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CORROSION INHIBITION OF MILD STEEL IN BOILING HYDROCHLORIC ACID BY SOME THIAZOLE DERIVATIVES

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The influence of some thiazole derivatives namely, 2- benzylideneamino-4-phenylthiazole (BAPT), 2-cinnamylideneamino-4-phenylthiazole (CAPT), 2-dimethylaminobenzylideneamino-4-phenylthiazole (DAPT), 2-furfurylideneamino-4-phenylthiazole (FAPT) and 2-salicylideneamino-4-phenylthiazole (SAPT) on corrosion inhibition of mild steel in 15% hydrochloric acid solution under boiling conditions has been studied using weight loss method. All the tested thiazole derivatives showed very good inhibition efficiency. Potentiodynamic polarization measurements reveal the fact that all the investigated thiazoles are of mixed type inhibitors 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: Acidization, corrosion inhibitor, hydrochloric acid, mild steel, potentiodynamic polarization.

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 up near bore channels in the formation and hence to increase flow of oil. To reduce the corrosive attack of the acid, inhibitors are incorporated with acid solution during acidization process [1].

Most of the organic compounds used as effective corrosion inhibitors during acidization include acetylenic compounds, unsaturated aldehydes, nitrogen and sulfur containing heterocyclic compounds, quaternary salts and condensation products of carbonyls and amines [2-3]. Among various compounds available, acetylenic alcohols are widely used as acidizing inhibitors because of their effectiveness and commercial availability. However, these inhibitors suffer from the following drawbacks (i) they are effective only at high concentration and (ii) they produce toxic vapours under acidizing process [4].

In view of the above mentioned demerits of acetylenic alcohols, there always exist a need for development of new acidizing inhibitors.

Most of the commercial inhibitor formulations are found to include aldehydes and amines as essential ingredients. Turbina *et al.* [5] have observed that condensation products of carbonyls and amines which are known as anils or Schiff's bases give higher inhibition efficiency than that for constituent carbonyls and amines. A few Schiff's bases (derived from aromatic aldehydes and amines) have been studied as corrosion inhibitors for mild steel in hydrochloric acid [6]. It was found that the inhibition efficiency for the investigated Schiff's bases is much higher than that for corresponding amines and aldehydes. These observations have led us to the synthesis of a few anils by condensing a few 2-amino-benzothiazoles with salicylaldehyde [7] and aminotriazoles with salicylaldehyde [8] with an idea of evaluating their inhibitive properties on corrosion of mild steel in acidic solutions. These anils have been found to be effective as acid corrosion inhibitors for mild steel. The inhibition efficiencies of all these compounds have been found to be greater than that for corresponding amines and salicylaldehyde. In view of the excellent performance of the condensation products of amines and aldehydes, we have synthesized five condensation products (anils) namely, BAPT, CAPT, DAPT, FAPT and SAPT by condensing 2-amino-4-phenylthiazole and different aldehydes to study their inhibiting action on corrosion of mild steel in 15% boiling HCl. All of the five anils studied in the present investigation are new. The choice of these anils as acid corrosion inhibitors is based on several considerations (i) in addition to the presence of an aminophenylthiazole ring, the presence of π-bond of an azomethine group

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and that of phenyl group can induce greater adsorption of the inhibitor molecules on the metal surface, (ii) the presence of substituents like $N(CH_3)_2$ and -OH can further improve inhibition by increasing the electron availability and the solubility of the compounds, (iii) all the compounds can be synthesized conveniently from relatively inexpensive raw materials.

EXPERIMENTAL METHOD

Materials and test solutions

The parent compound, 2-amino-phenylthiazole was synthesized by a known method [9]. All the anils, viz., BAPT mp = 420 K, CAPT mp = 453 K, DAPT = 411 K, FAPT mp = 415 K and SAPT mp = 443 K were prepared by the method described elsewhere [10]. All the compounds were purified by crystallization and the purity was ascertained by TLC. All of these compounds were characterized by 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. Propargyl alcohol, 99% (MERCK) was used for comparative studies with the anils synthesized.

Mild steel (AISI 1079) specimens of size 2 cm by 2 cm by 0.6 cm (0.788 in. by 0.788 in. by 0.236 in.) having composition, C = 0.14%, Mn = 0.35%, Si = 0.17%, S = 0.25%, P = 0.03% and remainder Fe were used for weight loss measurements. The experiments were performed in a 500 ml three neck borosil round bottom flask using a condenser for half an hour at 378 ± 2 K. All the coupons were prepared, cleaned and evaluated as per ASTM G1-72 [11]. For potentiodynamic polarization studies, mild steel strips of the same composition embedded in araldite with an exposed area of 1 cm^2 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 PARC potentiostat/galvanostat (model 173), universal programmer (model 175) and with X-Y recorder (model RE 0089). A platinum foil of 3 x 3 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 as per ASTM G3-74 and ASTM G5-87 [11].

RESULTS AND DISCUSSION

Weight loss measurements

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

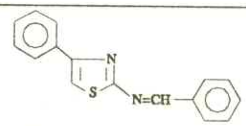
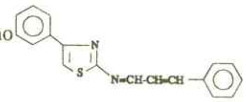
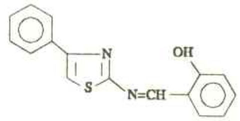
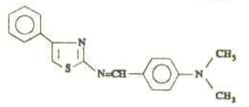
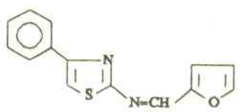
$$P(\%) = \frac{(R^0 - R) \times 100}{R^0} \qquad (1)$$

where R^0 and R are the corrosion rates in the absence and presence of an inhibitor, respectively. Percent inhibition efficiency increases with concentration of all the anils in 15% boiling HCl. All the anils studied have exhibited an excellent performance (94% inhibition efficiency) as inhibitors on the corrosion of mild steel in boiling 15% HCl. Among the tested anils the order of percent inhibition efficiency at a concentration of 2000 ppm has been found to be as follows:

CAPT	SAPT	BAPT	FAPT	DAPT	PA
98.2	97.9	94.8	94.0	90.8	23.8

CAPT has been found to give the best performance at a concentration of 2000 ppm. This can be

TABLE I: Studied organic compounds

Designation	Structure	Abbreviation
2-Benzylideneamino-4-phenylthiazole		BAPT
2-Cinnamylideneamino-4-phenylthiazole		CAPT
2-Salicylideneamino-4-phenylthiazole		SAPT
2-Dimethylamino benzylideneamino-4-phenylthiazole		DAPT
2-Furfurylideneamino-4-phenylthiazole		FAPT
Propargyl alcohol	HC ≡ CCH_2OH	PA

explained on the basis of the presence of an additional -C=C- bond between carbon atoms in conjugation with azomethine -C=N- group. These extensively delocalized π-electrons favour greater adsorption on the metal surface as compared to other compounds, thereby, giving rise to very high value of percent inhibition efficiency (98%) at a concentration of 2000 ppm. Higher IE of condensation product of cinnamaldehyde and thiosemicarbazide than that of the benzaldehyde and thiosemicarbazide was earlier explained on these lines [12]. Higher IE of anil derived from 2-amino-phenylthiazole (APT) and cinnamaldehyde than APT and benzaldehyde [13] was also found. Commercial acidizing inhibitors like acetylenic alcohols give maximum percent inhibition efficiency at a concentration of 3000-7000 ppm. Propargyl alcohol is widely used as a commercial acidizing inhibitor, hence, it is chosen as the basis for comparison of inhibitive performance with the synthesized anils in boiling 15% HCl solution (378 ± 2 K). All the investigated inhibitors match the performance of propargyl alcohol.

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

Concn of inhibitors (ppm)	Corrosion rate (mmpy)	Inhibition efficiency (%)
15% HCl (Blank)	12526	—
PA		
1000	10994	12.2
2000	9543	23.8
3000	177	98.6
4000	142	98.9
5000	37	99.7
BAPT		
1000	1847	85.3
2000	650	94.8
3000	268	97.8
CAPT		
1000	403	96.8
2000	227	98.2
DAPT		
1000	2256	82.0
2000	1142	90.8
3000	1109	91.1
4000	724	94.2
5000	413	96.7
FAPT		
1000	1188	90.5
2000	747	94.0
3000	704	94.3
SAPT		
1000	653	94.7
2000	256	97.9

Potentiodynamic polarization studies

Potentiodynamic polarization studies were carried out in 15% HCl without and with different concentrations of all the inhibitors. The various electrochemical parameters calculated from Tafel plots are given in Table III. I_{corr} values decrease significantly in presence of the inhibitors. These observations indicate that all anils are effective inhibitors for the corrosion of mild steel in 15% HCl. E_{corr} values are slightly shifted in presence of the inhibitors suggesting that these inhibitors inhibit the corrosion of mild steel in 15% HCl by controlling both the anodic and cathodic reactions.

Adsorption isotherms

The surface coverage (θ) of each concentration was calculated using the following equation

$$\theta = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}} \qquad (2)$$

where I^0_{corr} and I_{corr} are the corrosion current densities in the absence and presence of an inhibitor, respectively. A plot of θ vs Log C gives a straight line suggesting that the adsorption of the tested anils on mild steel/acidic solution interface obeys Temkin's adsorption isotherm (Fig. 1).

Mechanism of inhibition

The plausible mechanism of the inhibition of corrosion of mild steel in 15% HCl may be explained on the basis of adsorption. In aqueous acidic solutions, the investigated thiazoles (anils) can exist as cationic species [14] like other azoles [15]. These cationic species may adsorb on the cathodic sites of the mild steel and decrease the evolution of hydrogen. These protonated thiazoles can also be adsorbed on the metal surface on specifically adsobred chloride ions [16-17]. Similar synergistic mechanism has also been proposed by Granese *et al.* [18] to explain the higher inhibition efficiency of some nitrogen containing heterocyclics in acidic solutions. The adsorption of these compounds on anodic site through lone pairs of electrons on nitrogen and sulphur atoms and π electrons of the phenyl and thiazole ring and azomethine group may decrease anodic dissolution of mild steel.

CONCLUSION

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

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	—
PA			
250	-516	0.06	98.3
500	-522	0.06	98.3
750	-523	0.06	98.3
BAPT			
250	-516	0.05	98.6
500	-540	0.04	98.9
750	-530	0.04	98.9
1000	-520	0.04	98.9
CAPT			
250	-528	0.08	97.7
500	-536	0.05	98.5
750	-536	0.04	98.8
DAPT			
500	-526	0.25	92.8
750	-536	0.17	95.1
1000	-532	0.15	95.7
FAPT			
250	-538	0.15	95.7
500	-516	0.10	97.1
750	-518	0.08	97.7
SAPT			
250	-544	0.10	97.1
500	-546	0.07	98.0
750	-546	0.07	98.0
1000	-564	0.16	95.4

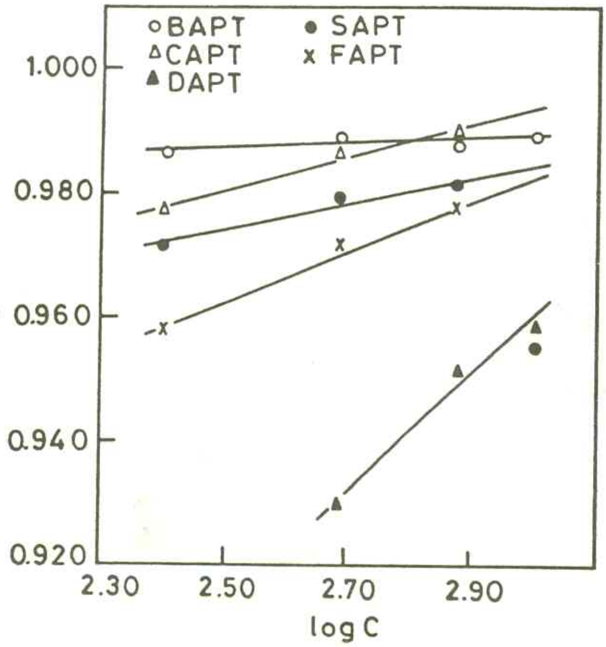


Fig.1: Temkin adsorption isotherm plot for different concentration of inhibitors on mild steel in 15% HCl

- all the investigated thiazoles namely BAPT, CAPT, DAPT, FAPT and SAPT are effective inhibitors against corrosion of mild steel in 15% boiling HCl solution and is comparable in performance of propargyl alcohol.
- they are mixed type inhibitors.
- they inhibit corrosion by adsorbing on the mild steel surface.
- their adsorption on the mild steel from 15% HCl solution obeys Temkin's adsorption isotherms.
- they represent a possible alternative to the use of propargyl alcohol, since they are solid compounds and do not produce toxic vapours during acidizing process.

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