Evaluation of acridine, $p$-amino benzaldehyde and diethanol amine as corrosion inhibitors for carbon steel in citric acid

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Acridine, $p$-amino benzaldehyde and diethanol amine have been shown to exhibit increasing inhibition efficiencies with concentration of the respective inhibitors. The temperature coefficient of inhibition was found to be negative for all the three inhibitors and the activation energy for the process increased on addition of inhibitors. All these compounds follow both Langmuir and Freundlich adsorption isotherms. The heat of adsorption obtained by Langmuir equation indicated the adsorption to be of physical in nature. The negative free energy and the entropy of adsorption were higher for acridine and $p$-amino benzaldehyde than that for diethanol amine which explained the better performance shown by acridine and $p$-amino benzaldehyde in protecting carbon steel in citric acid in comparison to that of diethanol amine.

Equipments used for transporting water or process chemicals are likely to develop a corrosion product film which affects the heat transfer and fluid flow. In nuclear power reactors, the corrosion leads to additional problem of high radiation field. Periodic removal of these corrosion products from the heat transfer surfaces is thus a necessity. Chemical cleaning can be carried out either with inhibited mineral acid or with a mixture of dilute organic acids. The latter process, known as dilute chemical cleaning, is preferred because of low base metal corrosion. Carbon steels are used as construction material in primary heat transport systems of chemical and process industries. The dilute chemical cleaning formulations contain an organic acid (which is a source of H$^+$ ions), a complexing agent to chelate Fe$^{2+}$ ions and a reducing agent. Citric acid is one of the commonly used organic acid along with different complexing agents$^{1-2}$. The addition of inhibitors is essential for further lowering of corrosion rate. The selection of inhibitors is based on the criteria of their effectiveness at low concentrations, less toxicity, thermal stability and less deleterious effect on the equipments used. Sulphur containing compounds cannot be used as they can cause stress corrosion cracking in stainless steel components which may be a part of the circuit. Among other class of compounds, the amines are most effective. Further, the aromatic amines are, in general, more efficient as compared to the aliphatic amines at a lesser concentration$^3$. Investigations have shown acridine to be an effective inhibitor for acid corrosion of aluminum base alloys,$^4$,$^5$ copper$^7$ and iron$^8$. Hoar and Khera$^9$ have studied the inhibition characteristics of diethanol amine for the corrosion of mild steel in acidic medium. The present study is devoted to the evaluation of the corrosion behaviour of carbon steel in citric acid in a temperature range of 303–348 K with acridine (ACDN) and $p$-amino benzaldehyde (PABD) (both are aromatic amines) and diethanol amine (DEA, aliphatic amine). The probable mechanism for inhibition has been explained with the help of various thermodynamic parameters determined by weight loss method.

Experimental Procedure
Carbon steel specimens (C–0.11 %, Mn–0.35 %, S–0.03 %, Si–0.04 %) were annealed at 1198 K for 30 min followed by furnace cooling. Dimensions of the specimens were $20 \times 20 \times 2.5$ mm. These were polished up to 600 grit, thoroughly degreased, dried and weighed before immersion. Effect of temperature was studied at 303, 318, 333 and 348 K and the accuracy of temperature measurement was ±1K. The exposure time was 24 h in all immersion tests. The corrosion rates were determined from the observed weight loss data. To check the reproducibility, each experiment was carried out four times and the values were within ±5% of the mean value reported here.
Results and Discussion

The data obtained for the rate of dissolution of carbon steel with different concentrations of citric acid at 333 K are fitted to Eq.(1)

$$R' = K C^n$$

where $R'$ is the corrosion rate, $C$ is the concentration of citric acid and $K$ is the rate constant. The exponent ($n$) which represents the order of reaction, was found to be 0.8. This is shown in Fig.1, which suggests that the reaction between iron (major component of carbon steel) and citric acid is nearly unimolecular.

Earlier work\(^2\) has shown that citric acid possesses a good dissolving capacity for the corrosion products, at a concentration of 9.6 mM at 333 K. All experiments have, thus, been carried out at this concentration of citric acid. This medium results in base metal dissolution rate of 980 mdd (0.52 µm.h\(^{-1}\)) which is likely to cause slight surface roughness\(^10\). In order to achieve a smooth surface, the addition of inhibitor is mandatory.

The inhibitor efficiency ($I$) at various temperatures and concentrations of inhibitor was calculated from weight loss data using the expression

$$I = (R_o - R_i)/R_o \times 100$$

where $R_o$ and $R_i$ are corrosion rates in uninhibited and inhibited citric acid, respectively. Plots of inhibitor efficiency versus concentration at 333 K are shown for ACDN, PABD and DEA in Fig.2. Initially, the efficiencies of all three inhibitors increase with the concentration of inhibitors. In case of PABD and ACDN, there is practically no change in inhibition efficiency at concentrations greater than 1.43 mM; the efficiency is about 85% in both the cases. On the other hand, the inhibition efficiency of DEA exhibits slow increase with concentration and reaches a maximum of 80% at 48 mM.

The effects of temperature on the performance of the inhibitors is shown in Fig.3. The concentrations of the inhibitors were 0.83, 0.56 and 9.5 mM for PABD, ACDN and DEA, respectively. It has been observed that the inhibition efficiency decreases with increasing temperature for all the three inhibitors. However, while the drop is rapid in case of DEA, a marginal decrease is observed with other two inhibitors in the temperature range studied. The inhibition efficiencies are found to be in the order: PABD > ACDN > DEA, except at 303 K, where the efficiency of DEA was similar to that of ACDN. This is probably due to a faster rate of desorption of DEA with increasing temperature as compared to the other two inhibitors.

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Fig. 1—Variation of corrosion rate of carbon steel with concentration of citric acid at 333 K

Fig. 2—Dependence of inhibitor efficiency on the inhibitor concentration. (a) (O) p-amino benzaldehyde, (□) acridine and (b) (△) diethanol amine in 9.6 mM citric acid at 333 K
For a metal dissolution reaction, the corrosion rate \( R \) is related to the rate constant \( K \) and hence it is possible to write the Arrhenius equation\(^{11}\) as

\[
\log R = A - \frac{E}{RT}
\tag{3}
\]

where \( E \) is the activation energy for the corrosion reaction and \( A \) is a temperature-independent constant. Fig. 4 shows the plots of \( \log R \) against \( 1/T \) for uninhibited and inhibited citric acid. The values of activation energy are obtained from the slopes of these plots and are listed in Table 1. It can be seen that the presence of inhibitors causes a rise in activation energy for the dissolution of carbon steel in citric acid. These results along with the decrease in inhibitor efficiency with temperature are in agreement with the observations made by Putilova et al\(^{12}\). It may be pointed out that DEA results in higher activation energy in comparison to those with PABD and ACDN, but the corrosion rates are higher with the former case. The magnitude of activation energy indicates more about the mechanism of the process taking place at the interface rather than its speed or kinetics.

Assuming that the adsorption of the inhibitor results in a monolayer whereby each site accommodates one adsorbed molecule, and at any time a fraction \( \theta \) of the metal surface is covered. The fraction available for interaction with the acid is \( (1 - \theta) \). Then \( \theta \) can be written as

\[
\theta = \frac{R_o - R}{R_o}
\tag{4}
\]

Langmuir\(^{13}\) and Freundlich\(^{14}\) adsorption isotherms have been drawn using the data obtained from weight loss experiments and these are shown in Figs 5 and 6. The Langmuir equation can be written as

\[
\log [\theta/(1 - \theta)] = \log C + \log B
\tag{5}
\]

where \( C \) is the concentration of inhibitor.

According to Kaminski and Szklarska-Smialowska\(^{15}\), \( B \) is related to the free energy of adsorption \( \Delta G_{ads} \) as

\[
B = \exp (-\Delta G_{ads}/RT) \times 1/55.5
\tag{6}
\]

Eqs (5) and (6) have been used to calculate the free energy of adsorption for all the three inhibitors at different temperatures. The plot of free energy of adsorption as a function of temperature is shown in Fig. 7. According to Gibbs-Helmholtz relation, the slope of these lines is equal to \( \Delta S_{ads} \).
and the intercepts on free energy axis give the corresponding heat of adsorption. The values of the heat of adsorption, the free energy of adsorption and the entropy of adsorption are given in Table 1. The values of heat of adsorption are less than 25 kJ/mol indicating that the adsorption process is physical in nature in case of all the three inhibitors. The negative values of \( \Delta G_{ads} \) indicate the spontaneous adsorption of inhibitors on the surface of carbon steel. The values of \( \Delta G_{ads} \) and \( \Delta S_{ads} \) are higher for ACDN and PABD compared to DEA. This is in agreement with the observed lower efficiencies for DEA than both PABD and ACDN. According to Ateya et al.\textsuperscript{16}, the thermodynamic parameters are the algebraic sum of the values for adsorption of inhibitor molecules and desorption of water molecules on the carbon steel surface. The gain in entropy which accompanies the substitutional adsorption process is attributed to increase in the solvent entropy.

References