Corrosion inhibition of mild steel in sulphuric acid by n-octylamine and iodoacetic acid

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The influence of iodoacetic acid (IAA) on the corrosion inhibition of mild steel in 0.5 M sulphuric acid (H$_2$SO$_4$) containing octylamine (OA) has been studied using weightloss, polarization and a.c. impedance techniques. Corrosion data obtained by different methods are consistent. IAA and OA individually retard the corrosion of mild steel in sulphuric acid. The addition of IAA enhances the inhibitor efficiency of OA considerably. Adsorption of inhibitors follows quasi-substitution process at the interfaces. OA cations are adsorbed by coulombic interaction on the metal surface, which is pre-occupied by IAA molecules as dipoles. Adsorption model is suggested to account the synergistic action of IAA on the corrosion inhibition of mild steel in sulphuric acid solution by OA.

Sulphuric acid is known to be the working horse in the pre-treatment (pickling) of mild steel components in metal finishing industries. Inhibitors are generally used in industries for surface treatment process to control both metal dissolution and acid consumption. Nitrogen containing compounds have been used as effective metallic corrosion inhibitors. Amines are good corrosion inhibitors for mild steel, where inhibitor efficiency enhances in the presence of anions. Usually adsorption of inhibitor molecules at the corroding metal surface-solution interface plays a dominant role in combating corrosion. Haloacetic acids are dipoles and control the corrosion of metals by structurally rearranging themselves at the metal-solution interface through adsorption. The aim of the present work is the study of effect of IAA on the corrosion inhibition of mild steel in sulphuric acid solution by n-OA by weightloss, polarization and electrochemical impedance spectroscopic measurements (EIS). The obtained corrosion data from different approach are compared. The co-operative inhibiting action of IAA and OA are explained by considering models involving adsorption of inhibitor molecules at metal-solution interface.

Experimental Procedure
All solutions were prepared using AR grade chemicals and double distilled water. Mild steel (C, 0.15%, Mn, 1.02%, Si, 0.8%, and P, 0.25%) in the form of cylindrical rod ($1cm^3$) embedded in Teflon holder was used. The surface was mechanically polished on emery paper (4/0 to 6/0) degreased with trichloroethylene and then washed before use. Corrosion rate was evaluated during weightloss measurement by estimating the amount of iron dissolved by colorimetric method, using 1-10 phenonthroline. Galvanostatic polarization studies were made by using potentiostat/galvanostat (PAR EG and G, USA model 362). A platinum foil of area $2\times2cm^2$ and a saturated calomel electrode (SCE) were used as auxiliary and reference electrodes, respectively.

During polarization measurement, the sweep rate was maintained as 1 mV s$^{-1}$. A.C impedance measurements were carried out at the open circuit potential using an electrochemical interface (1186 Solartron) from 0.1 Hz to 20 kHz by applying 4mV A.C voltage. Nyquist plots were made from these experiments. $R_{ct}$ and $C_{dl}$ values were evaluated as described earlier. Experiments were repeated to ensure reproducibility.

Results
Mild steel was dissolved for various periods of immersion in 0.5 M sulphuric acid solution at 303K without and with definite concentration of IAA ($1\times10^{-4}$ M), OA ($1\times10^{-3}$ M) and the mixture of both IAA ($1\times10^{-4}$ M) and OA ($1\times10^{-3}$ M). Mild steel was found to dissolve at a steady rate (Fig. 1). The
corrosion rate was decreased by the presence of IAA or OA. The extent of decrease in the corrosion rate was appreciable in the presence of both IAA and OA.

Anodic and cathodic polarization was carried out under galvanostatic condition in 0.5 M H₂SO₄ solution containing 1×10⁻³ M OA and different concentrations (1×10⁻⁴ to 1×10⁻² M) of IAA at 303K in the current density range (0.1 to 100 mA/cm²). Cathodic Tafel slopes were evaluated. Tafel slopes in H₂SO₄ solution was found to increase by the presence of inhibitors. The increase in polarization was observed in 0.5 M sulphuric acid solution containing definite concentration of both IAA and OA and it was more than that observed in presence of IAA or OA alone. Inhibitor efficiency (%IE) was calculated for a given concentration of the inhibitors by using the equation,

\[ %\text{IE} = \frac{i_{\text{cor}}^0 - i_{\text{cor}}}{i_{\text{cor}}^0} \times 100 \]  

where \( i_{\text{cor}}^0 \) and \( i_{\text{cor}} \) are the corrosion current densities of mild steel without and with inhibitor respectively.

The corrosion current density for \( i_{\text{cor}} \) for each inhibitor was evaluated by using the equation

\[ i_{\text{cor}} = b_a b_c / 2.303 R_p (b_a + b_c) \]  

where \( b_a \) and \( b_c \) are the anodic and cathodic Tafel slopes respectively and \( R_p \) is the polarization resistance.

Fig. 2 shows polarization curves obtained in 0.5 M sulphuric acid solution without and with inhibitors. Polarization data at different concentrations of IAA and OA are given in Table 1. Both anodic and cathodic kinetic parameters in 0.5 M sulphuric acid are not changed much in the presence of inhibitors. From these results it is evident that IAA influences the inhibition efficiency of OA.

Electrochemical impedance spectroscopic (EIS) technique is frequently used to evaluate corrosion rate at open circuit potential (OCP), which has an advantage over polarization technique. A physical description of any model for such a system is based on type of interface existing at the immediate vicinity of a corroding surface. The electrical properties of the interface affect the corrosion characteristics of the metal surface.

Fig. 3 represents Nyquist plots for mild steel in 0.5 M sulphuric acid and in the presence of various concentrations of OA. Similar results along with IAA are given in Fig. 4. Nyquist plots (Figs 3 & 4) are almost semi circulars in appearance but are not perfect semi circles and this difference is due to frequency dispersion. From these results the value of charge transfer resistance \( (R_\Omega) \), double layer capacitance \( (C_d) \) and inhibitor efficiency \( (%\text{IE}) \) are calculated and given in Table 2. \( R_\Omega \) value increases with the increase in the concentration of OA.

![Graph](image-url)

**Table 1—Galvanostatic polarization parameters for mild steel in 0.5 M H₂SO₄ containing different concentrations of IAA and OA at 303 K**

<table>
<thead>
<tr>
<th>IAA (M)</th>
<th>OA (M)</th>
<th>(-E_{\text{cor}}) (mV)</th>
<th>(b_a) (±5mVdec⁻¹)</th>
<th>(b_c) (±5mVdec⁻¹)</th>
<th>(i_{\text{cor}}) (µAcm⁻²)</th>
<th>(IE) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1×10⁻⁴</td>
<td></td>
<td>490.0</td>
<td>38.0</td>
<td>120.0</td>
<td>240.0</td>
<td>41.5</td>
</tr>
<tr>
<td>1×10⁻³</td>
<td></td>
<td>525.0</td>
<td>45.0</td>
<td>130.0</td>
<td>140.0</td>
<td>45.6</td>
</tr>
<tr>
<td>1×10⁻²</td>
<td></td>
<td>515.0</td>
<td>50.0</td>
<td>140.0</td>
<td>75.0</td>
<td>68.7</td>
</tr>
<tr>
<td>1×10⁻⁴</td>
<td></td>
<td>480.0</td>
<td>45.0</td>
<td>132.0</td>
<td>80</td>
<td>66.0</td>
</tr>
<tr>
<td>1×10⁻³</td>
<td></td>
<td>494.0</td>
<td>49.0</td>
<td>138.0</td>
<td>76.0</td>
<td>68.0</td>
</tr>
<tr>
<td>1×10⁻²</td>
<td></td>
<td>495.0</td>
<td>51.0</td>
<td>141.0</td>
<td>70.0</td>
<td>70.0</td>
</tr>
</tbody>
</table>
Fig. 2—Galvanostatic polarization (anodic and cathodic) of mild steel in 0.5 M H₂SO₄ (●), in presence of 1x10⁻³ M OA (O), 1x10⁻⁴ M OA (Δ) and 1x10⁻³ M OA + 1x10⁻⁴ M IAA (■) at 303 K.

extent of increase in $R_{ct}$ value further increases by the presence of IAA. The reverse trend is observed in the case of dependence of $C_{dl}$ on inhibitor concentration.

Discussion
The variation of weightloss with time in the present system (Fig. 1) indicates the absence of passivating film on the corroding metal surface. Under this situation, corrosion of mild steel in acidic solution is the result of consecutive steps: anodic dissolution of iron and the cathodic evolution of hydrogen. Corrosion inhibition is a surface process, which involves the specific adsorption of inhibitor molecules at the metal-solution interface. The extent of inhibition depends on the nature of the surface (surface heterogeneity and surface charge) and structure of the inhibitor molecule.

The metal surface in aqueous solution is always covered with adsorbed water dipoles. Hence, adsorption of inhibitor molecules at the metal-solution...
Table 2—Impedance parameters for mild steel in 0.5 M H₂SO₄ containing 2x10⁻³ M IAA and in the presence of various concentrations of OA at 303 K

<table>
<thead>
<tr>
<th>OA (M)</th>
<th>Rₑ (Ohm)</th>
<th>Cₑ (μF)</th>
<th>iₑ (μAcm⁻²)</th>
<th>IE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1x10⁻³</td>
<td>32 (69)</td>
<td>21.7 (11.7)</td>
<td>115 (63)</td>
<td>40 (68)</td>
</tr>
<tr>
<td>2x10⁻³</td>
<td>60 (85)</td>
<td>15.6 (7.1)</td>
<td>102 (58)</td>
<td>46 (70)</td>
</tr>
<tr>
<td>4x10⁻³</td>
<td>82 (107)</td>
<td>11.1 (4.3)</td>
<td>98 (41)</td>
<td>48 (79)</td>
</tr>
<tr>
<td>6x10⁻³</td>
<td>121 (183)</td>
<td>8.9 (3.1)</td>
<td>94 (32)</td>
<td>51 (83)</td>
</tr>
<tr>
<td>8x10⁻³</td>
<td>136 (264)</td>
<td>4.6 (2.5)</td>
<td>70 (29)</td>
<td>63 (85)</td>
</tr>
<tr>
<td>1x10⁻²</td>
<td>239 (315)</td>
<td>2.3 (1.0)</td>
<td>61 (24)</td>
<td>68 (88)</td>
</tr>
</tbody>
</table>

Values in presence of 2x10⁻³ M IAA are given in the parenthesis.

Table 3—Comparison of Inhibitor efficiency by impedance and polarization methods in 0.5 M H₂SO₄ containing 2x10⁻³ M IAA and in presence of different concentrations of OA at 303K

<table>
<thead>
<tr>
<th>OA (M)</th>
<th>% Inhibitor Efficiency</th>
<th>EIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1x10⁻³</td>
<td>44 (70)</td>
<td>40 (68)</td>
</tr>
<tr>
<td>2x10⁻³</td>
<td>46 (73)</td>
<td>46 (70)</td>
</tr>
<tr>
<td>4x10⁻³</td>
<td>49 (78)</td>
<td>48 (79)</td>
</tr>
<tr>
<td>6x10⁻³</td>
<td>51 (80)</td>
<td>51 (82)</td>
</tr>
<tr>
<td>8x10⁻³</td>
<td>59 (85)</td>
<td>63 (85)</td>
</tr>
<tr>
<td>1x10⁻²</td>
<td>61 (91)</td>
<td>68 (88)</td>
</tr>
</tbody>
</table>

Values in presence of 2x10⁻³ M IAA are given in parenthesis.

interface is similar to quasi-substitution process¹⁵, which is well documented,

Inhibitor (soln) + nH₂O (ads) ↔ Inhibitor (ads) + nH₂O (soln) 

IAA is a dipole with high polarizability. It adsorbs strongly on the metal surface and inhibits the corrosion process. OA undergoes protonation in aqueous acidic solution and available in the form of cations (OAH⁺). The OAH⁺ ions (R⁺) preferentially concentrate on the surface pre-occupied by IAA dipoles because of coulombic attraction. The extent of adsorption and corrosion inhibition by two types of inhibitors depends on the relative concentration of inhibitors.

On the basis of early literature on the subject and the observed corrosion data of the present system, one could propose two adsorption models—one at lower concentrations of IAA and OA (Fig. 5a) and another at lower concentration of IAA and higher concentration of OA (Fig. 5b). Stabilization of adsorbed IAA by means of electrostatic interaction between negative pole of IAA (X) and OAH⁺ (R⁺) leads to greater surface coverage and hence greater inhibition. This is further in support of increase in Rₑ or decrease in Cₑ by the presence of inhibitor (Table 2) for the cooperative action. At lower concentration (1x10⁻⁴) of OA [X]>[R⁺], it is possible that R⁺ cations are weakly bound to the negative pole of IAA [X], which can be adsorbed directly on the metal surface (model 6A).

On increasing the concentration of OA (1x10⁻³), R⁺ cations [X]<[R⁺] tend to draw the adsorbed X⁻ dipole into the solution and hence co-adsorption of X⁻ and R⁺ cations is possible (model 6B). The impedance measurements are based on the consideration that an electrochemical cell representing the corroding system is analogous to an electric circuit consisting of an array of resistors and capacitors. This allows the use of equivalent circuit, which represents the present electrochemical system. Fig. 5e is a simple Randles type of equivalent circuit proposed to the corroding mild steel surface and sulphuric acid solution containing inhibitor molecules. For such equivalent circuit, Z can be shown to be

\[ Z = Z₀ - jωZ' \]  ... (4)

where, \( Z₀ = Rₑ + Rₐ + 1 + ω^2 Cₑ^2 Rₑ^2 \)  ... (5)

and \( Z' = ω Cₑ Rₑ^2 1 + 1 + ω^2 Cₑ^2 Rₑ^2 \)  ... (6)

where ω is frequency at which \( Z' \) is maximum and j is imaginary component.
Surface Coverage ($\theta$) is calculated for each concentration of IAA or OA from the impedance data. Variation of $\theta$ in the presence of OA in different concentrations of IAA follows the Langmuir isotherm. A plot of $C/\theta$ against $C$ (inhibitor concentration) gives a straight line (Fig. 5).

**Conclusion**

(i) Octylamine inhibits the corrosion of mild steel in 0.5 M sulphuric acid solution and extent of corrosion inhibition enhances by the presence of trace concentration of IAA.

(ii) Corrosion data from weightloss, polarization and EIS techniques are comparable under identical experimental conditions.

(iii) Corrosion inhibition involves interfacial adsorption of Octylamine cations and Idoacetic acid in the form of quasi-substitution process.

(iv) Synergistic action of Idoacetic acid towards corrosion inhibition is explained by considering the coulombic and electrostatic attractions of Octylamine cations and negative pole of dipolar Idoacetic molecule on the corroding surface respectively.

(v) Adsorption model and electrical circuit are proposed to account the corrosion inhibition and capacitive behaviour prevailing at the interface.

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