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Influence of Some Thiophene Derivatives on the Corrosion of Iron in Nitric Acid Solution

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Corrosion of iron in $2\,M\,HNO_3$ has been studied by the electrochemical polarization and weight loss measurements. The effect of some thiophene derivatives has been investigated. The results show that the inhibitors under consideration, influencing both the cathodic and anodic process, are adsorbed on the metal surface in molecular form. They do not change the mechanism of the reaction between iron and nitric acid, but decrease its rate. This effect is controlled by the values of their dipole moments. The weight loss technique also gave the same order of inhibition efficiency of the tested inhibitors.

(Keywords: Corrosion; Thiophene)

Der Einfluß einiger Thiophen-Derivate auf die Korrosion von Eisen in salpetersauren Lösungen

Es wurde die Korrosion von Eisen in $2\,M\,HNO_3$ mittels Messungen der elektrochemischen Polarisation und des Gewichtsverlustes untersucht. Dabei wurde der Einfluß einiger Thiophenderivate überprüft. Die Ergebnisse zeigen, daß die Inhibitoren, die den kathodischen und den anodischen Prozeß beeinflussen, an der Metalloberfläche in molekularer Form adsorbiert werden. Dabei wird der Reaktionsmechanismus der Reaktion zwischen Eisen und Salpetersäure nicht geändert, es wird jedoch die Geschwindigkeit herabgesetzt. Dieser Effekt ist mit den Dipolmomenten korrelierbar. Die Gewichtsverlustmessungen ergaben übereinstimmende Resultate.

Introduction

One of the most important considerations in any industry today is the reduction in overall cost in protection and maintenance of materials used. Because iron is the back bone of industrial constructions, the inhibition of iron corrosion in acid solutions of organic inhibitors has been studied in considerable detail. The inhibitory effects of alcohols, amides, amines, anilines, azoles, mercaptans, oximes and thioethers have been studied to mention but a few[1—9]. In nearly all cases there was evidence of chemisorption of the inhibitor and it was observed that the inhibitors were of mixed type, that is, both the anodic and cathodic polarization curves were affected. *Carossiti* et al.[10] and *Kaminski*[11] have studied the inhibition of iron corrosion in sulfuric acid by nitriles and thiophene derivatives, respectively. A higher efficiency was observed. In the present investigation corrosion of iron in $2M$ nitric acid was studied. Influence of thiophene, 2-acetylthiophene, 2-thiophenecarboxaldehyde and 2-thiophenecarboxylic acid has been studied.

The object of this work is to suggest effective inhibitors towards corrosion of iron by nitric acid.

Experimental

Iron test pieces of 99.99% purity were used. All chemicals used were of AR grade quality. The solution of $2M\,HNO_3$ was prepared with distilled water. The specimens of iron used for the weight loss measurements were of 2 × 2 cm size. The preparation, testing and cleaning procedures were those adopted by *Fouda*[12]. All experiments were carried out at 30 ± 1 °C. Inhibitive efficiencies were calculated from the weight loss values using the following equation:

$$\%\ \text{Inhibition} = \frac{W_B - W_I}{W_B} \cdot 100$$

where W_B = weight loss in $2\,M$ HNO_3 solution and W_I = weight loss in inhibited solution.

For the galvanostatic measurements electrodes were constructed from analytical reagent grade iron wire having a diameter of 0.053 cm. A 2 cm length of wire was inserted in the small opening of a tube so that about 1 cm extended beyond the end of the tube. The same procedures for the potential measurements were adopted as those described by *Gatos*[13].

The inhibitive efficiency was calculated employing the formula:

$$\%\ \text{Inhibition Efficiency} = \frac{I - I'}{I} \cdot 100$$

where I and I' are the corrosion current without and with inhibitor, respectively.

The inhibitors used in our investigations are listed in Table 1. The purity of these substances was checked by gas chromatography. Table 1 contains the dipole moments of the compounds under considerations. They characterize quantitatively the changes of the electron density in defined position caused by introduction of the given substituent into the thiophene molecule.

Results and Discussion

Anodic and cathodic *Tafel* plots of iron in unhibited HNO_3 and in thiophene solutions are shown in Fig. 1. For comparison, polarization curves measured in $2\,N$ HNO_3 solution are also plotted. The corrosion

Table 1. *Inhibitors used in the experiments*

No.	Compound	Formula	Dipole moment (μ/D)
1	Thiophene	C_4H_4S	0.53 (14)
2	2-Thiophenecarboxylic acid	$C_4H_3S—COOH$	1.96 (15)
3	2-Acetylthiophene	$C_4H_3—COCH_3$	3.37 (14)
4	2-Thiophenecarboxaldehyde	$C_4H_3S—CHO$	3.55 (14)

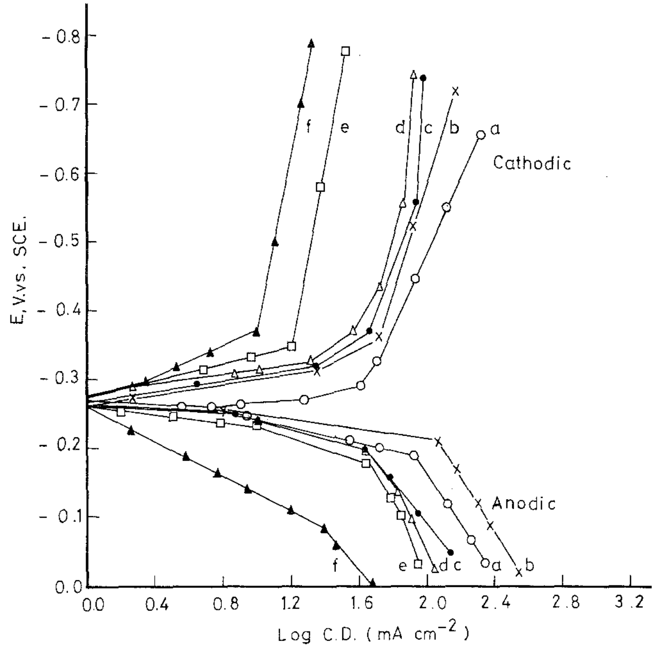


Fig. 1. Anodic and cathodic polarization curves of iron in uninhibited 2 *N* HNO_3 and in 2 *N* HNO_3 containing different concentrations of 2-thiophenecarboxaldehyde (**4**); *a* 2 *N* HNO_3 in H_2O; *b* 2 *N* HNO_3 in alcohol; *c* 0.5 ml **4**; *d* 1.0 ml **4**; *e* 1.5 ml **4**; *f* 2.0 ml **4**

current density for iron in 2 *N* HNO_3 is: $i_{corr} = 13.8\ mA\ cm^{-2}$ for cathodic polarization but it equals to $5.25\ mA\ cm^{-2}$ for anodic polarization. Addition of inhibitors induces a decrease in i_{corr}. The slope of cathodic curves (*Tafel* lines) changed from 40–125 mV per current decay. The anodic polarization curves in 2 *N* HNO_3 have a slope of 70–125 mV. In the

Table 2. *Cathodic Tafel parameters of corrosion of iron in* 2 *M* HNO_3 *at* $30 \pm 1\,°C$

Inhibitor	Concentration of inhibitor ml/100 ml	I_{corr} mA	$-E_{corr}$ w. r. to SCE, mV	% Inhibition
HNO_3	—	13.80	270	—
2-Thiophene-carboxaldehyde	0.5	4.17	270	69.80
	1.0	3.80	270	72.46
	1.5	1.21	270	91.23
	2.0	1.00	270	92.76
2-Acetyl-thiophene	0.5	6.41	280	53.55
	1.0	5.51	280	60.07
	1.5	4.71	283	65.87
	2.0	2.93	285	78.77
	2.5	1.90	280	86.23
2-Thiophene-carboxylic acid	0.5	8.71	285	36.70
	1.0	6.61	285	52.14
	1.5	5.01	280	63.69
	2.0	3.31	290	76.01
	2.5	2.00	295	85.51
Thiophene	0.5	8.71	260	36.90
	1.0	6.46	285	53.23
	1.5	5.25	290	61.98
	2.0	4.17	290	69.80
	2.5	2.14	295	84.51

presence of the inhibitors, the straight line part of the anodic curves is shorter than in pure acid solutions, and its slope oscillates between 25 and 60 mV per decade.

Results of Tables 2 and 3 show that the inhibitors under consideration influence both the cathodic and anodic process.

As follows from measurements of the corrosion rate, the compounds being studied are weak inhibitors. Comparison of effects of different compounds at the same concentration of 0.5–2.0 ml per 100 ml medium (Tables 2 and 3) shows that the thiophene has the smallest protective ability.

Substitution of one hydrogen atom in thiophene by an electrophilic (2-COOH, 2-$COCH_3$, 2-CHO) group, increases the inhibitor efficiency; this increase is directly proportional to the dipole moment (Table 1).

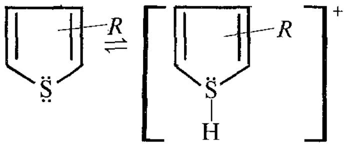
Most probably, the molecules of the inhibitor lie flat on the metal surface and the adsorption of these compounds on the metal/electrolyte phase boundary results from the interaction of π-electrons of the thiophene ring with surface metal atoms. The same mode of adsorption

Table 3. *Anodic Tafel parameters of corrosion of iron in* $2\,M$ HNO_3 *at* $30 \pm 1\,°C$

Inhibitor	Concentration of inhibitor ml/100 ml	I_{corr} mA	—E_{corr} w. r. to SCE, mV	% Inhibition
HNO_3	—	5.25	285	—
2-Thiophene-carboxaldehyde	0.5	3.47	270	33.93
	1.0	3.31	260	36.90
	1.5	2.63	280	49.88
	2.0	1.00	260	92.76
2-Acetyl-thiophene	0.5	4.82	270	8.19
	1.0	4.21	270	19.81
	1.5	3.80	275	27.62
	2.0	2.50	260	52.38
	2.5	2.00	265	61.90
2-Thiophene-carboxylic acid	0.5	6.92	260	—31.81
	1.0	5.76	285	—9.71
	1.5	4.37	290	+16.83
	2.0	2.88	290	+45.05
	2.5	2.63	290	+49.88
Thiophene	0.5	10.96	260	—108.76
	1.0	7.94	285	—51.12
	1.5	3.63	290	30.86
	2.0	3.47	290	33.90
	2.5	3.16	290	39.81

was assumed by *Conway* and *Barradas*[16] for pyridine on mercury in $1\,N$ HCl.

The inhibition efficiency increases in the order: 2-thiophenecarboxaldehyde > 2-acetylthiophene > 2-thiophenecarboxylic acid > thiophene. This can be explained in the following way: in strong acid solutions at $pH \simeq 0$, one can expect that thiophene and its protonated form exist in equilibrium:



By substituting one hydrogen atom in thiophene by a strong withdrawing group this will increase the positive charge of the cationic form and reinforce its adsorption as a result of the increased coulombic

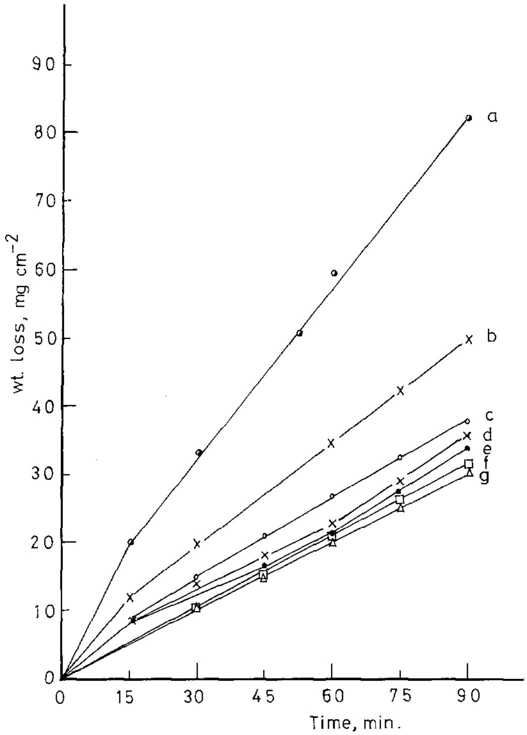


Fig. 2. Weight loss-time curves for different concentrations of 2-thiophene-carboxaldehyde (**4**); *a* 2 *N* HNO_3 in H_2O; *b* 2 *N* HNO_3 in alcohol; *c* 0.5 ml **4**; *d* 1.0 ml **4**; *e* 1.5 ml **4**; *f* 2.0 ml **4**; *g* 2.0 ml **4**

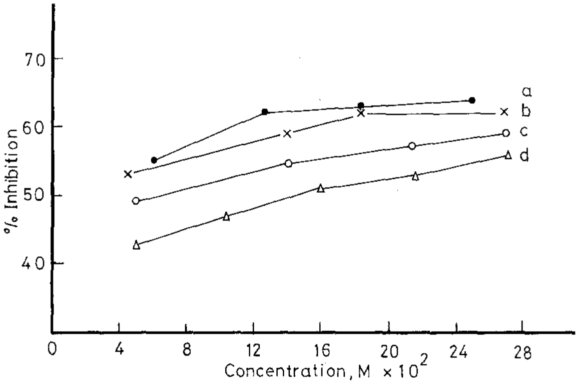


Fig. 3. Percentage inhibition—concentration curves for all additives used; *a* 2-thiophene-carboxaldehyde; *b* 2-acetylthiophene; *c* 2-thiophenrecarboxylic acid; *d* thiophene

interaction[10]. Also these substituting groups will increase the dipole moment of the molecule (Table 1). Therefore, one can expect an increase of its adsorption ability and its inhibitor efficiency as well.

The effect of thiophene derivatives on the dissolution of iron in 2 *N* HNO_3 solution was also studied by the weight loss method. Fig. 2 represents the weight loss-time curves of 2-thiophenecarboxaldehyde. These curves are straight lines passing from the origin and are characterized by an initial increase in weight loss. This linearity of the weight loss with time from the beginning was interpreted by *El-Hosary* et al.[17] as the breakdown of the oxide film and the start of the attack. Fig. 3 shows that the compounds used follow the same order when arranged according to the current efficiency at the same concentration.

The agreement of the results obtained by the two methods supports the given arrangement of the additives used in inhibiting the corrosion of iron metal in 2 *N* HNO_3 solution.

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