Corrosion inhibition of stainless steel 302 by 1-methyl-3-pyridine-2-Yl–thiourea in acidic media

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The corrosion inhibition of stainless steel type 302 (302 SS) with different concentrations (0.004-0.007 M) of 1-methyl-3-pyridine-2-Yl–thiourea (MPT) in acid solutions was investigated by potentiostatic polarization measurements. The effect of temperature (283-323±1 K) on corrosion parameters was examined. The open circuit potential values in the presence and absence of MPT noted before and after experiments indicated the formation of passive film on the surface of the samples. It was found that corrosion potential \( (E_{\text{corr}}) \) increases with increasing MPT concentrations, while, corrosion current \( (i_{\text{corr}}) \) decreases. Inhibition efficiency of MPT is slightly more in 1 M H\(_2\)SO\(_4\) than in 1 M HCl. The inhibitor functions through adsorption and follows Temkin isotherm in both the acids. Activation energy \( (E_a) \) and Gibbs free energy \( (\Delta G_{\text{ads}}) \) for adsorption of MPT are calculated. The values of \( \Delta G_{\text{ads}} \) decreased (attained more negative values) with increasing temperature.

**Keywords**: Corrosion, Stainless steel, MPT, Polarization behaviour, Temkin isotherm

Austenitic stainless steels (SS) are the commonly used construction materials, owing to their excellent resistance to general corrosion, high strength, workability and weldability. However, they are susceptible to localized corrosion in the presence of aggressive ions such as chloride ions, which limit their use in seawater. Stainless steel type 302 is susceptible to corrosion in several media such as oxidizing solutions, most organic chemicals and sterilizing solutions. Oldfield and Todd\(^1\) employed stainless steel type 302 in Multi-Stage Flash (MSF) desalination plants, and it was economically feasible over the other methods. The results of his work show that Type 302 stainless steel, which is representative of the austenitic grades with similar chromium content, has excellent resistance to the normal gases (CO\(_2\), O\(_2\) and N\(_2\)) in MSF plants. The use of inhibitors is one of the most practical methods of protecting against corrosion; especially for materials in acid media\(^2\), most of the well known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms. Numerous studies on corrosion inhibition using organic compounds have been reported\(^3-16\). The choice of 1-Methyl-3-pyridine-2-Yl–thiourea (MPT) is based on the fact that substituents to thiourea increase further its electron densities for their adsorption on the metal surface. In the present work, the corrosion inhibition properties of MPT (Fig. 1) against 302 SS in acidic solutions have been investigated.

**Experimental Procedure**

Stainless steel type 302 (302 SS) samples were of the compositions (in wt.%): 0.15% C, 1% Si, 2% Mn, 8-10% Ni, 18% Cr, 0.045% P, 0.03% S, Fe (balance). The stainless steel sheet of 1.2 cm\(^2\) area was mechanically polished with different grades (400, 800, 1200, and 1500) of emery papers in sequence. After polishing the specimens were washed with double distilled water and were used as working electrode for the test solution. A saturated calomel

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*Fig. 1—Chemical structure of MPT*
electrode (SCE) was used as reference electrode and a platinum plate as the counter electrode. The solutions were prepared with addition of different concentrations (0.004 - 0.007 M) of MPT to 1 M of acid solutions (H₂SO₄, HCl). The inhibitor was synthesized according to the procedure reported in the literature and the structure of compound was characterized by spectral data and its purity was confirmed by thin-layer chromatography (TLC). Potentiodynamic studies were performed by a potentiostate, CG, CV & PG system model DPSWx.

Prior to polarization measurement, the 302 SS working electrode was immersed in the experimental solution for ~30 min to attain a stable value of open circuit potential (OCP). Experiments were carried out at different temperatures (283-323±1 K) controlled by a thermostat. The anodic and cathodic polarization curves were obtained at a scan rate of 1 mVs⁻¹. The electrochemical parameters were obtained from the results of polarization studies done at 283-323 K. These parameters include the corrosion potential (E_corr), corrosion current density (i_corr), inhibition efficiency (η%) and surface coverage degree (θ). Also activation energy (E_a) and thermodynamic parameters such as, Gibbs free energy (ΔG_ads), adsorption enthalpy (ΔH_ads) and adsorption entropy (ΔS_ads) were calculated.

**Results and Discussion**

Figures 2 and 3 show the polarization curves for stainless steel 302 in 1 M HCl and 1 M H₂SO₄ with and without various concentrations of MPT at 283 K. Addition of this inhibitor hindered the acid attack on the stainless steel electrode and a comparison of curves in both of the cases with respect to the blank sample, revealed that increasing concentration of the inhibitor gives rise to a consistent decrease in anodic and cathodic current densities and the corrosion potential (E_corr) shifts to +ve direction, indicating the inhibitor to be of anodic in character and the formation of a surface film. The corrosion current densities (i_corr) were obtained by extrapolation of the Tafel lines. The variations of the inhibition efficiency (η%) and the degree of surface coverage (θ) with the molar concentration of inhibitor were calculated by using the following formulas:

\[ η = \left( \frac{i_0 - i_1}{i_0} \right) \times 100\% \]  \hspace{1cm} (1)

\[ θ = \frac{η}{100} \]  \hspace{1cm} (2)

where \( i_0 \) and \( i_1 \) are the corrosion current densities in the absence and presence of the inhibitor, respectively. Corrosion current densities were determined by the intersection of the extrapolated Tafel lines and the corrosion potential for 302 SS in acid solutions. The values of corrosion current density (i_corr), corrosion potential (E_corr), and calculated inhibition efficiencies (η%) and surface coverage (θ) are listed in Tables 1 and 2. The values of η and θ were found to increase with increase in inhibitor concentration. A maximum efficiency of 97% was observed at a concentration of 0.007 M inhibitor in the case of sulphuric acid solution. The inhibiting effect of MPT can be attributed to parallel adsorption at the metal solution interface. The parallel adsorption
takes place due to the presence of one or more active center available on MPT for adsorption on metal surface. The result of previous work indicates that, the inhibition efficiency achieved for stainless steels using 2,2'-[bis-N(4-dimethylamino salicyl aldimin)]1,1'-dithio (DASD) inhibitor decreases in the following order: 302 > 304 > 308 > 316, corresponding to the decreasing percentage of Fe atoms in the SS 302 to SS 316. In other words when the percentage of Fe atoms is decreasing the amount of Ni and Cr increases. This phenomena does not depend only on the nickel and/or chromium but is also dependent on the surface properties and the interaction between surface film and the adsorbed ligands. The adsorption possibly takes place due to the presence of active center for adsorption of metal cations. For example Fe$^{2+}$ ions created from anodic reaction entering the solution, would make a complex with the inhibitor near the surface. This complex would be adsorbed by physical bonding with metal surface covered with Cr$_2$O$_3$ film which is not protective enough in this media. So a stronger film is formed which protects the metal from corrosive media.

**Effect of temperature**

The effect of temperature on cathodic and anodic polarization curves for the 302 SS is shown in Figs 4 and 5. The results of these curves revealed that corrosion current density ($i_{corr}$) increases with increasing temperature, so that highest current density ($i_{corr}$) values were observed at 323±1K while corrosion potential ($E_{corr}$), decreased with increasing temperature. This proves that the inhibition occurs through the adsorption of the inhibitor on the surface. The activation energy of the corrosion process can be calculated using the following equation:

$$k = A \exp \left(-\frac{E_a}{RT}\right) \quad \ldots(3)$$

where $E_a$ is the activation energy, $A$ is the frequency factor, $T$ is the absolute temperature, $R$ is the gas
constant and \( k \) is the rate of metal dissolution reaction and is directly related to corrosion current density \( (i_{\text{corr}}) \). Plotting \( k \) versus 1/\( T \), the value of \( E_a \) can be calculated from the slopes of straight lines (Figs 6 and 7). The values of \( E_a \) are 15.13 and 11.6 kJ mol\(^{-1}\) for blank sample and 21.2 and 18.3 kJ mol\(^{-1}\) for 0.007 M of inhibitor in hydrochloric acid and sulphuric acid solutions respectively. The activation energy is higher in the presence of inhibitor than in the absence of inhibitor. This type of inhibitor retards the corrosion process at ordinary temperature\(^{26,27} \) whereas the inhibition is considerably decreased at elevated temperature.

Adsortion isotherm

The results indicate that \( i_{\text{corr}} \) decreases with the addition of MPT in both acids, and it is due to the increase in the blocked fraction of electrode surface by adsorption. The free energy of adsorption (\( \Delta G_{\text{ads}} \)) at different temperatures was calculated from the following equation:

\[
\Delta G_{\text{ads}} = -RT \ln (55.5K) \quad \ldots(4)
\]

where \( K \) is given by

\[
K = \frac{\theta}{C (1-\theta)} \quad \ldots(5)
\]

where \( \theta \) is the degree of coverage on the metal surface, \( C \) is the concentration of inhibitor in mol L\(^{-1}\), the value of 55.5 is the concentration of water in solution expressed in mol\(^{-1}\) and \( K \) is the equilibrium constant. The values of \( \Delta G_{\text{ads}} \) are given in Table 3.
Table 3—Free energy of adsorption ($\Delta G_{ads}$) for 302 SS in acidic media in the absence and presence of various concentrations of inhibitor.

<table>
<thead>
<tr>
<th>Concentration of MPT (M)</th>
<th>$\Delta G_{ads}$ (kJ mol$^{-1}$)</th>
<th>283 K</th>
<th>293 K</th>
<th>303 K</th>
<th>313 K</th>
<th>323 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>In 1 M HCl</td>
<td></td>
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<td></td>
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<td></td>
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<tr>
<td>0</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>0.004</td>
<td></td>
<td>51.0</td>
<td>53.1</td>
<td>54.5</td>
<td>57.4</td>
<td>59.5</td>
</tr>
<tr>
<td>0.005</td>
<td></td>
<td>51.5</td>
<td>54.1</td>
<td>55.4</td>
<td>57.9</td>
<td>59.9</td>
</tr>
<tr>
<td>0.006</td>
<td></td>
<td>53.1</td>
<td>55.3</td>
<td>57.3</td>
<td>59.8</td>
<td>63.3</td>
</tr>
<tr>
<td>0.007</td>
<td></td>
<td>55.5</td>
<td>56.5</td>
<td>58.2</td>
<td>61.0</td>
<td>63.8</td>
</tr>
<tr>
<td>In 1 M H$_2$SO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.004</td>
<td></td>
<td>57.6</td>
<td>59.3</td>
<td>61.3</td>
<td>63.6</td>
<td>64.3</td>
</tr>
</tbody>
</table>

The negative values of $\Delta G_{ads}$ suggest the strong interaction of the inhibitor molecules onto the alloy surface$^{29,30}$. The values of surface coverage ($\theta$) were plotted against log C for different concentrations of the MPT. The straight line (Figs 8 and 9) thus obtained indicates that the adsorption of MPT on the 302 SS surface follows Temkin’s adsorption isotherm$^{31,32}$ in acidic media [Temkin isotherm: exp(-2$\alpha$)$\theta$/$KC$; $\alpha$ = molecular interaction parameter].

The results obtained from variations of adsorption free energies with the temperature (Figures are not shown) (Table 3) reveal that the $-\Delta G_{ads}$ decreases in the range of 283-323±1 K. The large negative values of $-\Delta G_{ads}$ indicate the spontaneous adsorption of the inhibitor and are usually characteristics of strong interaction with the metal surface. Generally values of $\Delta G_{ads}$ up to -20 kJ mol$^{-1}$ are consistent with the electrostatic interaction between the charged molecules and the charged metal (physical adsorption), while those which are more negative than -40 kJ mol$^{-1}$ involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (chemisorption)$^{33,34}$. The large values of $\Delta G_{ads}$ and its negative sign are usually characteristic of strong interaction and a highly efficient adsorption$^{26}$. The high value of $\Delta G_{ads}$ shows that in the presence of acidic media chemisorption of MPT may occur. Morad & El-Dean$^{35}$ stated that although some researcher results fit Langmuir isotherm, some authors attributed corrosion inhibition to physisorption while the results of others were interpreted as chemisorption.

Other thermodynamic parameters, such as adsorption enthalpy, $\Delta H$, and adsorption entropy $\Delta S$, can be derived from these data. Since $\Delta G = \Delta H - T\Delta S$, a plot of $\Delta G$ versus $T$ is a straight line with a slopes of 0.211 kJ mol$^{-1}$K$^{-1}$ and 0.177 kJ mol$^{-1}$K$^{-1}$ between 283-323 K. The overall results are in agreement with the values of IE. Using the values of $\Delta S$, adsorption enthalpies $\Delta H_{ads}$ were found to be 55.0 kJ mol$^{-1}$ and 57.5 kJ mol$^{-1}$ in hydrochloric acid and sulphuric acid solutions respectively.

The possible mechanisms for chemisorption can be attributed to the donation of $\pi$-electron in the aromatic rings, the presence of three nitrogen atoms and one sulphur in inhibitor molecule as reactive centers, electrostatic adsorption of the protonated azo compound in acidic solution on the metal surface. The slightly higher corrosion rate of 302 SS in hydrochloric acid solution in comparison to sulphuric acid solution may be attributed to the higher aggressiveness of hydrochloric acid compared to sulphuric acid. Such results have been reported earlier$^{37}$. Different researchers$^{38-40}$ have given different values of inhibition efficiency for steel in H$_2$SO$_4$ and HCl solutions, in the presence of inhibitors and some of them show better efficiency for the H$_2$SO$_4$ than HCl. Furthermore, in H$_2$SO$_4$, it seems that adsorption through the lone pairs of heteroatom and...
Π-electrons of the MPT molecule outweigh the adsorption due to the cationic form of the MPT molecule on the metal surface, i.e., in the presence of acid solution the N and S heteroatoms of the inhibitor molecules easily accommodate their pair of electrons to the d orbital of Fe$^{2+}$. This may be possible due to the shape of the sulphur and nitrogen orbitals of the heterocyclic compound.

Conclusions

The following conclusions may be drawn from the results of the study:

(i) MPT acts efficiently in 1 M sulphuric acid than in 1 M hydrochloric acid, perhaps the adsorption through the lone pairs of heteroatoms and Π-electrons of the MPT molecule outweighs the adsorption due to the cationic form of the MPT molecule on the metal surface. This adsorption is due to the shape of the sulphur orbitals of the heterocyclic compound.

(ii) The corrosion current density of 302 SS in acidic media decreases with an increase of MPT concentration while corrosion potential increases.

(iii) MPT inhibited corrosion by adsorption from acid solutions onto the steel surface following Temkin’s adsorption isotherm.

(iv) The calculated values of thermodynamic parameters ($\Delta G$, $E_a$, $\Delta H$, and $\Delta S$) show that the presence of inhibitor increase the activation energy whereas the negative values of $\Delta G$ indicate the spontaneous adsorption of the inhibitor on the surface of stainless steel.

References

31 Frumkin A, J Phys Chem, 166 (1925) 466.