Inhibition effect of some aniline compounds on corrosion of mild steel in 3% HF

S Vishwanatham & Emranuzzaman
Department of Applied Chemistry, Indian School of Mines, Dhanbad 826 004, India
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The corrosion inhibition efficiencies (IE%) of aniline (AL), p-toluidine (PTD), p-anisidine (PAD), p-phenetidine (PPD) and N,N-dimethyl aniline (DMA) have been evaluated in 3% HF by weight loss and potentiostatic polarisation methods. PAD is the best inhibitor and IE% can be classified in the following order: PAD > PPD > PTD > DMA > AL. The effect of temperature (range 303-333 K) on the corrosion behaviour of mild steel in plain HF solution and inhibited acid was also studied. The corrosion rate increased with increasing temperature both in uninhibited and inhibited acid and the values of IE% of all the inhibitors depend on temperature. The inhibitors act as mixed adsorption type inhibitors. Adsorption of AL, DMA and PTD on mild steel in 3% HF interface corresponds to Langmuir adsorption isotherm model while PAD and PPD appear to adsorb on the metal surface according to Temkin adsorption isotherm.

Experimental Procedure

In the acidization operation of oilwell for enhanced oil recovery, HF or some other acid is pumped into oilwell to remove pluggings of CaCO₃ or scales. As the acids severely affect the casing and tubing of the oilwell, some corrosion inhibitors are added along with the acids. Some commercial inhibitors are being used for acidization treatment of oilwell. Quaraishi et al. have studied the inhibition characteristics of a heterocyclic compound (synthesized inhibitor) along with propargylic alcohol (a commercially available acidizing inhibitor) in 15% HCl. Several classes of organic substances have been tested for pure iron and plain steel in HF solutions. Aniline compounds have been found to be effective inhibitors for mild steel in HCl whereas these compounds have not been investigated as corrosion inhibitors for mild steel in HF. The paper describes corrosion inhibition behaviour of mild steel in 3% HF in presence of some aniline compounds.
where \( I \) is current density, \( D \) is specimen density and eq wt is the specimen equivalent weight. The details regarding corrosion studies and potentiostatic experiments are reported earlier\(^{14,15}\).

**Results and Discussion**

The results of the effect of various concentrations of inhibitors are presented in Table 1. \( I_{E\%} \) of inhibitors was calculated by using the equation,

\[
I_{E\%} = \frac{W_u - W_i}{W_u} \times 100
\]

where \( W_u \) is the average weight loss of mild steel sample in 3% HF solution without inhibitor and \( W_i \) is the average weight loss of the sample in 3% HF containing inhibitor. PAD has shown maximum inhibition of 94.9% at 50.0 mM concentration, while AL exhibited 72.7% inhibition at the same concentration. \( I_{E\%} \) of all the inhibitors increases with increase in inhibitor concentration. pH variations of the test solutions after addition of 50.0 mM concentration of the inhibitors were found to be 3.65, 3.70, 3.76, 3.76 and 3.67 in case of AL, PTD, PPD, PAD and DMA respectively whereas it was 3.64 in case of plain acid solution. Though, there is slight shift (\( \approx 0.12 \)) of pH in basic region after addition of the inhibitors to the test solution, the inhibition effect may be mainly due to addition of the inhibitors. PAD is the best inhibitor and \( I_{E\%} \) of the additives decreases in the following order:

PAD > PPD > PTD > DMA > AL

\( I_{E\%} \) of all the tested inhibitors in 3% HF at room temperature gradually decreased with exposure period (Table 2). The, inhibition conferred by AL, DMA, PTD, PPD and PAD after 36 h exposure was found to be 67.0, 70.7, 70.8, 81.7 and 84.8% respectively. The relative decrease in \( I_{E\%} \) with time is less pronounced in case of PAD.

The degree of surface coverage(\( \theta \)) at each case was calculated\(^{16}\) from the results of weight loss test using the equation,

\[
\theta = \frac{W_u - W_i}{W_u - W_m}
\]

where \( W_u \) and \( W_i \) are weight loss in uninhibited and inhibited solution and \( W_m \) is the weight loss in case of maximum inhibition. \( \theta \) when plotted against log concentration showed a linear plot indicating Temkin adsorption isotherm\(^{17}\) in the case of PPD and PAD (Fig.1). In the case of PTD, DMA and AL a straight line relationship is observed (Fig.2) when log \( \theta /1-\theta \) is plotted against log inhibitor concentration and hence, Langmuir adsorption isotherm\(^{17}\) is obeyed. Corrosion rates are generally decreased with increase of inhibitor concentration at all temperatures. At the same temperature and inhibitor concentration PAD is more efficient than the other tested inhibitors for retarding the corrosion of the mild steel in 3% HF. Activation energies, \( E_a \) were calculated from slopes of the Arrenhius plots (Fig. 3) and heat of adsorption (Fig. 4) was calculated from slopes of the plots of log \( \theta /1-\theta \) vs 1/\( T \). The values of \( E_a \) in the inhibited solutions are found to be higher compared to that in the uninhibited one and increased with inhibitor concentration which indicates that dissolution of
values of heat of activation ($\equiv 11-16$ kcal) and heat of adsorption ($\equiv 13-21$ kcal) may be attributable to chemisorption.

Fig. 5 shows variation of open circuit potential ($OCP$) with time. $OCP$ of AL, PTD, PAD, PPD and DMA is found to be -570, -570, -550, -590 and -560 mV respectively which shows more positive value than the uninhibited solution ($OCP = -690$ mV). The positive shift of potential and its early steady state in case of inhibited solution is attributed to the formation of protective surface film. Polarisation measurements of mild steel were carried out at 25.0 mM concentration of the inhibitors. Fig. 6 shows the polarisation curves for mild steel in 3% HF without and with 25.0 mM of the inhibitor at room temperature. Inspection of the figure reveals that all the inhibitors significantly lowered $i_{corr}$ values indicating corrosion inhibition. The values of $OCP$ in the presence of inhibitors are shifted towards the noble direction. The shift of the cathodic and anodic partial curves in the presence of inhibitors suggests that these inhibitors are adsorbed on the surface of the mild steel and affect both anodic and cathodic areas.
Table 2—Effect of exposure period on inhibitor efficiency of aniline compounds for corrosion of mild steel in 3% HF

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Exposure period, h</th>
<th>Inhibitor efficiency, IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>Nil</td>
<td>(460.9)</td>
<td>(402.3)</td>
</tr>
<tr>
<td>AL</td>
<td>74.9</td>
<td>74.7</td>
</tr>
<tr>
<td>PTD</td>
<td>78.7</td>
<td>77.0</td>
</tr>
<tr>
<td>PAD</td>
<td>90.8</td>
<td>91.3</td>
</tr>
<tr>
<td>PPD</td>
<td>87.7</td>
<td>85.9</td>
</tr>
<tr>
<td>DMA</td>
<td>78.5</td>
<td>76.9</td>
</tr>
</tbody>
</table>

Values in parentheses indicate corrosion rate in mpy.

The inhibition of the cathodic reaction may be due to onium ions (RNH₃) produced in the acid solution.

RNH₂ + H⁺ = RNH₃ (from acid solution)

RNH₃ + M = (RNH₃)_ads

The onium ions may adsorb on cathodic areas on the metal (M) surface by means of electrostatic attraction¹⁸. The inhibition of the anodic partial reaction may be attributed to chemisorption of unprotonated inhibitor molecule on the anodic metal surface through the co-ordination between the metal and solitary electron pair on nitrogen atom (Fig. 7). The inhibition of the anodic reaction may depend on the adsorptive power of the inhibitor, the coverage area and the spatial effect of the adsorbed molecule. The adsorptive power depends on density of the electron cloud on the polar atom and its electron releasing power. Since the metal and the compound are Lewis acid and bases, stability of the adsorption bond is closely related to the hard and soft acids and bases (HSAB).
principle. According to concept of the HSAB principle\textsuperscript{19,20}, "hard" acids and bases are atoms and ions holding valency electrons tightly and "soft" acids and bases are those holding the electrons loosely. Most of polar organic compounds($R_nX$) acting as corrosion inhibitors are chemically adsorbed on surface of bulk metal, $M$ forming a charge transfer complex\textsuperscript{21} bond between their polar atom and the metal as 

$M + R_nX: \rightleftharpoons M:XR_n$

In the case of aniline compounds also the inhibitor efficiency may be due to formation of similar charge transfer complex. In a study of the inhibition efficiency of mild steel in HCl in presence of toluidines, Balezin et al.\textsuperscript{11} reported that toluidines are capable of forming similar insoluble surface complexes which offer corrosion protection. Aniline is a weaker base due to resonating structures. In aniline the N-atom is bonded to an $sp^2$ hybridised carbon atom but, the unshared electron pair on N-atom can interact with the delocalised $\pi$-orbitals of the nucleus. If aniline is protonated stabilisation is prohibited. Aniline molecule is energetically unprofitable to take up proton and therefore, functions as a weak base. An electron releasing group(\textemdash CH$_3$), that has plus inductive effect (+I), on aniline increases its basicity because it reduces the resonance of an NH$_2$ group. In the case of PAD, the methoxy group having a strong resonance (+R) effect increases the basicity resulting in relatively high corrosion inhibition.

**Conclusion**

The inhibition of the aniline compounds is due to their adsorption. PAD and PPD obey Temkin adsorption isotherm, whereas AL, DMA and PTD exhibit Langmuir adsorption isotherm. (+R) effect of the substituents on aniline tends to increase the basicity of PAD. PAD conferred maximum inhibition of 94.9% at 50.0 mM concentration in 3% HF. The aniline compounds act on both cathodic and anodic reactions and hence, they are mixed inhibitors.

**References**