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A thermodynamical, electrochemical, theoretical and surface investigation of diheteroaryl thioethers as effective corrosion inhibitors for mild steel in 1 M HCl

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ABSTRACT

The inhibition effect of three diheteroaryl thioethers (DHATs) namely 5,5'-thiobis (4-phenylthiazol-2amine) (DHAT-1), 4,4'-(5,5'-thiobis(2-aminothiozole-5,4-diyl)) diphenol (DHAT-2) and 4,4'-(5,5'-thiobis(2-aminothiazole-5,4-diyl))bis (benzene-1,3-diol) (DHAT-3) on mild steel corrosion in 1 M HCl was studied by weight loss, electrochemical, scanning electron microscopy (SEM), atomic force microscopy (AFM) and theoretical calculation methods. Among the studied compounds DHAT-3 exhibited maximum inhibition efficiency ($\eta\%$) of 96.99% at 11.2 × 10^{-5} mol/L concentration. The potentiodynamic studies revealed that investigated DHATs act as mixed type inhibitors. Adsorption of the DHATs on the mild steel surface in 1 M HCl obeys the Langmuir adsorption isotherm. The results of theoretical calculation, SEM and AFM studies were found to be consistent with the weight loss and electrochemical results.

1. Introduction

Iron and its alloys are one of the most inspired construction materials for various industrial applications due to their excellent structural and mechanical strength [1]. However, they are very prone to corrosion during industrial processes such as acid pickling, acid cleaning, ore production, oil well acidification and acid descaling. Acid solutions particularly HCl, are used during these processes to remove detrimental corrosion products (scale and rust) from the metallic surfaces [2]. The poor corrosion resistance of mild steel in acidic solution needs utilization of corrosion inhibitors during such processes. Consumption of organic compounds is one of the most effective and economic approaches in metallic corrosion protection [3–7]. Organic compounds containing heteroatoms (N, O, S, and P), heterocyclic rings, polar functional groups and extensive conjugation are of particular interest as they block the active sites present on the metallic surface and thereby reducing the corrosion of metals in aggressive corrosive media [8, 9].

Considering the excellent corrosion inhibition properties of organic compounds containing nitrogen, oxygen and sulfur, we herein synthesized and studied the adsorption ability of the three diheteroaryl thioethers (DHATs) containing two thiazole rings, namely 5,5'-thiobis (4-phenylthiazol-2amine) (DHAT-1), 4,4'-(5,5'-thiobis(2-aminothiozole-5,4-diyl)) diphenol (DHAT-2) and 4,4'-(5,5'-thiobis(2-aminothiazole-5,4-diyl))bis (benzene-1,3-diol) (DHAT-3) on mild steel surface in 1 M HCl. Recently, a large number of thiazoles derivatives were reported as effective corrosion inhibitors for various metals and alloys including mild steel, copper and aluminum in acid, basic and neutral corrosive media using theoretical and experimental methods [10–16]. The selection of these compounds based on the facts that: the DHATs (a) can be synthesized from commercially available starting materials, (b) contain various adsorption centers including $-NH_2$, –OH groups and heteroatoms along with extensive conjugation in form of hetero aromatic rings (c) they were effective even at very low concentration and (d) they were highly soluble in test medium. Moreover, owing to their utilization in treatment of various malignant diseases, the DHATs can be considered as nontoxic, biocompatible and environmental friendly green corrosion inhibitors [17,18]. The study was conducted using weight loss, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, scanning electron microscopy (SEM), atomic force microscopy (AFM) and quantum chemical calculation techniques.

2. Experimental

2.1. Inhibitors synthesis

The DHATs used in present study were synthesized according to the scheme shown in Fig. 1 [19]. The chemical structure, abbreviations, IUPAC name and analytical data of the synthesized diheteroaryl

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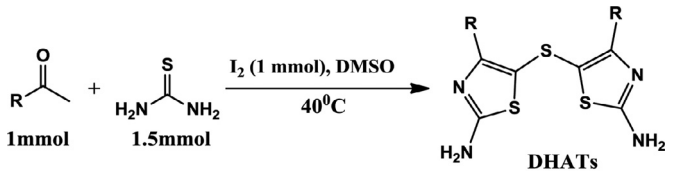


DHAT-1, R- = Ph DHAT-2, R- = 4-HOC$_6$H
DHAT-3, R- = 2, 4-(HO)C$_6$H$_4$-

Fig. 1. Synthetic route of studied diheteroaryl thioethers.

thioethers are given in Table 1. Purity of the compounds was confirmed by thin layer chromatographic method.

2.2. Preparation of electrodes and test solution

The mild steel specimens having dimension 2.5 × 2 × 0.025 cm were used for all weight loss experiments. Whereas, mild steel having size 8 × 1 × 0.025 cm with exposed area 1 cm^2 were used for all electrochemical measurements. The chemical composition of the mild steel was: (wt%): C = 0.076, Mn = 0.192, P = 0.012, Si = 0.026, Cr = 0.050, Al = 0.023, and remainder Fe. Before performing the experiments, the mild steel surface were successively cleaned with SiC emery papers of different grades (600, 800, 1000 and 1200), washed with double distilled water, degreased with acetone and finally dried under hot air blower. The test solution (1 M HCl) was prepared by dilution of analytical grade HCl (MERCK, 37%) in double distilled water.

2.3. Weight loss experiments

The weight loss experiments were performed in 100 mL test solution containing different concentration of DHATs on rectangular mild steel specimens. The immersion time was 3 h at 308 K. At each concentration, triplicate experiments were performed and mean value was reported. Percentage inhibition efficiency (η%) was calculated using following equation:

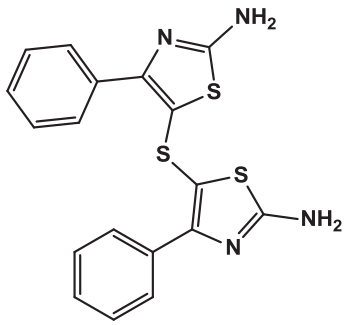
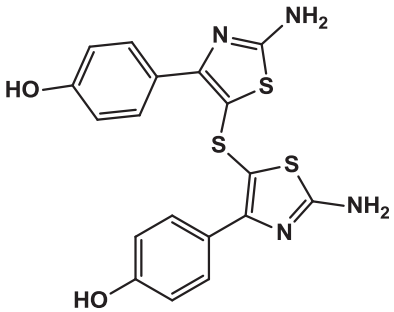
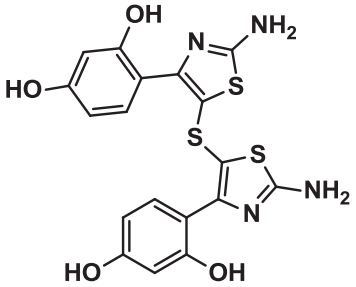
$$\eta\% = \frac{w_o - w_i}{w_o} \times 100 \quad (1)$$

Where w_0 and w_i are the values of weight loss of mild steel in absence and presence of DHATs, respectively. The corrosion rate for mild steel corrosion was calculated using following equation:

$$C_R = \frac{87.6w}{A\,t\,D} \quad (2)$$

Where w is the weight loss of mild steel (mg), A the area of the working electrode (cm^2), T is the exposure time (h) and D the density of working electrode (7.85 g/cm^3).

Table 1
IUPAC name, molecular structure, molecular formula, melting point and analytical data of studied DHATs.

S. No.	IUPAC name and abbreviation of inhibitor	Chemical structure	Molecular formula and M.P. and analytical data
1	5, 5′ – thiobis(4 – pheny1thiazol – 2 – amine) **(DHAT-1)**		$C_{18}H_{14}N_4S_3$ (mol. wt. 382.03), 209–213 °C; IR spectrum (KBr cm^{-1}): 3354, 3252, 1673,1608, 1517, 1480, 1352, 1130, 771, 724: ^{1}H NMR (300 MHz, DMSO) δ (ppm): 7.85, 7.47, 7.32,
2	4, 4′ – (5, 5′ – thiobis(2 – aminothiazole – 5, 4 – diyl))diphenol **(DHAT-2)**		$C_{18}H_{14}N_4O_2S_3$, (Mol. wt. 414.03), 159–162 °C; IR spectrum (KBr cm^{-1}): 3408, 3228, 3117, 1670, 1642, 1548, 1524, 1507, 1428, 1339, 1225, 835, 753;^{1}H NMR (300 MHz, DMSO) δ (ppm): 7.63, 7.23, 6.85, 6.62–6.53
3	4, 4′ – (5, 5′ – thiobis(2 – aminothiazole – 5, 4 – diyl))bis(benzene – 1, 3 – diol) **(DHAT-3)**		$C_{18}H_{14}N_4O_4S_3$, (Mol. wt. 446.02), 239–241 °C;IR spectrum (KBr cm^{-1}):3509, 3328, 3252, 1770, 1648, 1631, 1523, 1498, 1353, 1228, 856, 789, 738: ^{1}H NMR (300 MHz, DMSO) δ (ppm): 7.78, 7.42, 6.89, 6.71–6.54, 6.23–6.21

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