵣᵣᵣᵣᵣ and polarization resistance Rᵣᵣᵣᵣᵣ were estimated from the Tafel plots. The inhibition efficiency was determined as follow:

\[ IE\% = \frac{i_o - i_i}{i_o} \times 100 \]  

Where, i₀ and iᵢ are the corrosion current densities without and with different concentration of SA, respectively [19].
2.3.2. Electrochemical impedance spectroscopy (EIS)

EIS estimations were completed utilizing AC signal (10 mV) at OCP in the recurrence scope of 10 Hz–50 M Hz. In all trials, the steel anode was likewise permitted to achieve its steady open-circuit potential (OCP). EIS outlines are assumed in the Nyquist and Bode portrayal. The data were analyzed by using Nova11.1. IE % was evaluated using the following equation:

$$IE\% = \frac{R_1 - R_0}{R_1} \times 100$$  \hspace{1cm} (5)

Where, $R_1$ and $R_0$ are the charge transfer resistance in the inhibited and uninhibited solutions, respectively.

2.4 SEM and EDEX investigation

The morphology of the carbon steel specimens was examined after exposure to 1 M HCl in the absence and presence of an optimum concentration of the SA inhibitor. JEOL 5410 SEM (Japan), equipped with an energy dispersive X-ray spectrometer to identify the morphological and chemical information of carbon steel.

3. Results and Discussion

The structure of sulphanilic acid (SA) was established by FT-IR spectroscopy in the range 500–4000 cm\(^{-1}\). Fig. 1 shows the FT-IR spectra of SA. A band at 2855 cm\(^{-1}\) relates to CH symmetric and anti-symmetric vibrations of SA. A peak at 1490 cm\(^{-1}\) shows the nearness of the benzene ring in aromatic compounds. Groups at 1572 and 1639 cm\(^{-1}\) of SA are the NH\(_2\) in SA [24].

![Fig. 1: FT-IR chart of sulphamic acid (SA)](image1)

### 3.1. Weight loss study

#### 3.1.1. Effect of SA concentration

The effect of SA on the inhibition efficiency of CS was studied in the range (200-1000 ppm) in 1 M HCl by using gravimetric method at room temperature for period. Plot exhibiting the variety of weight loss with time in the absence and presence of sulphanilic acid (200,400,600,800 and 1000 ppm) at 303 K has appeared in Fig. 2. The variation of weight loss with different SA concentration at different time is shown in Fig.3, the weight loss decreases with increasing of SA concentration.

![Fig. 2: The Variation of weight loss with time curves in 1M HCl solution without and with different concentrations of SA at 303 K.](image2)

![Fig. 3: Variation of Corrosion rate with SA concentration at room temperature](image3)
The corrosion rate and inhibition efficiency were determined by utilize weight loss information of different SA concentrations, using equation 1 and 2 are listed in Table 1. The inhibition efficiency increases with increasing SA concentration. This conduct can be clarified dependent on the cooperation of the inhibitor molecule with the CS surface by adsorption. The degree of adsorption increments with the increase the SA inhibitor lead to increase inhibition. The 1000 ppm is the optimum concentration that gives the most inhibition efficiency. The inhibitor molecule prevents dissolution by forming adsorbed protective film on the metal surface that isolate the CS surface from the deterioration medium. The presence of lone pair of electrons of nitrogen, and the presence of sulfur and the conjugated double bond of benzene ring in SA molecules increase the adsorption process.

3.1.2. Adsorption isotherm

Adsorption isotherm gives a better understanding of the electrochemical process on the metal surface. There are two types of interaction of organic molecules with the metal surface. The first one is the electrostatic attraction between the electrically charged metal surfaces with SA organic molecules, namely physisorption. The second type is charge transfer to the metal surface in order to form a coordinate type bond, namely chemisorptions. Adsorption isotherms are very important to determine the mechanism of 4-aminobenzenesulfonic acid (SA). It is important to know the mode of adsorption to understand this part of the study. The adsorption of inhibitor is a displacement reaction where the adsorbed water molecule is being removed from the surface of metal [25]. Surface coverage values were calculated by equation 3 from weight loss data and are listed in Table 1. The obtained values were fitted to Langmuir isotherm represented by Equation 6 [26], and the best fit to the experimental data was obtained.

\[
\frac{C}{\theta} = \left(\frac{1}{K_{ads}}\right) + C
\]  

(6)

Where, C is SA concentration, and K_{ads} is the equilibrium constant of adsorption/ desorption process.

Fig. 4 shows that the linear plot of C/θ vs. C in 1 M HCl solutions with and without SA, indicating that the adsorption of SA molecule followed Langmuir adsorption isotherms. From the intercepts of the straight lines, K_{ads} can be calculated then calculate the standard free energy of adsorption, (\Delta G_{ads}), as given by Equation 7 [27]:

\[
K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right)
\]

(7)

Where, T is room temperature, and R is gas constant (8.314 J K^{-1} mol^{-1})

The value of 55.5 is the concentration of water in the bulk solution replaced by 1000 in g/l.

![Fig. 4: Plot of C/θ vs. C in 1M HCl solutions in the absence and presence of SA](image)

Table 2:The values of adsorption parameters.

<table>
<thead>
<tr>
<th>Investigated inhibitor</th>
<th>K_{ads}</th>
<th>R^2</th>
<th>\Delta G_{ads} (KJmol^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphanilic acid</td>
<td>6.92</td>
<td>0.984</td>
<td>-14.99</td>
</tr>
</tbody>
</table>
Table 1: Corrosion rate (CR), Coverage surface (θ), and the inhibition efficiency (IE) of carbon steel in 1 M HCl in the absence and presence of a different concentration of SA obtained from weight loss data at 303 K

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>CR (mg cm⁻² h⁻¹)</th>
<th>Surface coverage θ</th>
<th>Efficiency (IE %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.140</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>200</td>
<td>0.045</td>
<td>0.678</td>
<td>67.85</td>
</tr>
<tr>
<td>400</td>
<td>0.040</td>
<td>0.711</td>
<td>71.14</td>
</tr>
<tr>
<td>600</td>
<td>0.031</td>
<td>0.778</td>
<td>77.85</td>
</tr>
<tr>
<td>800</td>
<td>0.020</td>
<td>0.857</td>
<td>85.71</td>
</tr>
<tr>
<td>1000</td>
<td>0.011</td>
<td>0.921</td>
<td>92.14</td>
</tr>
</tbody>
</table>

3.1.3. The Effect of Temperature

The optimal inhibition of CS was 92.14% in 1000 ppm SA at room temperature. To detect the stability of the formed protective film, the corrosion rate of SA inhibitor was studied in different temperature. The effect of temperatures (30, 40, 50, and 60°C) on the corrosion rate of the CS in 1 M HCl solutions in the absence and presence of best concentration of SA (1000 ppm) obtained by the weight-loss method was shown in Fig. 5.

![Fig. 5: The variation of corrosion rate (CR) and inhibition efficiency (IE%) with temperature of 1000 ppm SA concentration in 1M HCl](image)

It is seen that, the rate of corrosion in presence of the investigated inhibitor increases with the increase in the temperatures. The effect of temperature on the inhibited steel surface is highly complex due to several changes occur on the metal surface. As the temperature increases, the degree of surface coverage decreases due to desorption of SA inhibitor from the carbon steel surface. The surface becomes less protected and then the inhibition gradually loses its effectiveness. The value of apparent activation energy, E_a, was calculated using the Arrhenius Equation [30].

\[
C_R = Aexp\left(\frac{E_a}{RT}\right)
\]

Where, A is the pre-exponential factor, T is the absolute temperature and R is the universal gas constant and Fig. 6 show the linear regression plots between ln CR and 1/T gives a slope of - E_a/R. The calculated activation energy, E_a, and regulation factor, R, for CS in 1 M HCl solutions in the absence and the presence of SA are listed in Table 3. The values of E_a may be explained by the modification of the mechanism of the corrosion process in the presence of SA inhibitor molecules [31]. E_a of the inhibited metal is higher than the uninhibited one, indicating the more energy barrier is required for the corrosion reaction. According to reports, activation energy E_a due to chemical adsorption (> 80 KJ/mol) is considerably larger than due to physical adsorption (< 80 KJ/mol) [32,33].

Table 3: Thermodynamic parameters obtained from weight loss method

<table>
<thead>
<tr>
<th>parameters</th>
<th>Blank</th>
<th>1000ppm SA</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.495</td>
<td>2.778</td>
</tr>
<tr>
<td>R^2</td>
<td>0.9991</td>
<td>0.9949</td>
</tr>
<tr>
<td>E_a(kJ/mole)</td>
<td>19.430</td>
<td>53.490</td>
</tr>
<tr>
<td>ΔH_ads(kJ/mole)</td>
<td>16.791</td>
<td>50.851</td>
</tr>
<tr>
<td>ΔS_ads(kJ/mole)</td>
<td>-216.67</td>
<td>-119.97</td>
</tr>
</tbody>
</table>

ΔH_ads the apparent enthalpy of activation and ΔS_ads the entropy of activation values were obtained through the following equation:

\[
\ln\left(\frac{C_R}{T}\right) = \left[\ln\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S_{ads}}{R}\right)\right] - \frac{\Delta H_{ads}}{RT}
\]

Where, h is plank's constant and N is Avogadro's number.

The values of ΔH_ads and ΔS_ads listed in Table 3 were calculated from the slope and the intercept respectively of the straight line of ln CR/T vs 1/T as shown in Fig. 6. The positive values of ΔH reflect that the SA adsorption on the steel surface is endothermic process; meaning that dissolution of steel is difficult [34]. The negative values of ΔS_ads in
presence of the inhibitor imply that the activated complex in the rate-determining step was association rather than a dissociation step; the increase of entropy in presence of SA indicate that the disorder took place on going from reactants to the film formed on the metal/solution interface [35, 36].

![Graph](image.png)

Fig. 6: The relation of ln C.R and ln CR/T against 1/T in 1M HCl with and without of 1000 ppm of SA.

3.2. Electrochemical measurements

3.2.1. Potentiodynamic polarization studies

The polarization curves of CS in 1 M HCl with the expansion of different SA concentrations has appeared in Fig. 7.

![Graph](image.png)

Fig. 7: Tafel curves for CS in 1 M HCl without and with different SA concentration.

The corrosion parameters, for example, $E_{corr}$, $I_{corr}$, ($b_a$ and $b_c$) anodic and cathodic Tafel slope from the curves are given in Table 4. The corrosion current density $I_{corr}$ decreases with increasing SA concentration, so the corrosion rate decreases and both the resistance and the inhibition efficiency increase. Current density decline from $5.09 \times 10^{-3}$ Acm$^{-2}$ to $5.03\times10^{-4}$ Acm$^{-2}$ in absence and presence of1000 ppm of SA respectively, with inhibition efficiency 90.1%. The displacement of $E_{corr}$ is less than 85 mV indicates that the SA acts as mixed type inhibitor. Corrosion prevention and protection by adsorption of SA on the metal surface by donor atoms S, N and O. All corrosion parameter values listed inTable (4) indicate the protective film formed on the metal surface.

![Graph](image.png)

EIS is nondestructive method provides information about the surface properties. Nyquist and Bode plots of CS in 1M HCl without and with various concentrations of SA at open circuit potential have appeared in Figure 8(a –b) individually.
4-AMINOBENZENESULFONIC ACID AS EFFECTIVE CORROSION INHIBITOR

In the Nyquist plot appeared in Fig. 8 a, show the semicircle its diameter increases with the increase of the SA concentration. The high half-circle is credited to double layer capacitance [20, 21]. It is obvious that the impedance spectra is not an ideal half-circle and the discouraged capacitive circle compares to surface heterogeneity which might be the consequence of surface unpleasantness, or adsorption of the inhibitor atoms [22 - 24]. The charge transfer resistance increase with increasing SA concentration, its value is measure of electron transfer across the surface and is inversely proportional to corrosion rate [37]. The thickness of the formed SA film on the surface increases with the increase of SA concentration [26, 27]. Figure 8b shows the Bode plots shape for the inhibited and uninhibited carbon steel does not change indicates that the SA inhibitor doesn't change the corrosion mechanism. Bode plot shows two resistive region at low and high frequencies and a capacitive region in between.

The impedance data were analyzed using a simple equivalent circuit, it shown in Fig. 9, it consists of $R_s$ is the solution resistance, $R_{ct}$ is the charge transfer one and CPE is constant phase element is used instead of the capacitor to show good fitting of the double layer capacitor. EIS parameters are listed in Table 5. SA inhibitor enhances the $R_{ct}$ and decrease the $C_{dl}$ as shown in Fig (9). From $R_{ct}$ the IE% was calculated by equation (5). It is seen that IE% increase with increasing SA concentration. That increase proves the adsorption of SA on the metal surface forming protective film. The impedance of the CPE is expressed [38].

$$Z_{CPE} = \frac{1}{Y_0(\omega)^n} \quad (10)$$

Where, $Y_0$ is the magnitude of the CPE, $\omega$ is the angular frequency, $j$ is the imaginary unit, and $n$ is the CPE exponent.

The results obtained from EIS agree with the results obtained by polarization and weight loss measurements which indicate the ability of SA as corrosion inhibitor for CS in 1 M HCl solution.

3.3 SEM analysis

SEM investigations are carried out to confirm whether the SA inhibitor is adsorbed on the carbon steel surface or not. The SEM micrograph is shown in Fig.10. CS surface in 1M HCl is found to be severely affected and pit are present Fig.10 (a) which shows formation of porous surface of the outer oxide layer Fig.10 (b) shows the surface with 1000 ppm SA. It is seen that the roughness seems to be reduced with much less corroded area is observed which confirm adsorption of the SA on the active sites of the carbon steel surface, reveals a significant inhibiting effect of SA. To analysis the composition of the formed film was studied by EDX as shown in Fig 10 (c& d) it seen that in blank solution EDX show that the Fe and Oxygen are present. In presence of the optimal concentration of inhibitor peak for S, N and carbon appeared. Morphology and the EDX of surface prove that the protective film of SA on the carbon steel surface.
3.4. Mechanism of inhibition
Organic compounds act as corrosion inhibitors by adsorption on the metal surface. Adsorption takes place by electrostatic attraction, interaction of unshared electron pairs of hetero donor atoms N, O, S and interaction of the presence of conjugated bonds (π electron) in the inhibitor with vacant d-orbitals of carbon steel surface. Thus, adsorption is blocking the active surface sites, as a result reducing the corrosion rate by slowing the anodic and/or cathodic reaction and slowing the diffusion of aggressive species to the metal surface. In acidic solutions, Fe dissolves leaving negative charges on the CS surface which interact with the -NH$_2$ group of the SA molecule which has positively charged due to protonation. The electron pairs on the oxygen and nitrogen, the π-electrons of the heterocyclic on SA inhibitor molecules can be also adsorbed on the vacant d-orbitals of iron surface by donor–acceptor interactions.

4. Conclusions
All the estimations demonstrated that the sulphanilic acid has good inhibition properties against the carbon steel corrosion in HCl corrosive media. Potentiodynamic polarization estimations indicated that it acts as a mixed type inhibitor. EIS estimations likewise show that the inhibitor performance increments because of the adsorption of the particle on the metal surface. The inhibitor demonstrated the most extreme IE% at 1000 ppm convergence of the considered inhibitor. The IE% dictated by EIS, potentiodynamic polarization, and weight reduction consider are in acceptable understanding. The inhibitor follows the Langmuir adsorption isotherm during the time spent adsorption. SEM investigations indicated that there is a decline in the surface roughness of the inhibited surface in comparison with the uninhibited surface in HCl corrosive solution. From the above result, SA could be considered as corrosion inhibitor for mild steel.

Conflicts of interest
“There are no conflicts to declare”.

References
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