Corrosion kinetic studies of mild steel in methanol-hydrochloric acid solution

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The dissolution kinetics of mild steel and hydrogen evolution reactions in deaerated methanol-hydrochloric acid solutions at different concentrations of chloride and hydrogen ions have been investigated. The dissolution rate is found to increase with an increase in chloride content at constant acid concentration and the reaction order with respect to Cl⁻ is 1.12. The hydrogen evolution reaction rate slightly decreases as the concentration of Cl⁻ increases. The kinetic parameters derived from the electrochemical studies have been found to be very close to the values obtained by weight loss measurements. The reaction order for hydrogen evolution reactions is found to be very low (0.33).

The introduction of alcohols such as methanol and ethanol as an alternative fuel has created new corrosion problems in the automotive and alcohol manufacturing industries¹⁻⁵. This type of corrosion occurs during the contact between metal and methanol fuel and has been found to be divided into (a) corrosion by bulk methanol and (b) corrosion by methanol combustion products which is very common in fuel transport and in fuel storage equipments⁴⁻⁵. Corrosion rates of steel in methanol and methanol-water solutions are fairly well known⁶⁻⁹. However, the effect on corrosion rates in presence of impurities such as, chloride ions, acidity, and dissolved salts in methanol, methanol-water systems are of increasing interest for the researchers.

Keeping in view of the above practical applications of methanol, in the present work, a detailed study has been carried out on the effect of impurities such as Cl⁻, H⁺, etc. on the electrochemical behaviour of mild steel influencing the corrosion kinetics.

Experimental Procedure

Cold rolled mild steel (0.12% C) sheet test pieces (1 cm²) were polished with emery paper down to 600 grit, then rinsed in distilled water followed by methanol, dried in air and placed in desiccator. Methanol (0.1% water content), anhydrous LR grade lithium chloride, AR grade hydrochloric acid (37% by wt) were used for the preparation of solutions. All experiments were performed at 25°C in two types of solutions as given below;

(i) Fe/CH₃OH + 0.1 M HCl + LiCl

(Concentration of lithium chloride varied from 0.4 to 1.9 M)

(ii) Fe/mM LiCl + nM HCl

(m + n = 1)

The water content in the final solution was always kept constant and it was 0.5% by volume in 0.1 M HCl (maximum content in the experiment) solution of methanol.

Conventional weight loss and electrochemical measurements were carried out in deaerated solution of 0.1 M HCl in methanol.

The electrochemical studies were performed using a Princeton Applied Research Potentiostat (model 273) under galvanostatic mode. A saturated calomel reference electrode and platinum as counter electrode were used.

Results and Discussion

Role of chloride ion—The weight loss of mild steel specimens as a function of exposure time in methanol solution containing Cl⁻ ions at a constant H⁺ ion concentration (0.1 M) is shown in Fig. 1 at 25°C. The weight loss value increases linearly with increasing time which suggests the absence of any insoluble surface films during corrosion.
The relationship between corrosion rate and chloride ion concentration at a constant H⁺ ion concentration (0.1 M) is shown in Fig. 2. The corrosion rate increases linearly with an increase in Cl⁻ ion concentration. This suggests a direct participation of Cl⁻ ions in the dissolution process of the metal.

The anodic and cathodic polarization curves of mild steel in methanol + HCl + LiCl solutions were recorded keeping constant either the values of H⁺ ion concentration or Cl⁻ ion concentration. In the first set of experiments the H⁺ ion was kept constant. The experimental curves are given in Fig. 3. The chloride ion concentration was varied between 0.5 and 2.0 M. Increasing the chloride concentration shifted the polarization curves in a more active direction. This means that the rate of anodic reaction is increased by the Cl⁻. For all the Cl⁻ concentrations a Tafel slope of approximately 70 mV/decade was obtained in the vicinity of the corrosion potential. There is no remarkable difference between the cathodic polarization curves at all the concentration of Cl⁻ ions. At higher cathodic Tafel region, they tend to converge each other (beyond -550 mV) indicating the same mechanism in all the cathodic reactions. The cathodic Tafel slope remains almost constant, i.e., 120-125 mV/decade suggesting that the H⁺ ions (actually R−OH₂⁺ in the case of alcohols) take part in the cathodic reduction reaction.

The effect of the concentration of chloride ions on the corrosion potential is shown in Fig. 4. It is found that the corrosion potential changes linearly towards higher negative values with increase in the concentration of chloride ions and a relationship of the type:

$$\left[ \frac{\partial E_{corr}}{\partial \log [Cl^-]} \right] = -37 \text{ mV/decade} \quad \ldots (1)$$

has been observed.

The corrosion current density was determined by the intersection of the corrosion potential. The extrapolation of cathodic and anodic Tafel lines is
shown in Fig. 5. The corrosion current is found to increase with an increase in chloride ion concentration. The dependence of the corrosion current on the chloride ion concentration, as shown in Fig. 5, can be expressed by the relation:

$$\frac{\partial \log i_a}{\partial \log \text{Cl}^-} = 0.52$$  ... (2)

From the weight loss measurement the relationship between corrosion rate and chloride ion concentration is also deduced (Fig. 5) and a slope of 0.56 is observed; i.e.,

$$\frac{\partial \log \text{C.R.}}{\partial \log \text{Cl}^-} = 0.56$$  ... (3)

These values evaluated by the two techniques are in good agreement. This supports our observation that time has negligible role on the rate of corrosion (weight loss experiments were conducted by exposing the specimen for 3 h whereas polarization experiments were completed within 20 min).

The dependence of steel dissolution on the chloride ion concentration is shown in Fig. 6. The reaction order with respect to chloride ions is found to be 1.12, i.e.,

$$\frac{\partial \log i_a}{\partial \log \text{Cl}^-} = 1.12$$  ... (4)

where $i_a$ is the anodic current density at constant anodic potential $E_a$.

The positive anodic reaction order suggests that Cl$^-$ participates directly in the dissolution mechanism. Further, the shift of corrosion potential towards more negative direction additionally supports the anodic activity of Cl$^-$ ions on the dissolution kinetics.

The experimental results can be expressed as:

$$i_a = K_a [\text{Cl}^-]^{1.12} \exp \left( \frac{0.85 FE}{RT} \right)$$  ... (5)

By setting $E = E_{corr}$ and $i_a = i_c = i_{corr}$ in the above expression

$$i_{corr} = K_e [\text{Cl}^-]^{1.12} \exp \left( \frac{0.85 FE_{corr}}{RT} \right)$$  ... (6)

$$\log i_{corr} = 1.12 \times \log [\text{Cl}^-] + \frac{0.85 FE_{corr}}{2.3 RT}$$

or

$$\frac{\partial \log i_{corr}}{\partial \log \text{Cl}^-} = 1.12 + \frac{0.85 F}{2.3 RT} \frac{\partial E_{corr}}{\partial \log \text{Cl}^-}$$

or

$$\frac{\partial \log i_{corr}}{\partial \log \text{Cl}^-} = 1.12 + \frac{0.85}{2.3 RT} (-0.037) = 0.59$$

which is comparable with the experimental value (Eq. 2) obtained from the electrochemical study and very close to the value determined by weight loss method.

The anodic Tafel slope of 70 mV/decade obtained in this study is comparable to the values reported in the literature$^{10-12}$. But the anodic reaction order obtained for chloride ion is not in full agreement with the reported results$^{10-13}$. It may be due to the different experimental conditions, anions, degree of purity of metal, preparation of the surface and finally to different polarization methods and also sulphur content of the metal$^{14}$. In the present study, the specimen used was mild steel having 0.05% S content and therefore the value obtained is fairly comparable to the reported values$^{10-13}$.

**Effect of pH**—The anodic and cathodic polarization curves of mild steel in methanol + mM
HCl + nM LiCl (m + n = 1) solutions were recorded keeping the Cl⁻ ion concentration constant. The experimental curves are given in Fig. 7. An increase in hydrogen ion concentration shifted the polarization curves towards more negative direction. Both the anodic as well as cathodic polarization curves were affected and the open circuit potential has been found to move towards more negative direction with the increase in acidity at a constant chloride ion concentration.

Thus the effect of C₄H₄⁺ is quite similar to Cl⁻ addition as shown in Figs 8 and 9. It is also observed in this case that the corrosion potential moved towards more negative direction followed by an increase in corrosion current.

From the results of Fig. 7, it may be assumed that the ionization of iron in acid alcohol media is associated with the direct participation of solvent molecules, and not OH⁻ and RO⁻ ions. Otherwise, the anodic dissolution should be accelerated with decreasing HCl concentration, which is equivalent to the introduction of water. This, however, is not observed experimentally.

Further, a set of weight loss experiment was conducted keeping the Cl⁻ ion concentration constant. The experimental data are given in Fig. 9 along with corrosion current density values measured from the polarization curves. It was found that there was an increasing trend of corrosion rate with increasing acidity of the medium at a constant Cl⁻ concentration indicating that the corrosion rate is proportional to the acidity of the system.

It can, therefore, be concluded that, among the impurities present in the solution, acidity in terms of acid strength of hydrogen ion is the main factor governing the corrosion process.

The anodic reaction order with respect to acidity (H⁺ ion) for iron dissolution was determined from the polarization curves by a plot of log current vs log C₄H₄⁺ at a constant anodic potential. This plot is shown in Fig. 10 giving a slope of
The cathodic part of the reaction under control of hydrogen ion concentration can, therefore, be described as:

\[ i_e = K_e a_{H^+}^{0.4} \exp \left( \frac{-EF}{2RT} \right) \]  \( \cdots (12) \)

The kinetic parameters can be given as:

\[ \frac{\partial E_{corr}}{\partial \log C_{H^+}}_{Cl^-} = -37 \text{ mV/decade} \]  \( \cdots (13) \)

\[ \frac{\partial \log i_{corr}}{\partial \log C_{H^+}}_{Cl^-} = 0.36 \]  \( \cdots (14) \)

**Conclusion**

Corrosion of mild steel methanol + HCl + LiCl solutions proceeds through a direct participation of Cl⁻ ions in the dissolution process, which is associated with the participation of solvent molecules rather than hydroxyl ion or alkoxide ion. The dependence of corrosion rate on Cl⁻ ion concentration gives similar results as observed in the case of relation between corrosion current and Cl⁻ ion concentration, suggesting that time has negligible role on the rate of corrosion.

**References**