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Corrosion inhibition and adsorption properties of 3-amino-1,2,3-triazole on mild steel in H_3PO_4

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ABSTRACT

The corrosion inhibition of 3-amino-1,2,3-triazole (ATA) on the mild steel in phosphoric acid solution was studied using the weight-loss method and potentiodynamic polarisation and EIS measurements. The addition of ATA decrease the corrosion rate (CR) and consequently the inhibition efficiency increases with concentration. Examination of polarization curves indicates that ATA acts as a mixed-type inhibitor. ATA retards also the cathodic reaction with changing the mechanism of the hydrogen evolution reaction only at 10^{-2} *mol·L*$^{-1}$*. The adsorption of ATA on the steel surface obeys Temkin isotherm adsorption model. The free enthalpy energy has been evaluated.*

Keywords: Corrosion; Inhibition; Mild Steel; ATA; Phosphoric acid, Temkin.

INTRODUCTION

Mild steel is widely employed in industry because of its low cost and availability. Acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes. Inhibitors are generally used to control metal dissolution. The inhibition of corrosion in acid solutions can be secured by the addition of a variety of organic compounds and has been investigated by several workers [1-21]. Most of the well-known acid inhibitors are organic compounds containing O, S and/or N atoms [22-26]. However, the use of organic inhibitors in acid solutions can, in some cases, lead to enhancement of the metal corrosion [27], and stimulation of corrosion is related not only to the type and structure of the organic molecule but also depends on the type of acid and its concentration [11]. For example, the isomers of aminophenol inhibit the corrosion of mild steel in 1M HCl and accelerate it in 0.5M H_2SO_4 [28], and the results obtained for 1,3,4-oxadiazoles and 1,2,4,5-tetrazin reveal that these compounds are very good inhibitors and behave better in 1M HCl than 0.5M H_2SO_4 [29-30]. There are various organic inhibitors which tend to decrease the corrosion rate of steel and iron in acidic solutions. These substances in general, are effective through adsorption on the metal surface. 3-

amino-1,2,3-triazole (ATA) find more and more application toward corrosion protection of various metals in aggressive media [31–35].

Although phosphoric acid (H_3PO_4) is classified as a medium-strong acid, it causes severe damage on ferrous or ferrous alloy [36-38]. The objective of this work is to investigate the effect of 3-amino-1,2,3-triazole (ATA) on the corrosion of mild steel in 0.33M H_3PO_4. The activation and adsorption parameters were determined. Weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy methods were conducted.

MATERIALS AND METHODS

The mild steel used had the following chemical composition (0.09% P, 0.38% Si, 0.01% Al, 0.05% Mn, 0.21% C, 0.05% S and balance Fe). Steel samples are polished with different emery papers up to 1200 grade, washed thoroughly with bi-distilled water degreased and dried with acetone. The aggressive solution ($0.33\ mol\cdot L^{-1}$ H_3PO_4) is prepared by dilution of analytical grade 85% H_3PO_4 with double-distilled water.

The weight losses of samples were evaluated after exposure to $0.33\ mol\cdot L^{-1}$ H_3PO_4 containing various inhibitors. The solution volume is 100 cm^3. The steel specimen used has a rectangular from (1.5cmx1.5cmx0.05cm). The immersion time is 24 h at 298 K. In the case of the weight loss method, the relation determines the inhibition efficiency E_w %:

$$E_w\% = \left(1 - \frac{W_{corr}}{W^o_{corr}}\right).100 \qquad (1)$$

W_{corr} and W^o_{corr} are the corrosion rate of steel with and without the inhibitor, respectively.

The potentiodynamic polarization studies were carried out with steel strips having an exposed area of 1 cm^2. A saturated calomel electrode SCE and a platinum electrode are used as reference and auxiliary electrode, respectively. The current-voltage characteristics are recorded with a potentiostat/ galvanostat EG&G type Princeton Applied Research Model 263A. Before recording the cathodic polarization curves, the steel electrode is polarised at – 800 mV for 10 min. The potentiodynamic current potential curves were recorded by automatically changing the electrode potential from −800 mV to anodic potentials at a scanning rate of 1 $mV.s^{-1}$. The test solution is de-aerated with pure nitrogen. For electrochemical measurements, the inhibition efficiency is calculated by using corrosion current density as follows:

$$\eta\% = \left(1 - \frac{i_{corr}}{i^o_{corr}}\right).100 \qquad (2)$$

i_{corr} and i°_{corr} are the corrosion current density value with and without inhibitor, respectively, determined by extrapolation of cathodic Tafel lines to the corrosion potential.

The electrochemical impedance spectroscopy (EIS) measurements was carried out with a Tacussel electrochemical system which included a digital potentiostat model Voltalab PGW 100 computer at E_{corr} after immersion in aerated solution, the circular surface of steel exposing of 1cm^2 to the solution were used as WE. After determination of steady-state current at a given potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz were superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 30min of exposure. The impedance diagrams are given in the Nyquist representation.

RESULTS AND DISCUSSION

The effect of addition of ATA at different concentration on the corrosion of mild steel in 0.33 mol·L^{-1} H_3PO_4 was studied by weight loss at 298 K after 24h of immersion period. Fig. 1 shows the plots for both the variation of corrosion rate (CR) of mild steel in the presence of different concentrations of ATA in acid solution and corresponding efficiency E%. The figure shows that CR decreases with more ATA concentration increases. Consequently, the efficiency progresses with ATA presence but does not exceed 75% even at 10^{-2} mol·L^{-1}.

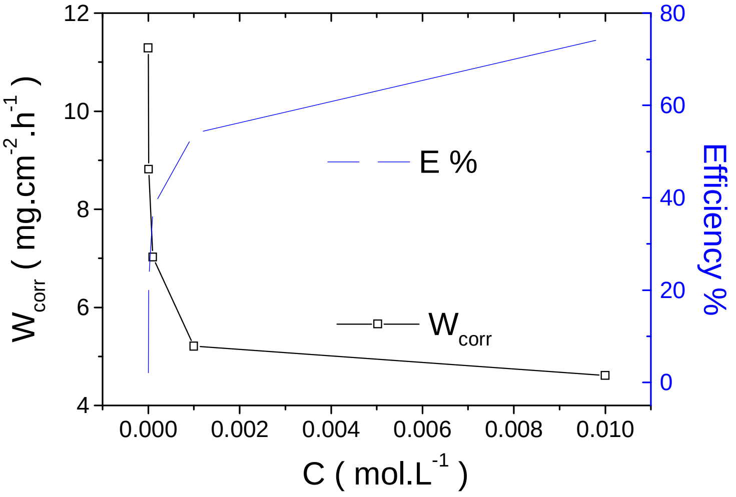

Figure 1: Evolution of corrosion rate of mild steel and inhibition efficiencies of ATA against the concentrations of ATA.

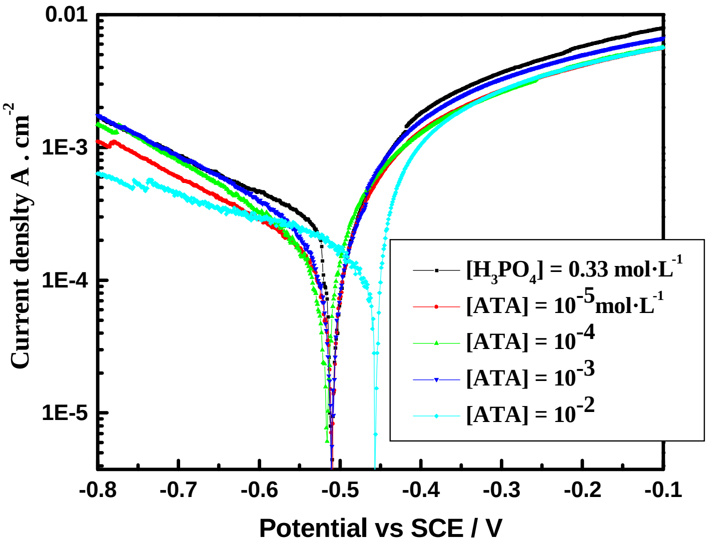

Fig. 2. Polarisation curves of mild steel in 0.33 mol·L^{-1} H_3PO_4 at different concentrations of ATA

The effect of ATA concentration (10^{-5} to 10^{-2} mol·L^{-1}) on the potentiodynamic anodic and cathodic polarization curves of steel has been studied in 0.33 mol·L^{-1} deaerated stirred H_3PO_4 solution. Obtained curves are collected in Fig. 2. Table 1 gives values of corrosion current (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (b_c) for ATA. We remark that the hydrogen evolution reaction is activation controlled since the cathodic portions rise to Tafel lines.

Table 1. Electrochemical parameters of mild steel in 0.33 mol·L^{-1} H_3PO_4 in the presence of different concentrations of ATA at 298 K

ATA (mol·L^{-1})	E_{corr}/mV(vs SCE)	I_{corr} (µA.cm^{-2})	b_c (mV.dec^{-1})	η (%)
0	-511	234	145	-
10^{-5}	-510	152	147	35
10^{-4}	-516	140	139	40
10^{-3}	-511	100	144	57
10^{-2}	-456	79	179	66

The presence of ATA did not affect the cathodic Tafel slope b_c until the concentration 10^{-2} mol·L^{-1}. Only at this later concentration, we may introduce that the mechanism of the cathodic process is modified. Kertit et al. [39] mentioned that the addition of triazoles did not change hydrogen reduction mechanism of mild steel in phosphoric acid. ATA presence was almost constant at concentrations below 10^{-2} mol·L^{-1}. At this concentration, E_{corr} shifted in the positive direction indicating that at higher ATA concentration a possible formation of iron II- ATA complex.

Sahin et al. pointed out in their work [40] that relative inhibition efficiencies of the compounds can be rationalised qualitatively under the assumptions that: (i) the inhibition is essentially based on the coverage of the metal surface by the inhibitor molecules, thus making the contact of corroding species difficult; (ii) attachment of the molecules on the metal surface is facilitated through the coordination of π-electron system to the metal atom; (iii) the stability of the complex is somewhat related to the molecule's being planar.

The maximum inhibiting effect observed at 10^{-2} mol·L^{-1} may be interpreted by both retardation of the cathodic reaction and anodic dissolution. These results indicate ATA in H_3PO_4 solution acts as a mixed-type.

Electrochemical impedance spectroscopy

More information about the metal/acidic solution characteristics is possible by electrochemical impedance spectroscopy (EIS). EIS diagrams of mild steel were plotted in acidic solution in the presence of ATA at 298 K after 12h of immersion at corrosion potential. Fig. 3 shows Nyquist plots obtained in uninhibited and inhibited acidic solutions at different concentrations of ATA. The parameters deduced are grouped in Table 2. Charge-transfer resistance values (R_t) and Double layer capacitance values (C_{dl}) were obtained from impedance measurements as described previously [41]. The following relation is used to calculate E (%):

$$E_I\% = \left(1 - \frac{R_t^o}{R_t}\right).100 \qquad (3)$$

where R_t and R_t^o are the charge-transfer resistance values with and without inhibitor, respectively.

Examination of Table 2 reveals that, more and more the ATA concentration increases, R_t rises to higher values showing that ATA inhibit corrosion reaction, and in the same time the decreasing of C_{dl} is interpreted by the adsorption of inhibitor molecules on the metal surface [41].

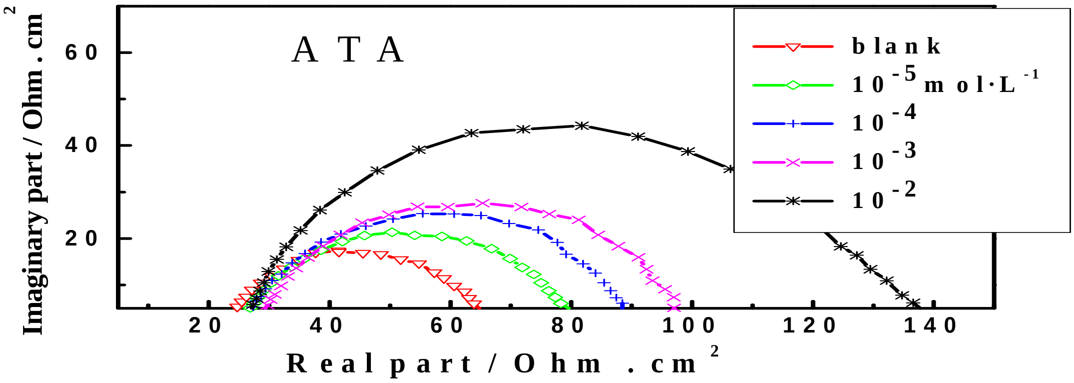

Fig. 3. Nyquist diagrams for mild steel in 0.33M H_3PO_4 containing different concentrations of ATA.

Table 3 Impedance parameters and inhibition efficiency for the corrosion of mild steel in 0.33M H_3PO_4 at various concentrations of ATA at 303 K

$C_{inhibitor}$ / (mol·L^{-1})	R_t (Ohm.cm^2)	f_o (Hz)	C_{dl} (µF.cm^{-2})	E (%)
0	47	79	43	-
10^{-5}	71	45	50	33
10^{-4}	74	48	45	37
10^{-3}	85	48	39	44
10^{-2}	127	46	27	63

Adsorption isotherm

Adsorption isotherms are very important for the understanding of the mechanism of organo-electrochemical reaction [42]. The most frequently used isotherms are Langmuir, Frumkin, Temkin, Parsons, etc. [43]. The degrees of surface coverage (θ) of different concentrations of ATA in 0.33M H_3PO_4 have been evaluated from weight loss measurements, where θ is the ratio E (%)/100. Examination of the various isotherm models indicates that the Langmuir isotherm is not adequate because the slope deviate from unity (1.661) and the Temkin isotherm model describes the adsorption phenomenon of ATA on the steel surface. The Temkin isotherm equation is:

$$\exp(f.\theta) = K_{ads}.C \qquad (5)$$

where C is the inhibitor concentration, K_{ads} the equilibrium constant of the adsorption process and ΔG_{ads} the standard free energy of adsorption, calculated as:

$$K_{ads} = \frac{1}{55.5}\exp(-\frac{\Delta G^{\circ}_{ads}}{RT}) \qquad (6)$$

Figure 4 shows the variation of θ against the logarithm of the inhibitor concentration. The linear correlation coefficient is 0.99994 close to unity. The obtained value of K_{ads}= 2065983. The negative value of $\Delta G°_{ads}$ = -46.75 kJ.mol^{-1} is generally interpreted by a spontaneous adsorption process of inhibitor onto the steel surface [44].

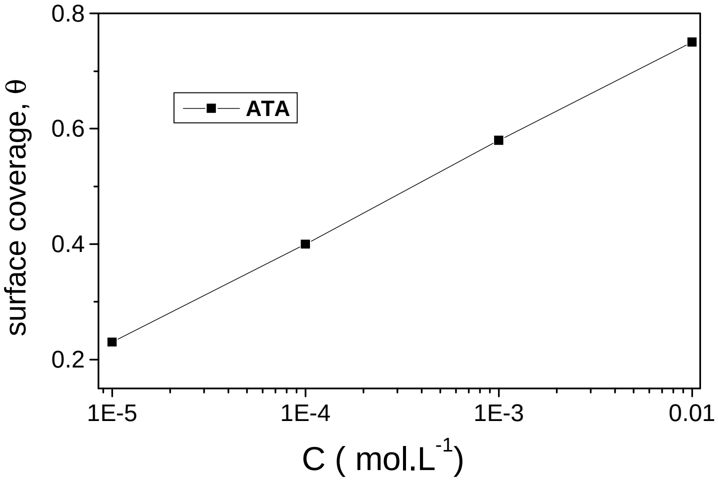

Fig.4. Temkin isotherm adsorption model on the steel surface of ATA in 0.33M H_3PO_4.

Temkin (1941) approached the development of an adsorption isotherm by considering a heterogeneous surface where no molecular interactions exist. He divided the surface into different patches, and since there are no interactions between molecules, in each patch the Langmuir isotherm can be applied. One advantage of the Temkin isotherm is that it considers the heterogeneity of the surface. However, like the Langmuir isotherm, it does not take into account lateral interactions between the adsorbates [45]. Temkin considered mostly solid electrode surfaces and here the question arises of heterogeneity—some sites on the metal surface (at ledges and corners of the structures on the surface) have metal atoms that are less bound to other metal atoms and so are more reactive to molecules that may try to adsorb there. Temkin stressed the idea that the surface of a metal would have all manner of heat adsorption, $\Delta H°_{ads}$ at the various types of sites. When adsorption begins (θ is at first small), the adsorbed molecules would bind to the more attracting sites (i.e., those with the greatest bonding power), where $\Delta G°_{ads}$ would be therefore highly negative. However, as the surface fills up, the more active sites (more negative $\Delta G°_{ads}$) become used up and therefore, for higher θ, ΔG_{ads} would be less negative [46]. This theory agreed well with our finding ($\Delta G°_{ads}$ = -46.75 kJ.mol^{-1}).

Generally, values of $\Delta G°_{ads}$ less negative than -40 kJ mol^{-1} are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption). On the other hand, values of $\Delta G°_{ads}$ more negative than -40 kJ mol^{-1} involve charge sharing or charge transfer from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) [47].

CONCLUSION

- ATA inhibit the corrosion of mild steel in 0.33M H_3PO_4 .
- Triazole examined acted as a mixed inhibitor in 0.33M H_3PO_4 at 10^{-2} mol·L^{-1}.
- The adsorption of ATA onto the steel surface in phosphoric acid follows the Temkin adsorption isotherm model.
- The weight loss, electrochemical impedance spectroscopy and polarization curves are in reasonably good agreement.

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