Inhibition of corrosion of mild steel by nitrite, hydrogen phosphate and molybdate ions in aqueous solution of sodium chloride

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Inhibition of mild steel in aqueous sodium chloride by sodium nitrite, disodium hydrogen phosphate and sodium molybdate with respect to the inhibitor concentration and temperature is reported here. Na$_2$MoO$_4$ shows highest efficiency (90.00%) followed by NaNO$_2$ (87.56%) and Na$_2$HPO$_4$ (85.36%). As such, the order of inhibition observed is Na$_2$MoO$_4$ > NaNO$_2$ > Na$_2$HPO$_4$. Thermodynamic as well as kinetic parameters including activation energy ($E_a$), change in free energy of adsorption ($\Delta G$), entropy of adsorption ($\Delta S$), corrosion current ($I_{corr}$), open circuit potential (OCP). Tafel slopes ($\beta_a$, $\beta_c$) and threshold limiting value (TLV) for protective film formation have also been calculated from weight loss and potentiostatic polarisation methods.

Sodium chloride is present in large concentrations in all types of water, potable as well as marine water. Sodium chloride concentration varies from 150 ppm to 2000 ppm in various types of water; for drinking water allowable below 1000 ppm$^1$, and 250 ppm for aesthetic value as per WHO guidelines. But, the presence of large concentration of sodium chloride$^2$ is harmful for water pipeline material because of aggressive behaviour of chloride ions towards corrosion and increase in conductivity of the solution by strong acid and strong base formed after hydrolysis in spite of a slight variation in pH of aqueous solution of sodium chloride.

Various studies have been carried out to mitigate the corrosion of metals due to sodium chloride by organic as well as inorganic inhibitors$^{3-7}$. The addition of these inhibitors in large amounts in potable water may change the quality of potable water resulting in various health hazards.

Sodium nitrite, disodium hydrogen phosphate, sodium molybdate are among the suitable inorganic corrosion inhibiting ions, which can control the corrosive behaviour of sodium chloride without affecting the quality of water to a great extent. Before controlling the corrosion in water pipelines, it is important to identify the factors which influence corrosion reactions as well as the mutual effect of ions on one another, particularly while investigating aqueous solutions containing mixture of ions$^8$.9.

Electrochemical and weight loss investigations for mild steel in aqueous solution of NaCl in presence of sodium nitrite, disodium hydrogen phosphate, and sodium molybdate as corrosion inhibitors are reported here.

Experimental

Weight loss studies were performed on heat-treated mild steel square specimens (2x2 cm$^2$ of 0.03 cm thickness). The chemical composition of mild steel was determined by known chemical methods$^{10,12}$ and found to be: C 0.22%, S 0.018%, Ni 0.25%, Mn 0.62%, P 0.022%, Mo 0.15%, Si 0.28%, Cr 0.095%, Cu 0.20%, besides iron. The specimens were degreased in benzene, washed with 50% acetone, dried and weighed. Cleaned specimens were suspended by a glass hook in the aqueous solution of sodium chloride (concentrations ranging from 200 to 3000 ppm) (pH-7) for 24 h. Corroded coupons were then cleaned in a solution of hydrochloric acid, 50 g/L stannous chloride and 20 g/L antimony(III) chloride$^{10}$ and weighed. Temperature of corrosive medium was controlled from 293 K to 353 K for 24 h immersion period. Experimental set up for polarisation measurements consisted of potentiostat/galvanostat model CL-95 of Elico with a sweep current generator and three electrode cell. All potential values were recorded on the saturated calomel (SCE) scale.

Results and Discussion

The effect of sodium chloride concentration on corrosion rate (mg/dm$^2$) and open circuit potential recorded immediately after the immersion of specimen in corrosive media against reference calomel electrode, is shown in Fig. 1. The Figure shows that cor-
Fig. 1 - Effect of sodium chloride concentration on (a) weight loss and (b) potential of mild steel in aqueous solution of sodium chloride.

The corrosion rate and inhibition efficiency (IE) (calculated on percentage basis) of mild steel increases with the increase in concentration of inhibitor and decreases with the increase in concentration of inhibitor and the increase in temperature. The inhibition efficiency increases with the increase in concentration of inhibitor and decreases with the increase in temperature. The inhibition efficiency increases with the increase in concentration of inhibitor and decreases with the increase in temperature. The inhibition efficiency increases with the increase in concentration of inhibitor and decreases with the increase in temperature. The inhibition efficiency increases with the increase in concentration of inhibitor and decreases with the increase in temperature.

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Table 1 - Effect of temperature on corrosion rate, inhibition efficiency (IE%), energy of activation (E_a), heat of adsorption (Q), free energy of adsorption (ΔG) and entropy of adsorption (ΔS) for mild steel in 600 ppm sodium chloride aqueous solution.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Conc. (mg/dm²)</th>
<th>Temperature (K)</th>
<th>Wt. Loss mg/dm²</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.03</td>
<td>308.15</td>
<td>28.125</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>318.15</td>
<td>34.625</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>328.15</td>
<td>40.625</td>
<td>100</td>
</tr>
<tr>
<td>NaNO₂</td>
<td>0.03</td>
<td>338.15</td>
<td>51.250</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>338.15</td>
<td>51.250</td>
<td>100</td>
</tr>
<tr>
<td>NaHPO₃</td>
<td>0.03</td>
<td>308.15</td>
<td>5.500</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>318.15</td>
<td>7.000</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>328.15</td>
<td>7.978</td>
<td>100</td>
</tr>
<tr>
<td>Na₂MoO₄</td>
<td>0.03</td>
<td>338.15</td>
<td>10.750</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>338.15</td>
<td>10.750</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>338.15</td>
<td>10.750</td>
<td>100</td>
</tr>
</tbody>
</table>

ΔS (JK/mol): 100.03, 100.03, 100.03, 100.03, 100.03, 100.03, 100.03, 100.03, 100.03

Where W_i is the weight loss of the inhibited medium and W_o is the weight loss of metal in inhibited medium. The weight loss in presence of NaCl in absence of inhibitors at different temperatures and at varying inhibitors concentration is shown in Table 1 along with inhibition efficiency, E_o, ΔG, ΔS, and Q values.
MEHRA & SONI: INHIBITION OF CORROSION OF MILD STEEL BY NITRITE

In solutions containing various inhibitors, $E_a$ values are found to be slightly higher, i.e., 19.20, 20.50, 22.22 kJ mol$^{-1}$ for NaNO$_2$; 18.19, 19.12, 21.11 kJ mol$^{-1}$ for disodium hydrogen phosphate; and 21.14, 24.52, 26.12 kJ mol$^{-1}$ for sodium molybdate (at 0.03, 0.05 and 0.10% inhibitor concentration, respectively).

Heat of adsorption ($Q$) and free energy of adsorption $\Delta G$ were calculated by using\textsuperscript{12}:

\[
\log C = \left[ \log \left( \frac{\theta}{1-\theta} \right) - \log \beta \right]
\]

where $\log \beta = -1.74 - (C_{AV}/2.303 RT)$ and $\theta$ and $(1-\theta)$ are the surface coverage and open surface at any temperature.

Heat of adsorption ($Q$) was computed using\textsuperscript{14}:

\[
Q = 2.303 R \left[ \left\{ \log \left( \frac{\theta_2}{1-\theta_2} \right) \right\} - \left\{ \log \left( \frac{\theta_1}{1-\theta_1} \right) \right\} \right] \left( \frac{T_2 - T_1}{T_1 x T_2} \right)
\]

where $\theta_1$ and $\theta_2$ are the fractions of the metal surface covered by the inhibitors at temperatures $T_1$ and $T_2$ respectively and $(1-\theta_1)$ and $(1-\theta_2)$ are the open surfaces which react with the studied aggressive ions.

Surface coverage ($\theta$) is calculated using:

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

where, $W_u$ is the weight loss in uninhibited corrosive medium and $W_i$ is the weight loss in inhibited corrosive medium.

The $Q$ values are very less at low inhibitor concentration, increase as the inhibitor concentration increases ranging from 3.3 to 6.6 kJ mol$^{-1}$ for NaNO$_2$, 2.0 to 5.3 kJ mol$^{-1}$ for Na$_2$HPO$_4$, and 3.8 to 7.0 kJ mol$^{-1}$ for Na$_2$MoO$_4$. The average $\Delta G$ value for all the cases are negative. The Na$_2$MoO$_4$ inhibitor gives more negative free energy of adsorption than NaNO$_2$ and Na$_2$HPO$_4$, supporting the order of reported inhibition efficiency for these inhibitors. The comparison with MoO$_4^2$ has not been investigated\textsuperscript{16-17}.

Thus, with the increase in concentration of inhibitors, $\Delta G$ becomes less negative depicting decrease in corrosion rate. Similarly, with temperature, $\Delta G$ becomes more negative indicating the increase in corrosion rate with temperature which supports the Arrhenious relationship of temperature and reaction rate. $\Delta S$ (as given in Table 1) has been calculated by using the Gibbs-Helmholtz equation:

\[
\log W_2/W_1 = E_a/2.303 R (1/T_1 - 1/T_2)
\]

where $W_1$ & $W_2$ are the corresponding weight loss at temperature $T_1$ and $T_2$ (K), respectively. The Figure also depicts the Arrhenius plots for weight loss at different temperature and concentration of various inhibitors. The higher slopes in presence of inhibitors show high activation energy value. The $E_a$ values given in Table 1 show that the energy of activation for the corrosion of mild steel in 600 ppm NaCl solution is ~ 17.79 kJ mol$^{-1}$.
Fig. 3—Potentiostatic polarisation curves for corrosion of mild steel in aqueous solution of 600 ppm sodium chloride at varying inhibitor concentration [(a) Blank, (b) NaNO₂, (c) Na₂HPO₄, (d) Na₂MoO₄]

\[ \Delta G = Q - T \Delta S \]

The values of \( \Delta S \) are higher for Na₂MoO₄ than NaNO₂ and Na₂HPO₄ which range from 100.3 to 106.00 JK⁻¹mol⁻¹ for NaNO₂, 98.47 to 104.14 JK⁻¹mol⁻¹ for Na₂HPO₄ and 117.629 to 124.7 JK⁻¹mol⁻¹ for Na₂MoO₄ (for 0.03-0.10% concentration).

A comparison of IE%, \( \Delta G \), \( \Delta S \), \( E_{in} \), \( Q \) reveals that negative value of \( \Delta G \), small \( Q \) value and high \( E_{in} \) values are associated with high inhibition efficiency.
Polarisation behaviour

Anodic and cathodic polarization curves for mild steel in 600 ppm NaCl solution (in absence and presence of inhibitor) are given in Fig. 3 at 35±1°C. With the increase in concentration of inhibitor, curves become anodically polarised indicating film formation at the anodic sites. The values of various kinetic parameters of Tafel plots are given in Table 2. The OCP values shift towards less negative with the increase in concentration of inhibitor. The values of log $\text{I}_{\text{corr}}$ and $\text{I}_{\text{corr}}$ (µA/cm²) also decrease in the presence of inhibitor. For blank solution, log $\text{I}_{\text{corr}}$ is 1.05 µA/cm², which decreases in presence of NaN0₂ by 0.32, 0.16, 0.06 µA/cm² for NaN0₂, 0.42, 0.14, 0.13 µA/cm² for Na₂HPO₄ and 0.27, 0.09, 0.08 µA/cm² for Na₂MoO₄ (at 0.03, 0.05 and 0.10% inhibitor concentration respectively). Inhibition efficiencies calculated from corrosion current obtained by extrapolation of Tafel slopes to OCP are also given in Table 2. In almost all cases, the Tafel plot efficiencies agree well with the values obtained from weight loss data.

Mechanism

The inhibiting behaviour of these inhibitors is due to the formation of thin films on the surface of metal. The metal surface in contact with aqueous solutions becomes electron deficient, i.e. positively charged and higher electron density centres in anions of inhibitors get adsorbed on the metal surface to form a protective film. In case of NaN0₂, nitrogen as well as oxygen atoms have high electron density, hence both act as reaction centres. Similarly, in Na₂HPO₄ phosphorous as well as oxygen atoms act as reaction centres and in Na₂MoO₄ oxygen atom acts as reaction center.

The adsorption models of NaN0₂, Na₂MoO₄ and Na₂HPO₄ are shown in Fig. 4, according to which Na₂MoO₄ has greatest inhibition efficiency due to strong adsorption on mild steel followed by NaN0₂ and Na₂HPO₄.

The TLV values (the concentration of inhibitors required to inhibit corrosion) were determined by varying inhibitor concentrations up to 2.0%. It was found that at 308.15 K, Na₂MoO₄ gives nearly 100% inhibition efficiency at 0.9%, NaN0₂ at 1.2% and Na₂HPO₄ at 2.0%. At these concentrations, the weight loss becomes zero for 24 h immersion period and protection efficiency becomes nearly hundred percent, TLV values for Na₂MoO₄, NaN0₂ and Na₂HPO₄ being 0.9%, 1.2% and 2.0% at 308.15 K.
Conclusions
The corrosion rate of mild steel has direct relationship to the concentration of NaCl in aqueous solution and has an inverse relationship with inhibitor concentration. The efficiency of inhibitors decreases in the order $Na_2MoO_4 > NaNO_2 > Na_2HPO_4$. The interaction between inhibitor and mild steel surface is accomplished by negative free energy, low $Q$ values high $\Delta S$ values, high $E_a$ values and high value of inhibition efficiency with increase in concentration of inhibitor.

References