Corrosion Inhibition of Carbon Steel in Hydrochloric Acid Using N-acetyl p-aminobenzene Sulfonamide

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The corrosion behaviour of carbon steel in 2 M HCl in the presence of N-acetyl p-aminobenzene sulfonamide (APAS) as inhibitor was investigated using weight loss measurements, as well as electrochemical measurements. The morphology of carbon steel surface was investigated using scanning electron microscopy (SEM) and Mössbauer spectrometry. The corrosion current was determined by using Tafel polarization. The inhibition efficiency increased with APAS concentration. The experimental results suggest that the presence of APAS in the solution increases the surface coverage (θ) and therefore, indicate the adsorption of APAS. The adsorption of this compound on the metal surface is found to obey Langmuir’s adsorption isotherm. Mössbauer spectroscopy has shown that at this stage the main product of corrosion is a non-stoichiometric amorphous Fe\(^{3+}\) oxyhydroxide, consisting in a mixture of \(\alpha\), \(\beta\) and \(\gamma\)FeOOH, where \(\gamma\)FeOOH is the main phase.

Keywords: N-acetyl p-aminobenzene sulfonamide, scanning electron microscopy (SEM), Mössbauer spectrometry

Corrosion in pipes, pumps, turbine blades, coolers, water heaters, and other systems made of steel causes enormous industrial expenses due to production downtime, accidental injuries, and replacement costs. Steel is an important metal in industrial applications, but it can be corroded in aqueous solutions, such as hydrochloric acid, because the chloride ions significantly promote the corrosion process.

Treatments with organic compounds have been proposed in order to provide corrosion protection [1-6]. A large number of aliphatic and aromatic compounds containing nitrogen, oxygen and sulphur atoms are found to cause a distinct decrease in corrosion rates of steel in hydrochloric acid [7-9]. The inhibition efficiency of organic compounds is strongly dependent on the structure and chemical properties of the layer formed on the metal surface under particular experimental conditions. The available results show that most inhibitors act by adsorption on the metal surface [10-13]. The strength of adsorption and hence the extent of inhibition is dependent on the nature of the organic compounds, nature of the metal and corrosive media.

The present study aims to determine the role of new inhibitor APAS in providing the protection film in case of generalized corrosion of carbon steel in hydrochloric acid.

Experimental part

The carbon steel used had the following composition (weight %): C=0.1%; Si=0.035%; Mn=0.4%; Cr=0.3%; Ni=0.3%, with the balance in Fe. The samples were mechanically polished with different grades of emery paper (down to 600), degreased with acetone and dried. A 2 M HCl acid solution was used as the blank corrosion test solution. The inhibitor used was N-acetyl p-aminobenzene sulfonamide (APAS-Merk) in concentrations of 0.1 mM; 0.2 mM; 0.3 mM; 0.4 mM;

Weight loss measurements

The corrosion rates of carbon steel were determined in 2 M HCl solution in the absence and presence of variable concentrations of APAS: 0.1 mM; 0.2 mM; 0.3 mM; 0.4 mM. The immersion time of the steel plates in the respective media was three hours, at room temperature. The morphology of carbon steel surface after corrosion in 2 M HCl solution, containing 0.1-0.4 mM APAS were examined with an electron microscope (Vega Tescan).

Electrochemical measurements

For the study of polarization a standard corrosion cell was used, with a working electrode made of carbon steel with an active surface of 4 cm\(^2\). The saturated calomel electrode (SCE) was used as a reference electrode. The auxiliary electrode was a carbon steel plate identical to the one used as the working electrode. The polarization was conducted in an electrochemical system Keithley 2420 3A Source Metter with a personal computer and Test Point software, at room temperature.

Mössbauer Spectrometry

Mössbauer spectrometry measurements were performed at room temperature in the transmission (TMS) and conversion electron spectroscopy (CEMS) using constant - acceleration spectrometer with a \(^{57}\)Co - Rh Source. The CEMS measurement, effected with our CEMS detector [14], were conducted with a high degree of accuracy, ensuring the same geometry of the detection space and the same gas flow rate for all the samples. The parameters of the Mössbauer spectra were calculated using a computer – fitting program, which assumes a Lorentzian line shape. The isomer shifts were referred to Fe. The information obtained by scattering methods is restricted to the layer to which the secondary radiation employed in the measurement can penetrate from the surface of the sample. In the \(^{57}\)Fe Mössbauer spectroscopy the penetration depth maximum of conversion electron is of the order of 250 nm.

Results and discussions

Weight loss measurements

The loss in the weight of carbon steel samples in 2 M HCl in absence and presence of various concentrations of APAS was determined. The results of weight loss measurements are shown as general corrosion rates,
The increase in APAS concentrations leads to a decrease in corrosion rate for both examined samples, indicating that the presence of APAS retards the general corrosion of samples in 2 M HCl. This fact suggests that the inhibition of the carbon steel corrosion in the presence of APAS occurs by adsorption on metal surface. The adsorption of APAS molecules also produces important modifications in the structure of the double electric layer. The effect of surface blockage becomes dominant, which leads to a decrease in the number of active centres. APAS is an organic compound that contains both N- and S- atoms in the molecule. APAS can be easily adsorbed on the surface of the metal. Up to date, most of the investigations suggest that APAS is bound to the surface mainly through S-atom bond and formation of a metal-S bond occurs. However, it has been suggested that APAS might bind to the carbon steel surface through its N-atom. APAS forms stable monolayer on the metallic surface, which increases the resistance on corrosion of carbon steel in 2M HCl solution. It seems that complex formation occurs between the APAS compound (as ligand) and different metal cations provided by the steel. These complex species can form a stable passive layer on the steel surface, thus decreasing the rate of corrosion. The inhibition efficiency increases with APAS concentration. The percentage inhibition efficiency (P) of APAS was calculated by applying the following equation:

\[
P = \frac{k_{\text{go}} - k_{\text{g}} \times 100}{k_{\text{go}}} \]

where \( k_{\text{go}} \) and \( k_{\text{g}} \) are, respectively, the corrosion rates in the absence and presence of a given inhibitor. The inhibition efficiencies calculated from the weight loss data are also plotted in figure 1.

By studying the inhibitor we have reached the conclusion that the experimental data characterize an adsorption isotherm of Langmuir type expressed by linearization form (equation 2); an example is shown in figure 2.

\[
\frac{1}{1 - \theta} = K \times c
\]

where \( \theta \) is degree of coverage (\( \theta = P/100 \)), \( K \) is the equilibrium constant of the adsorption-desorption process, \( c \) is concentration of the APAS. The data plotting gave a straight line; the slope of this line represent \( K \). It can be observed that \( K \) has a high value of 6657.5 L·mole\(^{-1}\). The equilibrium constants \( K \) vary towards the same direction, in the sense that higher values of \( K \) imply a better adsorption. The standard free energy of adsorption \( \Delta G_{\text{ads}} \) was calculated using equation (3):

\[
K = \frac{1}{55.5} \exp \left( -\frac{\Delta G_{\text{ads}}^0}{R \times T} \right)
\]

where \( R \) is the ideal gas constant, \( T \) is temperature and 55.5 is the molar concentration of water in the solution. The value \( \Delta G_{\text{ads}}^0 \) of is negative (-31.75 KJ·mol\(^{-1}\)), which shows that the process of adsorption is spontaneous.

The morphology of carbon steel surface after corrosion in 2 M HCl solution (fig. 3a), and in HCl solutions containing 0.1 mM APAS; 0.2 mM HBTC and 0.4 mM APAS was examined with electron microscopy.

Figure 3 shows the evidence of formation a thick film on the surface of carbon steel. The corrosion spots are reduced in intensity in the case of carbon steel corroded in 2 M HCl containing APAS (fig. 3b, 3c and 3d). It can be concluded that the inhibitor molecules are adsorbed on the carbon steel surface.

Electrochemical measurements

Figure 4 shows the polarization curves of carbon steel in 2 M HCl blank solution and in the presence of various concentrations of APAS. The increase in APAS concentrations leads to both anodic and cathodic current inhibition, but the reduction in the anodic current was more significant than that of cathodic current. This behaviour shows that the addition of APAS reduces anodic dissolution and also retards the hydrogen evolution reaction. The decrease of the corrosion current (\( i_{\text{corr}} \)) was associated with a shift of corrosion potential (\( E_{\text{corr}} \)) to a less negative values. This suggests that although inhibition is of mixed type, it is predominantly anodic inhibitor.

The corrosion current was calculated at intercept of the anodic and cathodic Tafel lines. The percentage inhibition efficiency (P) of APAS inhibitor was also determined from the polarization measurements according to the following equation:

\[
P = \frac{i_{\text{corr}} - i_{\text{corr}}'}{i_{\text{corr}}} \times 100
\]

where \( i_{\text{corr}}' \) and \( i_{\text{corr}} \) are the uninhibited and inhibited corrosion current densities, respectively obtained by extrapolation of the anodic and cathodic Tafel lines to the corrosion potential.
The values of inhibition efficiency increase with APAS concentration reaching a maximum value of 76.5% at 0.4 M APAS, nearly equal with the value obtained from loss weight data, 74.2% (fig. 5).

**Mössbauer Spectroscopy**

The CEMS spectra of the sample corroded in 2M HCl solution without APAS and in 2M HCl solution with APAS are shown in figures 6 and 7.

We obtained the TMS and CEMS spectra of a reference sample before corrosion and the results are identically with those reported in [15]. The best fitting of the TMS and CEMS spectra for the reference sample indicated the presence of a single sextet. The parameters of this sextet were practically the same as for a $\alpha$-Fe sample. The CEMS spectrum of the reference sample pointed out the existence of a magnetic anisotropy on the surface of the samples as a result of polishing. For the sample corroded in a solution of 2M HCl containing of APAS, the magnetic anisotropy is higher than for the corroded sample in HCl solution without inhibitor. Mössbauer spectroscopy shows thus, in the case of the corroded samples in a solution of 2M HCl containing of APAS, that the process of corrosion is considerable.
slowed down. Also Mössbauer spectroscopy shows that a superficial compound of Fe$^{3+}$ without a magnetic arrangement is formed on the surface of the corroded samples. By estimating its relative area and lines intensity of the sextet, it results that this compound has a smaller thickness than the layer formed in the corrosion process without inhibitor. The Mössbauer parameters of superficial compound found on corroded sample in solution without inhibitor (fig. 6) show the presence of Fe$^{3+}$ species and they are similar to those shown by amorphous Fe$^{3+}$ oxyhydroxides, superparamagnetic $\alpha$-FeOOH and/or $\gamma$-FeOOH, β-FeOOH and $\gamma$-FeOOH and Fe (OH)$_3$ [16-23]. At this stage it is expected that the main product of corrosion is a non-stoichiometric amorphous Fe$^{3+}$ oxyhydroxide, consisting of a mixture of $\alpha$, $\beta$ and $\gamma$-FeOOH. The Mössbauer parameters of the compound found for the corroded sample in the solution with inhibitor (fig. 7) do not differ significantly from the previous parameters. We consider that the APAS inhibitor acts as an incipient "rust transformer" and favors the formation of a "superficial closed layer". The inhibitor converts some constituents of rust into corrosion inhibiting oxide phases.

Conclusions

APAS is an inhibitor of carbon steel in a solution of 2 M HCl; it has an efficiency of 74.2% obtained by weight loss measurements respectively 76.5% by electrochemical measurements. APAS acts through adsorption on the metal surface; this was demonstrated by using SEM. The Mössbauer spectroscopy shows in the case of the corroded samples in a solution of 2 M HCl containing of APAS that the process of corrosion is considerably slowed down and a superficial compound of Fe$^{3+}$ without a magnetic arrangement is formed. The adsorption of APAS on the electrode surface is found to obey Langmuir's adsorption isotherm; the standard free energy ($\Delta G^\circ_{\text{ads}}$) is negative, showing that the adsorption process of APAS on the metal surface is spontaneous.

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