Research Article

Study of a Triazole Derivative as Corrosion Inhibitor for Mild Steel in Phosphoric Acid Solution

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The corrosion inhibition by a triazole derivative (PAMT) on mild steel in phosphoric acid (H₃PO₄) solution has been investigated by weight loss and polarization methods. The experimental results reveal that the compound has a significant inhibiting effect on the corrosion of steel in H₃PO₄ solution. It also shows good corrosion inhibition at higher concentration of H₃PO₄. Potentiodynamic polarization studies have shown that the compound acts as a mixed-type inhibitor retarding the anodic and cathodic corrosion reactions with predominant effect on the cathodic reaction. The values of inhibition efficiency obtained from weight loss and polarization measurements are in good agreement. The adsorption of this compound is found to obey the Langmuir adsorption isotherm. Some kinetic and thermodynamic parameters such as apparent activation energy, frequency factor, and adsorption free energy have been calculated and discussed.

1. Introduction

The use of inhibitors is one of the most practical methods for protection of metal against corrosion, especially in acidic media [1]. Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulphur, and oxygen atoms. Compounds with π-electrons and functional groups containing heteroatoms which can donate lone pair electrons are found to be particularly useful as inhibitors for corrosion of metals [2–5]. The exiting data reveal that most organic inhibitors act by adsorption on the metal surface. This adsorption is influenced by the nature and surface charge of metal, the type of aggressive electrolyte and the chemical structure of inhibitors [6]. The compounds containing both nitrogen and sulphur can give excellent inhibition in contrast to compounds containing only nitrogen or sulphur [7]. Triazole and triazole-type compounds containing nitrogen, sulphur, and heterocycle on the corrosion inhibition of metal in acidic media have attracted more attention because of their excellent corrosion inhibition performance [8–11]. The some new triazole derivatives have been still continuously synthesized and investigated as inhibitors for corrosion of metals in acidic solutions [12–14]. For example, Zhang et al. studied the corrosion inhibition of a newly synthesized oxadiazol-triazole derivative for mild steel in sulphuric solution, their results indicated that the compound was effective corrosion inhibitor for mild steel in acid solution and its efficiency attained more than 97.6% at 298 K [15]. The researches by Fouda and Ellithy showed that some 4-phenylthiazole derivatives could inhibit the corrosion of 304L stainless steel in hydrochloric acid solution, but the inhibition effect was not very excellent [16]. However, Synergistic effect occurred on addition of KSCN to acid containing 4-phenylthiazole derivatives which inhibited 304L stainless steel corrosion, and the phenomenon of synergism took place at very low concentrations for the systems studied. Wang et al. also investigated the effect of some mercapto-triazole derivatives synthesized containing different hetero atoms and substituents in the organic structures on the corrosion and hydrogen permeation of mild steel in hydrochloric acid solution and their results revealed that all the mercapto-triazole derivatives performed excellently as corrosion inhibitors [17]. Especially, some N- and S-containing triazole derivatives are environmentally friendly corrosion inhibitors compared with some commercial acid corrosion inhibitors which are highly toxic, such as chromate and nitrite [18].

Although phosphoric acid (H₃PO₄) is a medium-strong acid, it still shows strong corrosiveness on ferrous or ferrous
alloy [19, 20]. Little work appears to have been done on the inhibition of mild steel in H₃PO₄ solution. In this work, a triazole derivative containing nitrogen, sulphur, and aromatic ring was synthesized and had been studied on the corrosion inhibition of mild steel in H₃PO₄ solutions by weight loss and potentiodynamic polarization methods.

2. Experimental Method

2.1. Materials. Figure 1 shows the molecular structure of the investigated compound, which has been labelled PAMT.

The synthesis and characterization (spectral measurements) of the PAMT was as described and documented elsewhere previously [21].

The chemical composition wt% of mild steel was as shown in Table 1.

The specimens for the gravimetric determination were cut from steel sheet and measured approximately 4 cm × 1 cm × 0.05 cm. The working electrode (WE) for the potentiodynamic tests was cut from steel plate (1.0 cm²) and was embedded in chemical resistant epoxy resin. A platinum foil was used as the auxiliary electrode and the reference electrode was a saturated calomel electrode (SCE) coupled to a Luggin capillary whose tip was located between the working electrode and the auxiliary electrode. All solutions were prepared from bidistilled water and AR grade H₃PO₄ was used.

2.2. Procedures. The specimens were successively abraded with a series of SiC paper to a final finish using 1500 grade paper. They were then degreased in acetone, washed with bidistilled water, washed in acetone, dried, weighed, and immersed in the test solution (100 mL) for 120 min in air without bubbling. At the conclusion of a run the specimens were washed with bidistilled water and acetone, dried, and immediately weighed. The tests were then repeated at different temperature.

The working electrode was immersed in the test solution at natural potential for 40 minutes before measurement until a steady state appeared. To obtain the Tafel slopes, polarization curves were performed by polarizing to ±250 mv with respect to the free corrosion potential (Ecorr) at a scan rate of 0.5 mV/s. All the potentiodynamic measurements were performed by PARSTAT 2263 Potentiostat/Galvanostat (Princeton Applied Research). All runs were done at 30°C in air atmosphere without bubbling.

3. Results and Discussion

3.1. Weight Loss Tests and Adsorption Isotherm. A measure of the inhibition efficiency (IE) of PAMT in 2 mol/dm³ H₃PO₄ at 30°C at different inhibitor concentration levels was ascertained by the weight loss method. In each case the specimens were exposed for a 2 hr period. The inhibition efficiency is calculated as follows:

\[
\text{IE\%} = \left[ 1 - \frac{W_i}{W_u} \right] \times 100, \tag{1}
\]

where \(W_i\) and \(W_u\) are the weight losses per unit area per unit time in the presence and absence of the inhibitor, respectively. Figure 2 gives the corrosion rate values of mild steel in 2 mol/dm³ H₃PO₄ solution at different concentrations of PAMT. It is clear that the corrosion rates of the steel gradually decrease as the concentration of PAMT increases. Figure 3 shows the variation of inhibition efficiency with the concentration of the inhibitor. As shown, the inhibition efficiency increases with the increase of inhibitor concentration. The maximum inhibition efficiency is approximately 97%. This behavior could be attributed to the increase of the surface area covered by the adsorbed molecules of PAMT with the increase of its concentration.

The interaction of inhibitor with the surface of metal can be described by physical (electrostatic) adsorption, by chemisorptions, or by complexation that are influenced by the nature and charge of the metal, the chemical structure of the inhibitor, and the type of electrolyte. Adherence to the Langmuir adsorption isotherm is generally regarded to indicate chemisorptions, and this was tested for by Langmuir adsorption isotherm [22, 23]:

\[
\theta = \frac{KC}{(1 + KC)^2}, \tag{2}
\]
The equation (2) can be rearranged to:

$$\frac{C}{\theta} = C + \frac{1}{K},$$

where $K$ is the constant of adsorption, $C$ is the inhibitor concentration, and $\theta$ is the degree of surface coverage for different concentrations of the inhibitor. Here $\theta$ can be written as [24]:

$$\theta = \frac{(r_0 - r)}{(r_0 - r_m)},$$

where $r_0$ is the corrosion rate of the specimens without the inhibitor and $r_m$ is the smallest corrosion rate in the presence of the inhibitor.

Figure 4 shows the relation between $C/\theta$ and $C$ at 30°C. A straight-line relationship with a slope of unity is observed and the linear correlation coefficient is 0.9997. This behavior suggests that the adsorption of PAMT onto metal surface obeys the Langmuir adsorption isotherm. The value of $K$ for PAMT on mild steel in 2 mol/dm$^3$ H$_3$PO$_4$ at 30°C can be determined from the intercept of Figure 4: $K = 3.04 \times 10^4$ (dm$^3$/mol). The standard free energy of adsorption ($\Delta G_{ads}^o$) can be obtained according to the following [25]:

$$K = \left(\frac{1}{55.5}\right) \exp\left(-\frac{\Delta G_{ads}^o}{RT}\right),$$

where $T$ is the absolute temperature and $R$ is the universal gas constant. The 55.5 is the concentration of water in solution expressed in molar concentration. The value of $\Delta G_{ads}^o$ for PAMT as calculated from (5) in 2 mol/dm$^3$ H$_3$PO$_4$ at 30°C was $-36.12$ kJ mol$^{-1}$. The higher value of $K$ and the negative value of $\Delta G_{ads}^o$ indicate spontaneous adsorption of the inhibitor and are characteristics of a strong interaction with the metal surface [26]. The obtained $\Delta G_{ads}^o$ value points out that PAMT is strongly adsorbed on the metal surface. Generally, the values of $\Delta G_{ads}^o$ above $-40$ kJ mol$^{-1}$ are consistent with chemisorption, whilst those below $-20$ kJ mol$^{-1}$ involve electrostatic interaction [27, 28]. The value of $\Delta G_{ads}^o$ indicates that the adsorption of PAMT is predominantly by chemisorption.

### 3.2. The Effect of Acid Concentration and Temperature on Inhibition

Figure 5 shows the effect of changing H$_3$PO$_4$ concentration at 30°C on the inhibitor efficiency of PAMT at the $5 \times 10^{-4}$ mol/dm$^3$ level. Although the inhibitor efficiency decreases slowly with increasing H$_3$PO$_4$ concentration, for 7 mol/dm$^3$ acid level (corresponding to the concentration of H$_3$PO$_4$ produced by the dihydrate wet-method industrial process) the inhibition efficiency still reached to approximately 94.7%. At the 9 mol/dm$^3$ acid level (approximately that reached in the hemihydrate wet-method process) the inhibition efficiency was 94%.

Mathur and Vasudevan plotted the logarithm of the corrosion rate of iron against the molar concentration of H$_3$PO$_4$ and obtained a straight line relationship [29].
following rate equation was set up to describe the straight line relationship:

$$\log r = \log k + BC, \quad (6)$$

where $k$ is the specific reaction rate constant, $B$ is a constant for the reaction, and $C$ is the molar concentration of acid. Replacing $k$ with $Ae^{-E/RT}$ and expanding gives

$$\log r = \left(\log A + \frac{BC}{2.303}\right) - \frac{E}{2.303RT}, \quad (7)$$

where $E$ is the apparent activation energy, $A$ is the frequency factor and $R = 8.3141 \text{K}^{-1} \text{mol}^{-1}$. Both $k$ and $B$ may be obtained from the plot of $\log r$ against $C$, whilst $E$ and $A$ are calculated from a plot of $\log r$ against $1/T$.

In the present study of corrosion of mild steel in phosphoric acid solutions with and without the inhibitor straight line relationships were obtained. Equations (6) and (7) are shown graphically in Figures 6 and 7, respectively.

In the presence of PAMT, the magnitude of $r$ is suppressed as is its tendency to increase with the acidic concentration. Calculated kinetic parameters are listed in Table 2. The values of $k$ in (6) were obtained by extrapolation of the straight line in Figure 5. $k$ can be regarded as a “commencing rate” at zero acid concentration and the superiority of PAMT as an inhibitor is clearly apparent by comparing values of $k$ between the blank and in the presence of PAMT. The calculated values of $E$ (for $\text{H}_3\text{PO}_4$ at the 2 mol/dm$^3$ level) are also shown in Table 2. The value of the apparent activation energy in absence of inhibitor is 42.59 mol/dm$^3$. The value is also of the order of the activation energies encountered for the hydrogen evolution reaction [30]. This is in accordance with the fact that the hydrogen evolution reaction in absence of an inhibitor is the rate determining step for the corrosion reaction. Compared with the value of the apparent activation energy in the presence of $5 \times 10^{-4}$ mol/dm$^3$ PMAT, the difference is not considered to be significant. The presence of PAMT adsorbed on the metal does not act to change significantly the energy barrier for the corrosion reaction. PAMT does not change the mechanism of the rate-determining step of the corrosion process, although it significantly reduces the rate [31]. This result agrees with that reported previously [32, 33]. The frequency factor in the presence of the inhibitor is also not significantly changed.

3.3. Polarization Measurements. Anodic and cathodic polarization curves for electrodes in 2 mol/dm$^3$ phosphoric acid in the absence and presence of various concentrations of inhibitor are shown in Figure 8. The electrochemical parameters such as corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), and Tafel slopes ($\beta_a$, $\beta_c$) are calculated by using Tafel fit and listed in Table 3. The inhibition efficiency was calculated from the following:

$$\text{IE(\%)} = 100 \times \frac{(i_{corr}^0 - i_{corr})}{i_{corr}^0}, \quad (8)$$

where $i_{corr}^0$ and $i_{corr}$ are the corrosion current densities in the absence and presence of the inhibitor, respectively.

It is seen that PAMT shifts both the cathodic and anodic branches of the polarization curves of the pure acid solution to lower values of current density indicating the inhibition of both the hydrogen evolution (HER) and mild steel dissolution reactions. Some retardation of the anodic reaction is observed but cathodic polarization is clearly dominant. PAMT inhibited the hydrogen evolution more than anodic dissolution of mild steel. The corrosion potential is almost unchanged. These observations indicate that a mixed-type control and PAMT is an inhibitor of mixed-type with predominant effect on the cathodic reaction for the corrosion of mild steel in 2 mol/dm$^3$ $\text{H}_3\text{PO}_4$. It can also be seen that PAMT decreases the corrosion current densities at all the studied concentrations, meaning that the corrosion rate of steel is reduced significantly. The inhibition efficiency obtained from polarization measurement is in
metal surface. When PAMT is dissolved in H₃PO₄ medium, which enhances the adsorption of the compounds on the 3d vacant orbital of the sulphur atom possible [35], resulting from overlap of 3d electrons from Fe atom to the 3d vacant orbital of the sulphur atom possible [34]. The presence of mercapto substituent in the organic structures makes the formation of δπ-δπ bond resulting from overlap of 3d electrons from Fe atom to the 3d vacant orbital of the sulphur atom possible [35], which enhances the adsorption of the compounds on the metal surface. When PAMT is dissolved in H₃PO₄ medium, protonation can occur by the reaction of amino group with H₃PO₄. Amines and heterocycle nitrogen compounds may also adsorb through electrostatic interactions between the positively charged nitrogen atom and negatively charged metal surface. The protonated compounds may decrease the hydrogen evolution by adsorbing on the cathodic sites of the mild steel. The adsorption of amine can be influenced by the nature of anions in acidic solution [6]. Being specifically adsorbed, they create an excess negative charge towards the solution and favour more adsorption of the cations [7]. PAMT may adsorb anodic sites through nitrogen and sulphur atoms and aromatic and heterocyclic rings which are electron donating groups and decrease anodic dissolution of mild steel.

### 4. Conclusion

1. The corrosion rates of the steel gradually decrease as the concentration of PAMT increases. The inhibition efficiency increases with the increase of inhibitor concentration and the maximum inhibition efficiency is approximately 97% in 2 mol/dm³ H₃PO₄.

2. PAMT also shows good corrosion inhibition at higher H₃PO₄ concentrations corresponding to the concentrations of H₃PO₄ produced by the dihydrate or hemihydrate wet methods industrial process. The inhibition efficiencies still reach to approximately 94.7% and 94%, respectively.

3. The adsorption of PAMT on the mild steel surface in 2 mol/dm³ H₃PO₄ medium obeys a Langmuir adsorption isotherm. The negative value of ΔG°ads obtained from the study indicates that PAMT was strongly adsorbed on the steel surface and predominantly by chemisorption.

4. PAMT acts as a mixed-type inhibitor retarding the anodic and cathodic corrosion reactions with predominant effect on the cathodic reaction.

### References


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