

INFLUENCE OF SOME MULTIFUNCTIONAL TRIAZOLES ON CORROSION OF MILD- STEEL IN BOILING HYDROCHLORIC ACID SOLUTIONS

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Some new triazole based corrosion inhibitors namely, 4-benzylideneamino-3-hydrazino-5-mercapto-1,2,4-triazole, (BAHMT), 4-dimethylaminobenzylideneamino-3-hydrazino-5-mercapto-1,2,4-triazole (DAHMT), and 4-vanillideneamino-3-hydrazino-5-mercapto- 1,2,4-triazole (VAHMT) have been synthesized and their influence on corrosion inhibition of mild steel in 15% hydrochloric acid solution under boiling conditions has been studied using weight loss method. All the tested inhibitors except DAHMT showed > 90% inhibition efficiency. Potentiodynamic polarization measurements have been carried out at room temperature, which clearly reveal the fact that all investigated inhibitors are of mixed type and they inhibit corrosion of mild steel by blocking the active sites of the metal surface. The adsorption of these inhibitors on the mild steel surface from 15% HCl has been found to obey Temkin's adsorption isotherm.

Keywords: Mild steel, polarization, acidising inhibitor.

INTRODUCTION

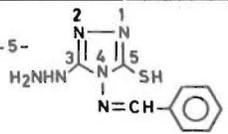
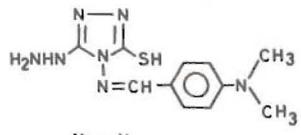
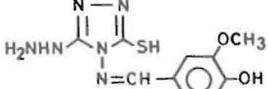
Acidization of petroleum oil and gas well is one of the important techniques for enhancing oil production. It is brought about by forcing a solution of 15-28% HCl into the well to open channels and to increase flow of oil and gas. Hydrochloric acid is the major acidizing agent. To reduce the corrosive attack of the acid, inhibitors are incorporated with the acid solution during the process of acidization [1].

A perusal of literature [2-3] reveals that most of the organic compounds used as effective corrosion inhibitors during acidization include acetylenic alcohols such as propargyl alcohol, hexynols and decynols are widely used as acidizing inhibitors because of their effectiveness and commercial availability. These acetylenics are hazardous as they produce toxic vapours during acidization and are effective only at higher concentration [4]. In view of the above mentioned demerits of acetylenic alcohols, there always exists a need for development of new acidizing inhibitors.

It is reported in the literature that the condensation products of carbonyls and amines which are known as anils or Schiff's bases give higher inhibition efficiency than that for the constituent carbonyls and amines [5-6]. These observations led us to synthesize a few condensation products derived from aminobenzothiazoles and salicylaldehyde [7], aminotriazole and salicylaldehyde [8]. All the investigated compounds were found to give excellent performance as corrosion inhibitors.

In the present investigation we have synthesized a few triazoles bearing both hydrazino and azomethine group in the same molecule, with an objective of evaluating their inhibiting action on corrosion of mild steel in boiling hydrochloric acid solutions. The studied compounds are: benzylideneamino-3-hydrazino-5-mercapto-1,2,4-triazole, (BAHMT), dimethylaminobenzylideneamino- 3-hydrazino-5-mercapto-1,2,4-triazole (DAHMT), and vanillideneamino-3-hydrazino-5-mercapto-1,2,4-triazole (VAHMT).

TABLE I

Designation	Structural formula	Abbreviation
4-Benzylidene amino-3-hydrazino-5-mercapto-1,2,4-triazole		BAHMT
4-Dimethylamino benzylidene amino-3-hydrazino-5-mercapto-1,2,4-triazole		DAHMT
4-Vanillidine amino-3-hydrazino-5-mercapto-1,2,4-triazole		VAHMT

Material and methods

The parent compound 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole, (AHMT) was synthesized by a known method [9]. All the tested azoles were synthesized in the laboratory by condensing AHMT with different aldehydes and were characterized by their IR spectra. The solutions of inhibitors were prepared in a mixture of organic solvents (5-10%). The structures of the anils are given in Table I.

Mild steel (AISI 1079) specimens of size 2.0 x 2.0 x 0.6 cm having composition, C=0.14%, Mn=0.35%, Si=0.17%, S=0.025%, P=0.03% and remainder Fe, were used for weight loss measurements. The experiments were performed in a 500 ml three neck glass cell using a condenser for half an hour at 278 ± 2 K. All the coupons were prepared and evaluated as per ASTM G1-72 and G31-72 [10].

For potentiodynamic polarization studies, mild steel strips of the same composition embedded in araldite with an exposed area of 1 cm² was used. The test electrodes were polished successively with emery papers of 1/0, 2/0, 3/0 and 4/0 grade and degreased with trichloroethylene. AR grade HCl (MERCK) and double distilled water were used for preparing test solution of 15% HCl for all the experiments. Potentiodynamic polarization studies were carried out using EG & G PAR potentiostat/galvanostat (model 173), universal

TABLE II: Corrosion parameters for mild steel in boiling 15% HCl (378 ± 2 K) in the absence and presence of different concentrations of inhibitors, derived from weight loss measurements

Concn of inhibitors (ppm)	Corrosion rate (mmpy)	Inhibition efficiency (%)
15% HCl (Blank)	12526.20	---
BAHMT		
1000	6022.31	52
2000	3403.31	73
3000	2412.96	81
4000	830.61	93
5000	874.55	93
DAHMT		
1000	10420.89	17
2000	7729.99	38
3000	6302.32	50
4000	6733.54	46
5000	4835.45	61
VAHMT		
1000	2986.41	76
2000	2468.46	80
3000	1470.04	88
4000	1336.93	89
5000	1116.05	91

programmer (model 175) and X-Y recorder (model RE 0089). A platinum foil of 3.0 x 3.0 cm and a saturated calomel electrode (SCE) were used as auxiliary and reference electrodes, respectively. All the experiments were carried out at constant temperature of 308 ± 2 K.

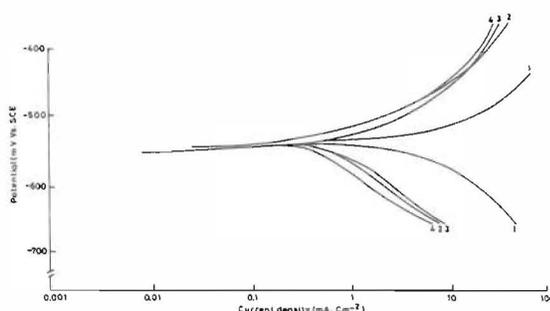


Fig. 1: Potentiodynamic polarization curves for steel in 15% HCl in the absence and presence of optimum concentrations of inhibitors 1. 15% HCl (Blank) 2. 1000 ppm VAHMT 3. 1000 ppm DAHMT 4. 1000 ppm BAHMT

RESULTS AND DISCUSSION

Weight loss method

Table II shows the values of corrosion rates and inhibition efficiencies obtained from weightloss measurements for different concentrations of the azole in 15% boiling HCl. From the calculated corrosion rate values, the inhibition efficiency, P(%) for each concentration was calculated using the following equation

$$I.E. (\%) = \frac{(R^0 - R)100}{R^0} \quad (1)$$

where R^0 and R are the corrosion rates in the absence and presence of an inhibitor, respectively.

It has been found from Table II that inhibition efficiency increases with the increase in concentration of the inhibitors. All compounds studied have exhibited an excellent performance (> 90% I.E) as inhibitors on the corrosion of mild steel in boiling 15% HCl except DAHMT, which exhibited an inhibition efficiency of 62%. Lesser inhibition efficiency shown by DAHMT as compared to other compounds may be attributed to the orientation of dimethylamino $-N(CH_3)_2$ group since it prevents flat orientation on the metal surface which decreases adsorption and inhibition. Similar explanation has been offered in [11]

TABLE III: Potentiodynamic polarization parameters for the corrosion of mild steel in 15% HCl at room temperature (308 ± 2 K) containing different concentrations of various inhibitors

Concn of inhibitors (ppm)	E_{corr} (mV vs SCE)	I_{corr} (mA/cm ²)	Inhibition efficiency (%)
15% HCl (Blank)	-542	3.50	---
BAHMT			
250	-551	0.80	77
500	-551	0.60	83
750	-553	0.50	86
1000	-551	0.35	90
DAHMT			
250	-549	1.50	57
500	-549	0.90	74
750	-551	1.00	71
1000	-549	0.60	83
VAHMT			
250	-551	0.70	80
500	-549	0.60	83
750	-545	0.50	87
1000	-547	0.45	87

to explain the discrepancy in the order of inhibition efficiency for isomers of anisidines, while studying the inhibition of anions on the performance of anisidines as corrosion inhibitors.

Potentiodynamic polarization studies

Potentiodynamic polarization studies were carried out in 15% HCl without and with different concentration of the inhibitors. The various electrochemical parameters calculated from Tafel plots are given in Table III.

It can be seen from Table III that the I_{corr} values decreases significantly in the presence of inhibitors. These observations indicate that all azoles are effective inhibitors for the corrosion of mild steel in 15% HCl. The E_{corr} values are slightly shifted in the presence of inhibitors suggesting that these inhibitors inhibit the corrosion of mild steel in HCl by controlling both the anodic and cathodic reactions. Inhibitors of this type are known as mixed type inhibitors. Fig. 1 shows the polarization behaviour of mild steel in 15% HCl in the absence and presence of optimum concentrations of inhibitors.

Adsorption isotherms

The surface coverage (θ) for each concentration was calculated from electrochemical measurements using the following equation

$$\theta = \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \quad (2)$$

where I_{corr}^0 and I_{corr} are the corrosion current densities in the absence and presence of an inhibitor, respectively. It was observed from Fig. 2 that a plot of θ vs log C gives a straight line suggesting that the adsorption of the tested azoles on

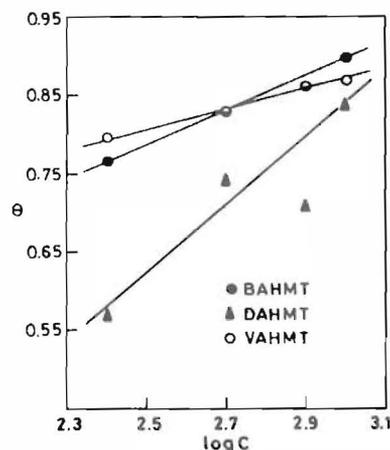


Fig. 2: Temkins adsorption isotherm plot for different concentration of inhibitors on mild steel in 15% HCl solution

mild steel/anodic solution interfaces obeys Temkin's adsorption isotherm.

The possible mechanism of the inhibition of corrosion of mild steel in HCl may be explained on the basis of adsorption. In aqueous acidic solutions, the investigated azoles can exist as cationic species [13] like other azoles [14]. These cationic species may adsorb on the cathodic sites of the mild steel and decrease the evolution of hydrogen. These protonated triazoles can also be adsorbed on the metal surface on specifically adsorbed chloride ions [14-15]. Similar synergistic mechanism has also been reported in [16] to explain the inhibitive action of some nitrogen containing heterocyclics in acidic solution. The adsorption of these azoles on anodic sites can take place through lone pairs of electrons of nitrogen and sulphur atoms, π electrons of the triazole ring and azomethine group.

CONCLUSIONS

The following conclusions can be drawn on the basis of present investigations.

1. All investigated triazoles namely BAHMT, DAHMT and VAHMT are effective inhibitors for corrosion of mild steel in 15% boiling HCl solution.
2. They are mixed type inhibitors.
3. They inhibit corrosion by getting adsorbed on the metal (mild steel) surface.
4. Their adsorption on the mild steel surface in 15% HCl solution obeys Temkin's adsorption isotherm.

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