

INHIBITION OF ACID CORROSION OF ALUMINIUM BY THIOPHENE AND ITS DERIVATIVES

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Studies were carried out on aluminium in acid solutions using ethoxylated fatty acids, derivatives of benzaldehyde and derivatives of phenanthroline. The corrosion rates were correlated with Hammett constants.

Keywords: Corrosion of aluminium in acids inhibitors, ethoxylated fatty acids derivatives of benzaldehyde Hammett constants, dipolemoments.

INTRODUCTION

Organic compounds with functional groups containing hetero-atoms are of particular interest as inhibitors. For compounds of similar structure with oxygen, nitrogen and sulphur as functional groups, the inhibitor efficiency follows the sequence $O < N < S$ [1]. Previous studies reported that carbonyl compounds[2] and sulphur containing organic compounds[3] inhibit the corrosion of mild steel in HCl [2] and H_2SO_4 [3] acid solutions.

Trials were made to inhibit the corrosion of aluminium in acid solutions using some ethoxylated fatty acids[4], benzaldehyde and some of its derivatives [5]. Also, phenanthroline and some of its derivatives, 2,2' bipyridyl and 2-pyridyl derivatives were investigated [6]. Studies were also performed to inhibit aluminium corrosion in halide media (mixtures of NaCl-NaBr and NaCl-NaI) by benzotriazole and 8-hydroxyquinoline [7]. Inhibition of alkaline corrosion of aluminium by condensation products of thiosemicarbozide with some aldehydes was also tried [8].

The present investigation reports the use of thiophene and some of its 2-substituted derivatives as inhibitors for aluminium corrosion in HCl acid solution.

EXPERIMENTAL

Pure aluminium (99.99%) was used in the present study. Flat specimens measuring (100 x 10 x 0.38 mm) were used for the gravimetric and hydrogen evolution was found to be constant over an extended time intervals satisfying the relation:

$$R = \frac{1}{A} \left[\frac{dV_{H_2}}{dt} \right] \text{ cm}^3 \text{ min}^{-1} \text{ cm}^{-2} \quad (1)$$

where A is the geometrical surface area of the specimens. The percent inhibition (PI) was determined applying the relation:

$$PI = \frac{R_0 - R_i}{R_0} \times 100 \quad (2)$$

where R_0 and R_i are the corrosion rates ($\text{mg}/\text{cm}^2 \cdot \text{hr}$) in uninhibited and inhibited 2 M HCl solutions respectively.

In the polarisation technique [10] Al was in the form of rod mounted in teflon holder to expose the bottom surface (0.01 cm^2). Corrosion rates were determined in terms of logarithm of corrosion current ($\log i_{\text{corr}}$) in 2 M HCl containing 10^{-3} M inhibitors.

Surface preparation included polishing with different grades of emery paper down to G 400, washing by distilled water, degreasing with acetone and drying with filter papers.

TABLE I: Thiophene and its 2-substituted derivatives

Compound	Formula	Hammett constant	Dipole moment (μ / D)	Electron density ⁽¹¹⁾	
				S	O
I Thiophene	C_4H_4S	0.000	0.53	-0.129	—
II 2-chlorothiophene	C_4H_3S-Cl	+0.226	1.60	—	—
III 2-thiophene carboxylic acid	$C_4H_3S-COOH$	+0.265	1.96	+0.035	-1.372
IV 2-acetyl thiophene	$C_4H_3S-COCH_3$	+0.516	3.37	+0.600	-1.384
V 2-thiophene carboxaldehyde	C_4H_3S-CHO	+0.570	3.55	+0.090	-1.387

Experiments were carried out at 293 ± 2 K in aerated unstirred 2 M HCl solution in absence and presence of different inhibitor concentrations. Thiophene and four of its 2-substituted derivatives (Table I) were used as inhibitors. All chemicals were of AR grade and solutions were prepared using distilled water.

RESULTS AND DISCUSSION

The inhibition efficiency of organic compounds is usually determined from their absorbability on the corroding metal surface. Therefore, the efficiency of the compounds under consideration will be discussed in terms of their adsorption on the metal surface. The data obtained from gravimetric and gasometric methods are more or less the same and gave an agreement as to the values of PI and the order of inhibition of the studied compounds. Inspection of Fig. 1 reveals that the compounds being used markedly decrease the rate of corrosion of aluminium in 2 M HCl. A linear increase of the present inhibition (PI) with inhibitor concentration is observed.

Comparison of the present age inhibition of the different compounds at all inhibitors concentration shows that compound I (thiophene) has the lowest values, whereas compound V (2-thiophene-carboxaldehyde) has the highest ones. In general the inhibiting action of these compounds can be arranged in a decreasing order as follows:

$$\text{compound: } V > IV > III > II > I$$

This sequence can be explained in terms of:

- i) the number of adsorption sites: It is clear that compounds I and II have only one

adsorption site, i.e., the hetero-sulphur atom in the thiophene ring. The other three compounds (III, IV, and V) have an additional adsorption site, i.e., the oxygen atom of the carbonyl group.

- ii) Electron density on adsorption sites: As is well known, the introduction of electrophilic substituents, namely, 2-COOH, 2-COCH₃ and 2-CHO (compounds III, IV, and V, respectively) in place of hydrogen atom in the thiophene ring increases the positive charge on the S-hetero atom and the negative charge on the oxygen atom of the carbonyl group.

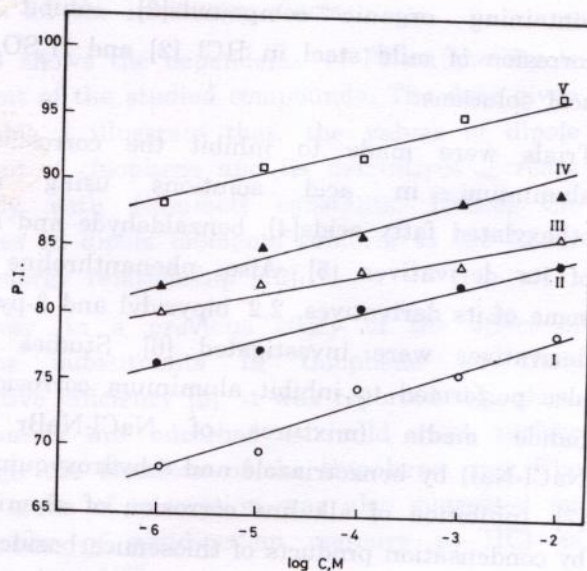


Fig. 1: Variation of percent inhibition (PI) with logarithm of inhibitor concentration
 (I) Thiophene (II) 2-Cl (III) 2-COOH
 (IV) 2-COCH₃ (V) 2-CHO

This fact is clear from the values of electron densities on both S and O atoms (Table II).

Therefore, inhibition by these compounds occurs through adsorption on both cathodic and anodic areas, respectively, as a result of coulombic interactions [12]. This argument explains the higher percentage inhibition of these compounds than that of compounds I and II.

iii) The electrophilic substituent (2-Cl, compound II) increases the positive charge, only on the S-hetero atom. Therefore, adsorption occurs strongly rather on the cathodic areas than on the anodic ones. This explains the low inhibiting action of compound II compared with those of compounds III, IV, and V; and its higher inhibiting action than that of compound I.

iv) For thiophene (compound I) its inhibiting effect arises from adsorption on the anodic areas. This adsorption occurs through the two electron pair present on the S-hetero atom.

Table I contains the values of Hammett constants (σ) calculated as reported in [13-14]. These constants are a quantitative measure of the ability of a certain substituent to charge the electron density at the reaction centre. A correlation is made (Fig. 2) between the Hammett constants and $\log i_{\text{corr}}$ (at 10^{-3} M of inhibitors) of the different

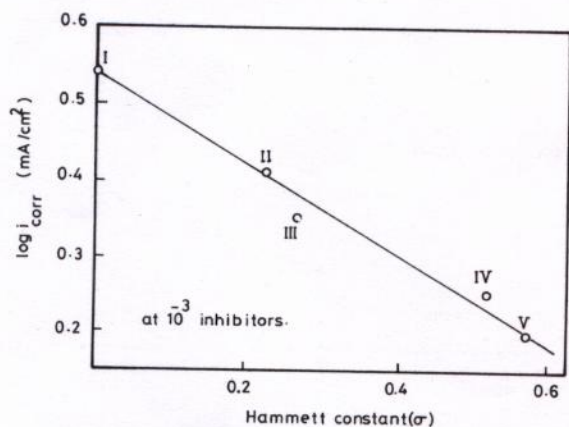


Fig. 2: Relation between Hammett constants (σ) of the substituents and logarithm of corrosion current (in presence of 10^{-3} M inhibitors)
 (I) Thiophene (II) 2-Cl (III) 2-COOH
 (IV) 2-COCH₃ (V) 2-CHO

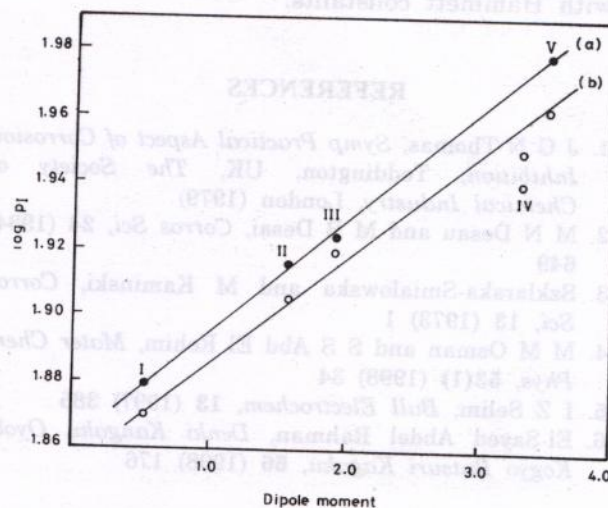


Fig. 3: Dependence of percent inhibition (PI) on dipole moments of thiophene and its derivatives
 (a) at 10^{-3} M of inhibitors (b) at 10^{-4} M of inhibitors
 (I) Thiophene (II) 2-Cl (III) 2-COOH
 (IV) 2-COCH₃ (V) 2-CHO

compounds. It is clearly seen that the corrosion rate decreases linearly with the increase of the values of σ . This is a further evidence that, electron density on the hetero-sulphur atom and oxygen atom (from C = O) are the determining factors for the inhibition effects.

Fig. 3 shows the dependence of PI on the dipole moment of the studied compounds. The data given in Table I illustrate that, the values of dipole moment of thiophene and its derivatives increase linearly with Hammett constants. Hence, the changes in dipole moments conform to the linear free energy relationship [15].

However, in a previous study of the effect of various substituents in thiophene on their inhibitive efficiency [5], it was reported that these compounds are adsorbed on mild steel surface through the electrons of the thiophene ring. The same mode of adsorption was also suggested for adsorption of pyridine on mercury in HCl as described in [16].

CONCLUSION

□ The corrosion rate decreases linearly with the increasing value of Hammett constants.

- The value of dipole moments, increases linearly with Hammett constants.

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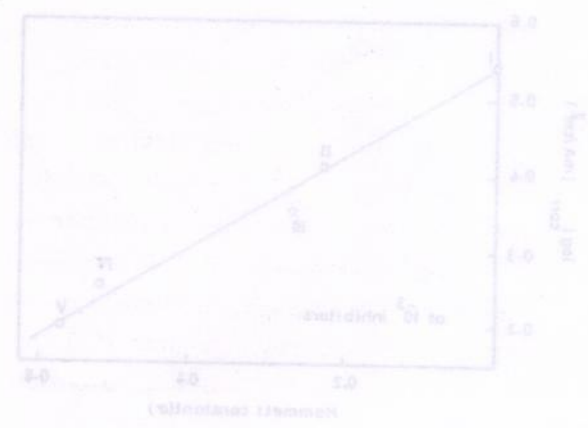


Fig. 2. Relation between Hammett constants (σ) of the substituents and logarithm of corrosion current (in presence of 10^{-5} M inhibitor): (I) Thiophene (II) 2-Cl (III) 2-COOH (IV) 2-COOH (V) 2-CHO