

EFFECT OF STEEL CORROSION BY SOME NEW TRIAZOLE DERIVATIVES IN BOILING HYDROCHLORIC ACID

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Abstract: Some new triazole derivatives, namely 4-aminobenzylidene-3-propyl-5-mercapto-1,2,4- triazole, 4-aminocinnamalidene-3-propyl-5-mercapto-1,2,4-triazole (ACPMT), 4-amino- salicylidene-3-propyl-5-mercapto-1,2,4-triazole (ASPMT), 4-aminovanillidene-3-propyl- 5-mercapto-1,2,4-triazole, and 4-aminodimethylamino-benzylidene-3-propyl-5-mercapto- 1,2,4-triazole (ADPMT), have been synthesised. Their inhibiting action on the corrosion of mild steel in 15%HCl under boiling conditions has been studied by the weight loss method. With the exception of ADPMT, all the triazole derivatives tested showed an inhibitor efficiency of >98%. Triazole compounds ACPMT and ASPMT showed an efficiency of >99%. Their efficiency has been found to be comparable with that of propargyl alcohol, a standard corrosion inhibitor for mild steel in boiling HCl. Potentiodynamic polarisation studies revealed that all the triazoles investigated are mixed type inhibitors inhibiting the corrosion of mild steel by blocking the active sites of the metal surface. The adsorption of these compounds on mild steel from 15%HCl has been found to obey Temkin's adsorption isotherm.

Keywords: Mild steel, polarization, acidizing inhibitor.

Introduction

Acidification of petroleum wells is one of the most important techniques for enhancing oil production. It is commonly brought about by forcing a solution of 15-28% HCl into the well to open up near bore channels in the formation and hence to increase the flow of oil. To reduce the aggressive attack of the acid on tubing and casing materials, inhibitors are added to the acid solution during the acidifying process [1].

A perusal of the literature [2, 3] reveals that the effective inhibitors used as acidifying corrosion inhibitors include acetylenic alcohols, alkenyl phenones, aromatic α , β unsaturated aldehydes, nitrogen containing heterocyclic compounds, quaternary salts, and condensation products of carbonyls and amines. Among the various compounds available, acetylenic alcohols are widely used as acidifying inhibitors because of their commercial viability and effectiveness. However, these inhibitors suffer from the drawbacks that they are effective only at high concentration and also are extremely toxic in their own right, causing problems of handling and waste disposal, and produce toxic vapours under acidifying process conditions [4]. In view of these disadvantages of acetylenic alcohols, there exists a need for the development of new acidifying inhibitors.

Triazoles such as benzotriazoles [5] and naphthotriazole [6] have been mainly used as corrosion inhibitors for copper. The inhibiting action of some aminohydrazinomercapto-triazoles on the corrosion of steel in H₂SO₄ has

been studied by Abd-El-Nabey et al. [7] The effect of aminomethyl-mercaptotriazole on corrosion and hydrogen permeation of mild steel in acidic solution has been evaluated by Muralidharan et al. [8] Recently, the present authors have investigated the influence of some triazole derivatives, namely 4-aminosalicylidene-3-hydrazino-5-mercapto-1,2,4-triazole, 4-aminosalicylidene-3-methyl-5-mercapto-1,2,4-triazole, and 4-aminosalicylidene-3-propyl-5-mercapto-1,2,4-triazole (ASPMT) on corrosion and hydrogen permeation in acidic solution [9]. All the triazoles investigated were found to be excellent corrosion inhibitors in both 1N H₂SO₄, and 1N HCl. Specifically, the triazole synthesised by the condensation of 4-amino-3-propyl- 5-mercapto-1,2,4-triazole (APMT) and salicylaldehyde showed the highest efficiency among the compounds studied, even at low concentration, in both the acid solutions at room temperature.

In view of the excellent performance of ASPMT as a corrosion inhibitor, the present authors have synthesised some additional triazoles, namely 4-aminobenzylidene-3-propyl-5-mercapto-1,2,4-triazole (ABPMT), 4-aminocinnamylidene-3-propyl-5-mercapto-1,2,4-triazole (ACPMT), 4-aminovanillylidene-3-propyl-5-mercapto-1,2,4-triazole (AVPMT), and 4-amino-dimethylaminobenzylidene-3-propyl-5-mercapto-1,2,4-triazole (ADPMT), with the objective of reducing the corrosion of mild steel in boiling 15% HCl. With the exception of ASPMT, the compounds tested are all new. The choice of these inhibitors is based on the fact that they can be synthesised conveniently from inexpensive raw materials.

Experimental

Inhibitor ASPMT was synthesised by a known method [10]. This involves refluxing an equimolar ratio of AMPT and salicylaldehyde in absolute ethanol for 3 h using 2 or 3 drops of piperidine as a catalyst. On cooling, the reaction mixture gave a solid product, which was purified by crystallising with ethanol. Other triazoles, namely ACPMT (melting point $t_m = 149\text{ }^{\circ}\text{C}$), ABPMT ($t_m = 162\text{ }^{\circ}\text{C}$), AVPMT ($t_m = 184\text{ }^{\circ}\text{C}$), and ADPMT ($t_m = 206\text{ }^{\circ}\text{C}$), were prepared by similar methods and were characterised by their IR spectra. Solutions of the inhibitors were prepared in a mixture of organic solvent (5% acetone and 5% alcohol).

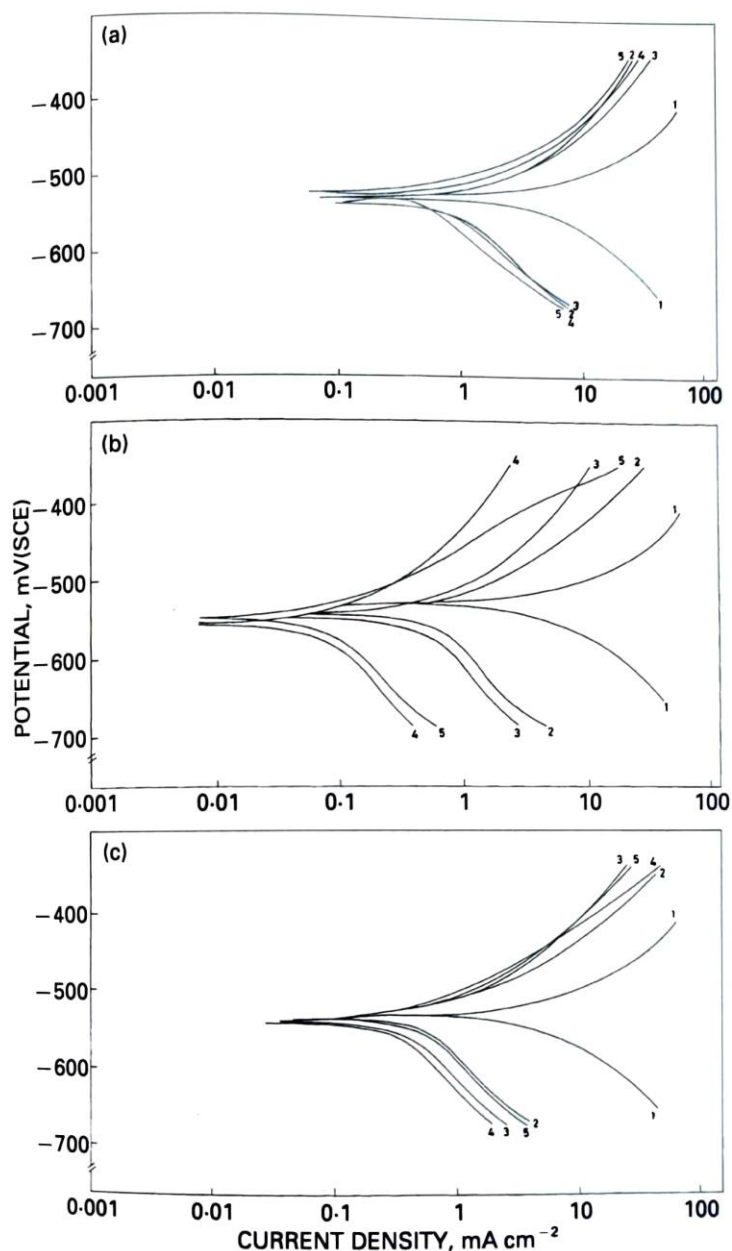
Weight loss measurements

Mild steel (AISI 1079) coupons of size $2 \times 2 \times 0.6\text{ cm}$ and composition Fe–0.14C–0.17Si–0.35Mn–0.03P–0.025S were used for weight loss measurement studies. Each experiment was performed for 30 min at $105 \pm 2\text{ }^{\circ}\text{C}$ as per ASTM test G1-72 (Ref. 11) in a 500 mL three neck borosil round bottom flask using a condenser. The volume of acid was kept at 20 mL cm^{-2} of metal as per ASTM G31-72 [11].

Electrochemical studies

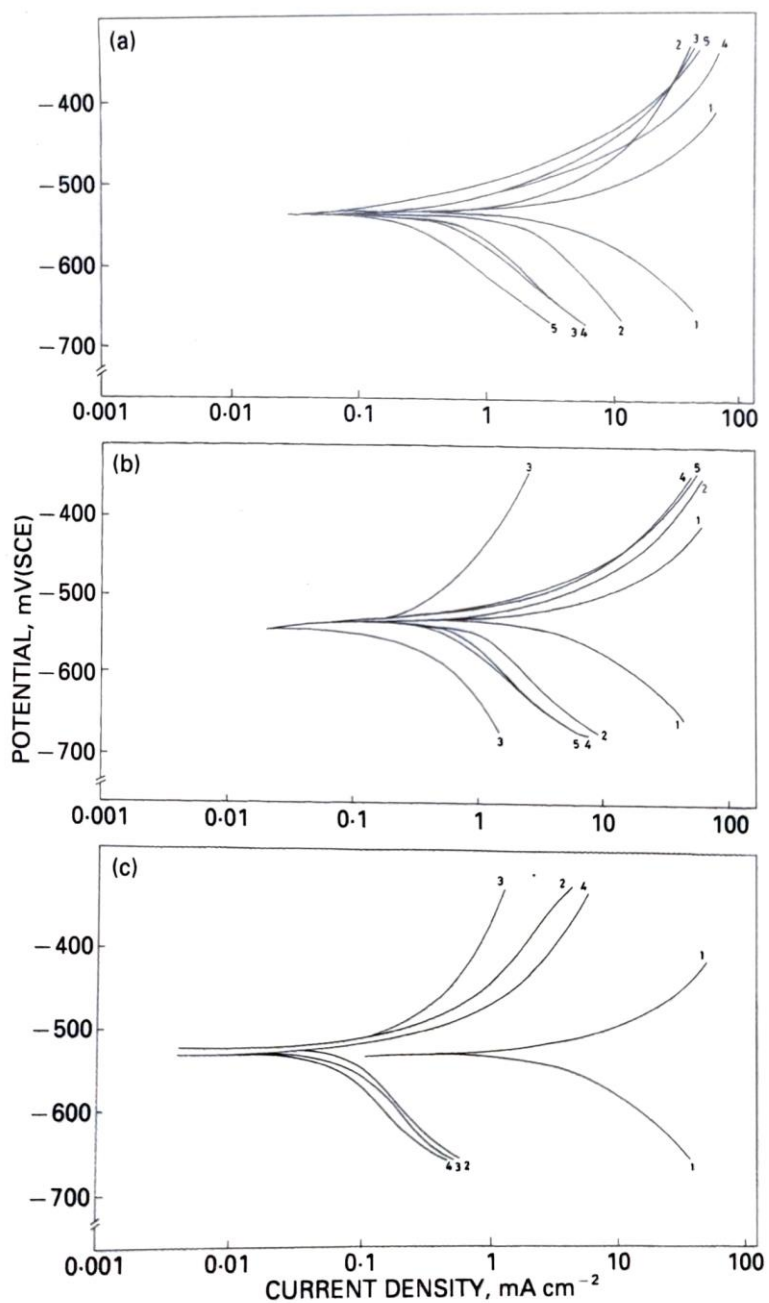
For potentiodynamic polarisation studies, mild steel strips of the same composition, embedded in araldite with an exposed area of 1 cm^2 , were used. The electrodes were polished with emery paper of 1/0, 2/0, 3/0, and 4/0 grades

and degreased with trichloroethylene. Analytical reagent grade HCl (Merck) and double distilled water were used to prepare solutions of 15% HCl for all experiments. Potentiodynamic polarisation studies were carried out using an EG&G Parc model 173 potentiostat-galvanostat, a model 175 universal programmer, and a model RE 0089 X-Y recorder. Platinum foil of size 3×3 cm was used as the auxiliary electrode, and a saturated calomel electrode (SCE) was used as the reference electrode for potentiodynamic polarisation studies. Each experiment was carried out at ambient temperature (35 ± 2 °C).



1: blank (15% HCl); 2: 250 ppm; 3: 500 ppm; 4: 750 ppm; 5: 1000 ppm
(a) ACPMT; (b) ASPMT; (c) AVPMT

Figure 1. Potentiodynamic polarisation curves for mild steel in 15% HCl in absence and presence of given concentrations of inhibitors.



1: blank (15% HCl); 2: 250 ppm; 3: 500 ppm; 4: 750 ppm; 5: 1000 ppm

(a) ABPMT; (b) ADPMT; (c) PA

Figure 2. Potentiodynamic polarisation curves for mild steel in 15% HCl in absence and presence of given concentrations of inhibitors.

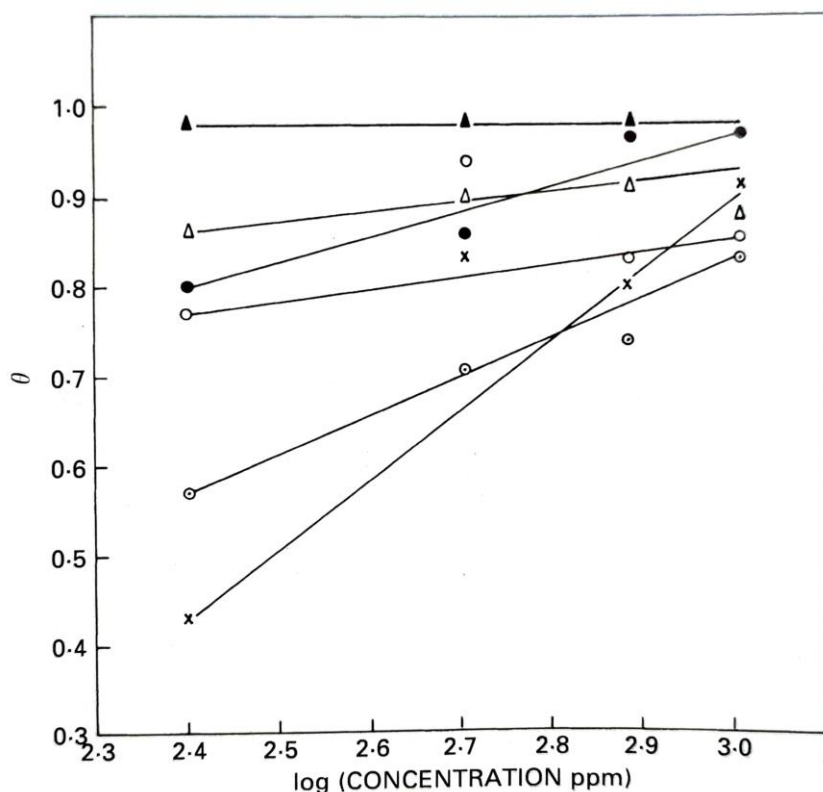
Results and Discussion

Weight loss measurements

The values of inhibitor efficiency and corrosion rate obtained from weight loss measurements for different concentrations of the inhibitors in 15% HCl. From the calculated weight loss values, the percentage inhibitor efficiency P was calculated using the equation

$$P = \frac{\text{uninhibited corrosion rate} - \text{inhibited corrosion rate}}{\text{uninhibited corrosion rate}} \times 100$$

With the exception of ADPMT, all of the compounds studied performed excellently (>98% inhibitor efficiency) as inhibitors of the corrosion of mild steel in boiling 15% HCl. The lower efficiency of ADPTM (81%) compared with the other compounds may be attributed to the orientation of the dimethylamino- $\text{N}(\text{CH}_3)_2$ group, which prevents flat orientation on the metal surface, thereby reducing adsorption and inhibition.



⊖ ACPMT; ● ASPMT; Δ AVPMT; × ABPMT; ○ ADPMT; ▲ PA

Figure 3. Temkin adsorption isotherm plot for different concentrations of various inhibitors on mild steel in 15% HCl

A similar explanation has been given by Rengamani et al.,[12] concerning the discrepancy in the order of inhibitor efficiency for isomers of anisidines, in a study of the inhibition of anions on the performance of anisidines as corrosion inhibitors. Among the five compounds, the order of inhibitor efficiency has been found to decrease in the order:

$$\text{ACPMT} > \text{ASPMT} > \text{AVPMT} > \text{ABPMT} > \text{ADPMT}.$$

Propargyl alcohol is widely used as a commercial acidifying inhibitor; hence, it was chosen as the basis for a comparison of inhibition performance with the prepared inhibitors in boiling HCl solution ($105 \pm 2^\circ\text{C}$). With the exception of ADPMT, all of the investigated inhibitors matched the performance of propargyl alcohol.

Electrochemical studies

Potentiodynamic anodic and cathodic polarisation scans were carried out at $35 \pm 2^\circ\text{C}$ in 15% HCl with different concentrations of all of the inhibitors. The I_{corr} values decreased significantly in the presence of the inhibitors. These observations indicate that the compounds synthesised are effective inhibitors for the corrosion of mild steel in 15% HCl. The E_{corr} values were only slightly shifted in the presence of the inhibitors, suggesting that they work by inhibiting both the anodic and cathodic reactions. Inhibitors that function in this way are known as mixed type inhibitors. Figures 1 and 2 show the polarisation behaviour of mild steel in 15% HCl in the absence and presence of different concentrations of various inhibitors.

Adsorption isotherms

Surface coverage θ values were obtained from electro- chemical measurements for different concentrations of various inhibitors using the equation

$$\theta = \frac{(I_{\text{corr}}^{\circ} - I_{\text{corr}})}{I_{\text{corr}}^{\circ}}$$

where I_{corr}° and I_{corr} are the corrosion current densities in the absence and presence of an inhibitor, respectively. It can be seen from Fig. 3 that a plot of θ versus log concentration gives a straight line, suggesting that the adsorption of all of the inhibitors at the mild steel/acidic solution interface obeys Temkin's adsorption isotherm.

Mechanism

A plausible mechanism of corrosion inhibition of mild steel in 15% HCl may be deduced on the basis of adsorption. In acidic solutions, the triazoles investigated can exist as cationic species like other azoles [13]. These cationic species may be adsorbed on the cathodic sites of the mild steel and reduce the evolution of hydrogen. The protonated triazole derivatives can also be adsorbed on the metal surface on specifically adsorbed chloride ions [14, 15]. The adsorption of these compounds at anodic sites through lone pairs of electrons of nitrogen and

sulphur atoms and through an electron of the triazole ring and azomethine group will then reduce the anodic dissolution of mild steel.

Conclusions

All of the investigated triazoles, ACPMT, ASPMT, ABPMT, AVPMT, and ADPMT, are effective inhibitors for the corrosion of mild steel in a 15% boiling HCl solution and, with the exception of ADPMT, are comparable in performance to propargyl alcohol. Also, these triazoles all exhibit a mixed inhibitor type mechanism. The inhibitors reduce corrosion by being adsorbed on the metal surface. They represent a possible alternative to the use of propargyl alcohol, since they are solid compounds and do not produce toxic vapours during the acidifying process.

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