Corrosion Inhibition of Mild Steel by Thiophene in Different Acid Solutions

A. A. Ismail¹, S. H. Sanad¹, A.G. Gad-Allah², E.M. Fayyad^{1,*}

¹ Physical Chemistry Department, National Research Center, Dokki, Cairo, Egypt ² Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt emfavad53@gmail.com

Abstract: The corrosion protection behavior of thiophene on mild steel electrodes in different acids solutions was manipulated using open-circuit potential (OCP), potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS) methods. The surface morphology of mild steel after 24 hours immersion in different acids without and with two different concentrations of thiophene was investigated by scanning electron microscope. The results showed that, the inhibition efficiency of thiophene is increased with high thiophene concentration. Comparing the value of R_p for mild steel in different acids at 0.05M thiophene, it was found that, they have the following order: $H_2C_2O_4 \ge H_3PO_4 > HClO_4 \ge HCl > HNO_3$, this showed that HNO₃ acid is the most corrosive media for mild steel.

[A. A. Ismail, S. H. Sanad, A.G. Gad-Allah, E.M. Fayyad. Corrosion Inhibition of Mild Steel by Thiophene in Different Acid Solutions. *J Am Sci* 2015;11(9):27-38]. (ISSN: 1545-1003). <u>http://www.jofamericanscience.org</u>. 4

Keywords: Thiophene, corrosion, mild steel, inhibition efficiency, EIS, SEM.

1. Introduction

The high mechanical strength, low cost and easy availability are the most important properties, making mild steel has notable economic and attractive materials for various applications. There are many ways to protect metals from corrosion. Adding corrosion inhibitors [1,2] is the most practical. common and economical method that used to protect the metals from acid attack which is widely used in industrial field as a chemical cleaning, descaling, pickling and in acidification of oil wells. Most used efficient inhibitors are organic compounds which containing hetero-atoms like sulpher, oxygen, nitrogen as well as an aromatic ring in their structures. They are considered the adsorption centers via them a protective film will be formed on the metal surface [3,4]. The structure of the inhibitors and the characterization of the environment are playing an important role in controlling the inhibition efficiency of the inhibitors [5]. Thiophene based compounds used in a wide range of applications because they are the precursors of many drugs, being used in the treatment of cancer [6], osteoporosis [7], hypertension [8], Alzheimer's disease [9] and as corrosion inhibitors [10] which is our interest. Numerous investigations on the corrosion and corrosion inhibition of mild steel in different acid media containing thiophene and thiophene derivatives under various conditions were done [11-20]. The aim of this paper is to compare the inhibition efficiency of thiophene on mild steel in different acid solutions which are hydrochloric, perchloric, oxalic, phosphoric and nitric acids using different methods. Moreover, investigating the effect of changing the concentration of thiophene on the inhibition efficiency of mild steel after three hours immersion in each acid.

2. Experimental Details

Measurements were performed using mild steel specimens of the following weight percentage composition. C= 0.13: Mn = 0.81: S = 0.015: P = 0.043; Si = 0.23; Al = 0.005; and the balance Fe. Spherical mild steel electrodes with diameter 0.4 cm were used. Pre-treatment of mild steel electrode was carried out by mechanical polishing using successively finer grade of emery papers (150, 400, 600, 1200 grades), then degreased by rubbing the electrode surface with a fine tissue paper soaked with acetone. The experiments were made with a 0.5 M solution of different acids (HCl, HClO₄, H₃PO₄, $H_2C_2O_4$ and HNO_3). All acids were used in pure grade as received, in the absence and presence of different concentrations of thiophene(0.001, 0.005, 0.01, 0.05 M). Thiophene was from Merck. Purification of thiophene was done. A constant concentration of 2% by volume of ethyl alcohol was used in all kinds of experiments with doubly distilled water. All experiments were performed in freshly prepared solutions at room temperature and the results were always repeated at least three times to check the reproducibility.

Open circuit potential measurements were recorded by Keithley 179 Trms Digital multimeter. Computer controlled potentiostat (PAR EG&G 283) was used to measure the potentiodynamic polarization curves of the working electrode (mild steel) relative to a saturated calomel electrode as a reference electrode in a conventional three components electrolytic cell. Platinum sheet was used as an auxiliary electrode. The measurements were done with a scan rate of 1 mV/s. Electrochemical impedance spectroscopy (EIS) measurements were performed using PAR EG&G 283 potentiostat coupled to frequency response detector EG&G model 1025. The excitation AC signal has an amplitude of 10 mV peak to peak in a frequency domain from 0.1 Hz to 100 KHz at a steady state open circuit potential (i.e., at the free corrosion potential). The data analysis software applied non-linear least squares fitting (NLLS) with Levenberg - Marquardt algorithm [21]. The surface morphology of the various electrodes have been studied using scanning electron microscope (SEM) of type Jeol - JXA -840A - Japan.

3. Results and discussion

3.1. Open-Circuit Potential Measurements:

The open-circuit potential (E_{OCP}) of mild steel electrodes in an inhibited and uninhibited acid solutions was measured and referred relative to a saturated calomel electrode (SCE). Measurements were collected as a function of the exposure time within a period of three hours following immersion of the electrodes in unstirred solutions of different acids at 25° C. The results were duplicated and the mean was computed and illustrated in Table (1).

Fig. 1 shows a representative potential/time curves under open-circuit conditions, obtained from mild steel electrode in 0.5M of HCl solutions as well as those containing different concentrations of thiophene. Generally, at higher concentrations of thiophene, E_{OCP} for mild steel in 0.5M solutions of all acids used (Table 1) shifts toward positive potential value with time. The positive shift of the potential is probably due to the development of a certain passive film on the metal surface. Shifting of the potential to more noble or more active value cannot serve a dependable criterion of decreasing or increasing the corrosion rate. This behavior indicates that the first adsorbed molecules of the inhibitors are attached to the most active anodic sites, usually considered to be the corners or edges of incomplete layers of atoms on the metal surface, this would interfere with the anodic reaction by hindering the escape of Fe⁺⁺ ions from the metal surface into solution and the attack of the metal would proceed at a reduced rate from less active anodic sites. It is noticed that the time necessary to attain stable values of E_{OCP} was about 30 minutes and independent of the metal composition or the thiophene concentration. According to Muller [22], the rapid attainment of a steady state in potential signifies that only a fraction of the electrode is covered with surface film which suffers from dissolution in the solution. This behavior can be explained by film repair - film removed equilibria.

By increasing the concentration of thiophene, more molecules would be adsorbed due to van der waal's forces between thiophene molecules and the substrate surface. The increasingly close packed film thus built up would further inhibit the anodic reaction, by steric hindrance to the escape of iron ions. At this stage, there is some inhibition of the cathodic reaction probably due to steric hindrance of the combination of the adsorbed hydrogen atoms to form molecules.



Figure 1: Variation of the open-circuit potential with time for mild steel electode in different concentrations of thiophene in 0.5M solutions of HCl at 25 °C.

in pres	m presence of which end concentrations of morphener										
		E _{OCP} , mV									
Conc. of	H	HCl		HCl HClO ₄		H ₃ PO ₄		$H_2C_2O_4$		HNO ₃	
thiophene	After	After	After	After	After	After	After	After	After	After	
(M)	3hrs.	24hrs.	3hrs.	24hrs.	3hrs.	24hrs.	3hrs.	24hrs.	3hrs.	24hrs.	
	immersion	immersion	immersion	immersion	immersion	immersion	immersion	immersion	immersion	immersion	
0.000	-520	-520	-485	-495	-528	-530	-465	-477	-477	-487	
0.001	-514	-518	-497	-497	-535	-539	-466	-466	-486	-496	
0.005	-500	-500	-497	-497	-531	-535	-476	-476	-478	-486	
0.010	-506	-495	-480	-495	-520	-530	-465	-465	-455	-477	
0.050	-500	-503	-480	-500	-517	-531	-465	-465	-/137	-448	

Table 1: Steady-state potentials of mild steel electrode in 0.5M solutions of different used acids in absence and in presence of different concentrations of thiophene.

3.2. Potentiodynamic Polarization Measurements

The electrochemical parameters necessary to calculate the kinetics of corrosion processes have been determined from potentiodynamic polarization curves for mild steel electrodes immersed in a 0.5 M solution of different acids for three hours without and with the addition of different concentrations of thiophene (0.001, 0.005, 0.01, 0.05 M) at room temperature (25° C) using a scanning rate of 1 mV/s and summarized in Tables (2 – 6). A representative (E/I) curves are shown in Fig. 2. The values for corrosion current densities and corrosion potentials were estimated from the intersection of the anodic and cathodic Tafel lines.

Tables (2, 3) elucidate potentiodynamic parameters of mild steel in 0.5M of HCl and HClO₄solutions in the absence and presence of different concentrations of thiophene. It is clear that the increase of the concentrations of thiophene does not have a significant change in corrosion potential except at higher concentration of thiophene (0.05M) in HCl, E_{corr} of a mild steel electrode shift towards the negative direction by about (-72 mV) Fig. 2.

Tables (4 - 6) show potentiodynamic parameters of mild steel in 0.5M of H₃PO₄, H₂C₂O₄ and HNO₃solutions in the absence and presence of different concentrations of thiophene. E_{corr} of mild steel in inhibiting acids is nobler than that of uninhibiting acids except at the lowest concentration of thiophene (0.001M) in case of HNO₃ is shifted to negative direction (\approx 27 mV).

With respect to corrosion current, it is clear that in different acids solutions, the corrosion current decreases as the concentration of thiophene increases. Also, the polarization resistance increases as the concentration of thiophene increases. The change in the Tafel slopes b_c and b_a with thiophene concentration is slightly in all acids solutions. Generally,this change is due to a variation in the mechanism of hydrogen evolution and the anodic dissolution process on the electrode surface which due to the effecting of the reaction at the double layer imposing a barrier to charge transfer [23].

The inhibition efficiency (IE) was calculated by applying Equation [1].

$$IE = \frac{IOCONT - ICONT}{IOCONT} \times 100$$
[1]

where i_{ocorr} and i_{corr} are uninhibited and inhibited corrosion current densities, respectively.

It was observed that the higher concentration of thiophene leads to higher inhibition efficiency in acid solutions reaching 99% in case of 0.5M oxalic acid solution, see Table (6). The highest inhibition efficiency of thiophene for mild steel immersed in an oxalic acid solution compared to that in other acids is attributed to the inhibitive character of it that make it at some time used as inhibitor for corrosion of steel [24]. The essential effect of the corrosion inhibition of thiophene is due to the presence of an electron donor group of sulpher atom in the molecular structure of the thiophene. In addition, the presence of the π -electrons in double bonds favor the adsorption of the inhibitor [14].

Comparing the inhibition efficiency and the values of R_P for mild steel in different inhibiting acids in the presence of 0.05M thiophene, Tables (2 – 6), it was found the order of inhibition decreases as the following:

 $H_2C_2O_4 \ge H_3PO_4 > HCl \ge HClO_4 > HNO_3$.

It can be seen that the inhibition efficiency of thiophene for mild steel in HNO_3 has a lower value than in other acids, this because HNO_3 acid is readily reducible provides an easy alternative cathodic reduction reaction that polarizes only a very small extent, resulting a high corrosion rate. The results of the open-circuit potential and the polarization measurements suggest that thiophene function through general adsorption on the whole metal surface and hence they affect both anodic and cathodic areas (mixed inhibitor).

Table 2: Electrochemical parameters of mild steel electrodes without and with addition of different concentrations of thiophene in 0.5M HCl solutions.

Conc. of	R _p	ba	bc	Ecorr	I _{corr}	IE
thiophene	(Ohm)	(V/decade)	(V/decade)	(mV)	(mA/cm^2)	(%)
0.000M	43	0.160	0.180	-460	5.38	
0.001M	130	0.129	0.155	-455	1.53	72
0.005M	234	0.118	0.135	-467	0.83	85
0.010M	322	0.096	0.306	-437	0.38	93
0.050M	412	0.131	0.136	-532	0.31	94

Conc. of	R _p	ba	bc	E _{corr}	I _{corr}	IE
thiophene	(Ohm)	(V/decade)	(V/decade)	(mV)	(mA/cm^2)	(%)
0.000M	105	0.140	0.170	-422	3.53	
0.001M	165	0.115	0.149	-411	1.35	61.7
0.005M	202	0.106	0.143	-405	1.00	71.6
0.010M	199	0.106	0.142	-430	0.98	72.3
0.050M	505	0.097	0.111	-410	0.25	92.8

Table 3: Electrochemical parameters of mild steel electrodes without and with addition of different concentrations of thiophene in 0.5M HClO₄ solutions.

Table 4: Electrochemical parameters of mild steel electrodes without and with addition of different concentrations of thiophene in $0.5M H_3PO_4$ solutions.

Conc. of	R _p	ba	bc	Ecorr	Icorr	IE
thiophene	(Ohm)	(V/decade)	(V/decade)	(mV)	(mA/cm^2)	(%)
0.000M	122	0.380	0.410	-497	5.83	
0.001M	202	0.202	0.312	-505	1.86	68.0
0.005M	344	0.151	0.261	-493	1.00	82.8
0.010M	487	0.101	0.141	-495	0.18	96.9
0.050M	1214	0.097	0.128	-469	0.14	97.7

Table 5: Electrochemical parameters of mild steel electrodes without and with addition of different concentrations of thiophene in $0.5M H_2C_2O_4$ solutions.

Conc. of	R _p	Ba	bc	E _{corr}	I _{corr}	IE
thiophene	(Ohm)	(V/decade)	(V/decade)	(mV)	(mA/cm^2)	(%)
0.000M	142	0.190	0.220	-512	3.050	
0.001M	3900	0.389	0.119	-438	0.115	96
0.005M	4500	0.211	0.111	-438	0.087	97
0.010M	4343	0.055	0.116	-458	0.086	97
0.050M	6468	0.055	0.107	-445	0.023	99

Table 6: Electrochemical parameters of mild steel electrodes without and with addition of different concentrations of thiophene in 0.5M HNO₃ solutions.

Conc. of	R _p	b _a	b _c	Ecorr	I _{corr}	IE
thiophene	(Ohm)	(V/decade)	(V/decade)	(mV)	(mA/cm^2)	(%)
0.000M	28	0.446	0.662	-451	29.0	
0.001M	158	0.320	0.244	-478	19.5	32.7
0.005M	180	0.209	0.690	-396	17.0	41.4
0.010M	310	0.156	0.271	-387	14.0	51.7
0.050M	400	0.177	0.319	-393	13.0	55.0



Figure 2: Potentiodynamic polarization curves of mild steel electrodes without and with immersion in different concentrations of thiophene in 0.5M HCl solution.

3.3. Electrochemical Impedance Measurements:

The corrosion behavior of mild steel in 0.5M solutions of five different acids (HCl, HClO₄, H₃PO₄, H₂C₂O₄ and HNO₃) in absence and presence of different concentrations of thiophene (0.05, 0.01, 0.005 and 0.001 M) were investigated by (EIS) at 25° C. Various impedance parameter such as polarization resistance (R_P), double layer capacitance (C_{dl}), solution resistance (R_s), phase shift (α) and inhibition efficiency (IE %) were calculated and obtained by line fitting to the semicircle given in Tables (7 -11). The obtained Nyquist impedance diagram in most cases does not show perfect semicircle, this may be attributed to the frequency dispersion as a result of the heterogeneity of the electrode surface and the type and nature of the medium and additives.

Comparing the value of R_p of the bare mild steel in each acid through different immersion times, it was found that the value of R_p (Tables7 -11) in all acids decreases as the time increases except in $H_2C_2O_4$ acid it increases. The value of R_p of mild steel in 0.5M HCl, HClO₄ and H₃PO₄ in the presence of 0.001M and 0.005M of thiophene decreases with immersion time, but in higher concentrations (0.01 and 0.05) of thiophene, the value of R_p increases as time increases and this improve that as concentration of thiophene increase, the efficiency increase Tables (7 - 9) and a representative Fig. 3 (a-d). R_p of mild steel in 0.5M H₂C₂O₄ acid in the presence of all different concentrations of thiophene increases with time Table (10). The presence of different concentrations of thiophene decreases the value of R_n for mild steel in 0.5M HNO₃ as time increase Table (11). At higher concentration of thiophene (0.05M), the efficiency has the higher value (91%).

In all used acids (HCl, HClO₄, H₃PO₄, H₂C₂O₄ and HNO₃), by comparing the diameter of the capacitive loop for different concentrations of thiophene after 180 minutes immersion time, it is found that the impedance diagrams show the same trend since the diameters of the capacitive loop increase with increasing concentration of thiophene, as shown in a representative curve Fig. 4. Also, the double layer capacitance (C_{dl}) decreases with increases in the concentration of thiophenein all acids, Tables (7 -11). This decrease is due to the adsorption of the inhibitor on the metal surface, causing a change in the double layer structure [25].

Comparing the values of R_P for mild steel in different inhibited acids at 0.05M thiophene after 3hrs immersion time, it was found that $H_2C_2O_4 \ge H_3PO_4 \ge HCIO_4 \ge HCIO \ge HNO_3$.

Table 7: Equivalent circuit parameters of mild steel after different immersion times in different concentrations of thiophene in 0.5M HCl solutions, at room temperature.

Conc.	of Time	R _s	R _P	C _{dl}	Α	IE %
thiophene(M)	(min)	$(\Omega.cm^2)$	$(\Omega.cm^2)$	(µF.cm ⁻²)		
0000	30	0.67	14.5	812	0.70	-
	60	1.05	12.5	736	0.69	-
	90	0.78	6.92	1227	0.75	-
	120	1.28	3.85	1976	0.80	-
	180	0.81	3.54	3325	0.70	-
0.001	30	1.38	42.85	289	0.79	66.6
	60	1.34	40.00	434	0.79	68.7
	90	1.24	31.96	524	0.79	78.0
	120	1.29	28.59	545	0.75	84.0
	180	1.18	25.52	589	0.80	86.0
0.005	30	1	48.13	114	0.80	69.5
	60	0.79	44.52	163	0.82	72.5
	90	0.86	39.88	219	0.79	82.7
	120	0.89	32.95	262	0.77	88.4
	180	0.96	25.69	318	0.80	86.0
0.010	30	0.83	73.80	121	0.88	79.7
	60	0.78	127.6	116	0.85	90.0
	90	0.88	158.0	118	0.86	95.6
	120	0.84	185.0	120	0.83	97.9
	180	1.13	194.5	118	0.83	98.0
0.050	30	1.62	73.40	56.8	0.88	79.7
	60	1.65	142.5	57.0	0.88	91.0
	90	2.30	233.7	48.8	0.88	97.0
	120	1.25	328.7	48.0	0.88	98.8
	180	1.09	372.0	44.0	0.88	99.0

Conc. of	Time	R _s	R _P	C _{dl}	Α	IE %
thiophene(M)	(min)	$(\Omega.cm^2)$	$(\Omega.cm^2)$	(µF.cm ⁻²)		
0000	30	1.04	21.16	321	0.77	-
	60	0.98	15.30	565	0.75	-
	90	1.05	12.45	736	0.78	-
	120	0.89	11.11	1015	0.79	-
	180	0.92	10.78	1387	0.79	-
0.001	30	1.10	36.6	91	0.75	43
	60	0.95	30.0	146	0.82	49
	90	1.19	21.4	169	0.81	41
	120	1.09	17.5	269	0.80	36
	180	1.09	15.0	418	0.84	29
0.005	30	1.39	41.8	109	0.86	49
	60	1.16	31.8	156	0.85	52
	90	1.64	30.0	230	0.84	59
	120	1.36	27.6	305	0.85	60
	180	1.10	27.0	400	0.85	61
0.010	30	3.10	64.5	358	0.85	66
	60	3.40	65.0	183	0.87	75
	90	2.06	81.2	204	0.88	85
	120	2.35	80.0	165	0.80	86
	180	2.10	99.7	108	0.79	89
0.050	30	0.66	479	46.8	0.86	95
	60	2.90	535	46.5	0.85	97
	90	2.70	648	46.9	0.84	98
	120	1.97	633	45.6	0.86	98
	180	1.97	633	46.0	0.86	98

Table 8: Equivalent circuit parameters of mild steel after different immersion times in different concentrations of thiophene in 0.5M HClO₄ solutions, at 297 °K.

Table 9: Equivalent circuit parameters of mild steel after different immersion times in different concentrations of thiophene in $0.5M H_3PO_4$ solutions, at $297^{\circ} K$.

Conc. of thiophene(M)	Time	R _s	R _P	C _{dl}	Α	IE %
	(min)	$(\Omega.cm^2)$	$(\Omega.cm^2)$	$(\mu F.cm^{-2})$		
0000	30	5.33	9.67	1090	0.70	-
	60	5.73	6.27	1052	0.80	-
	90	5.35	6.35	2210	0.70	-
	120	5.59	5.81	2485	0.71	-
	180	6.63	4.17	2435	0.69	-
0.001	30	7.8	44.1	359	0.79	77
	60	5.8	39.3	369	0.72	84
	90	5.9	31.4	363	0.72	79
	120	5.4	27.7	787	0.61	81
	180	6.4	24.9	730	0.63	83
0.005	30	3.79	55.5	222	0.80	82
	60	4.67	54.7	296	0.79	88
	90	4.21	48.8	354	0.79	87
	120	4.44	45.8	347	0.80	87
	180	5.40	42.8	389	0.78	90
0.010	30	3.99	63.8	200	0.77	84
	60	3,69	74.5	202	0.74	92
	90	4.18	86.9	177	0.75	92
	120	3.99	77.2	151	0.75	92
	180	3.99	96.6	111	0.78	96
0.050	30	3.85	217	132	0.78	96
	60	3.98	399	132	0.79	98
	90	3.89	561	128	0.82	99
	120	3.83	670	128	0.85	99
	180	3.59	774	125	0.80	99

Conc. of thiophene(M)	Time	R _s	R _P	C _{dl}	Α	IE %
	(min)	$(\Omega.cm^2)$	$(\Omega.cm^2)$	(µF.cm ⁻²)		
0000	30	2.05	19	596	0.81	-
	60	2.05	35	443	0.82	-
	90	1.74	99	427	0.82	-
	120	2.32	110	303	0.86	-
	180	2.81	150	276	0.87	-
0.001	30	2.36	82	194	0.85	77
	60	2.69	110	127	0.87	68
	90	2.60	239	107	0.86	58
	120	2.30	241	91	0.84	54
	180	1.46	426	86	0.84	65
0.005	30	2.69	104.0	160	0.86	82
	60	2.69	110.0	100	0.88	68
	90	2.27	332.7	97	0.88	70
	120	2.10	466.8	73	0.86	77
	180	2.60	523.4	66	0.83	71
0.010	30	2.30	241	94	0.86	92
	60	1.90	330	90	0.88	89
	90	2.20	567	91	0.88	82
	120	2.10	567	84	0.86	80
	180	2.20	800	66	0.83	80
0.050	30	1.77	317.0	59	0.89	94
	60	2.10	466.8	52	0.89	93
	90	2.60	523.4	54	0.84	81
	120	2.85	806.9	45	0.83	86
	180	2.00	1037	41	0.83	85

Table 10: Equivalent circuit parameters of mild steel after different immersion times in different concentrations of thiophene in 0.5M $H_2C_2O_4$ solutions, at 297 °K.

Table 11: Equivalent circuit parameters of mild steel after different immersion times in different concentrations of thiophene in 0.5M HNO₃ solutions, at 297 °K.

Conc. of	Time	R _s	R _P	C _{dl}	Α	IE %
thiophene(M)	(min)	$(\Omega.cm^2)$	$(\Omega.cm^2)$	(µF.cm ⁻²)		
0.0000	30	0.74	0.76	6899	0.63	-
	60	0.88	0.65	7700	0.70	-
	90	0.88	0.61	5542	0.70	-
	120	0.90	0.59	6900	0.79	-
	180	1.10	0.55	11250	0.79	-
0.001	30	0.64	1.84	512	0.70	59
	60	0.65	1.39	693	0.69	53
	90	0.73	1.22	925	0.75	50
	120	0.73	0.80	1178	0.65	27
	180	0.73	0.65	1237	0.65	17
0.005	30	0.96	2.55	317	0.75	70
	60	0.96	1.56	415	0.80	55.8
	90	1.04	1.48	799	0.79	60.9
	120	1.05	1.19	869	0.79	50
	180	1.06	0.75	1010	0.79	27
0.010	30	0.99	2.65	218	0.79	71
	60	1.10	2.22	307	0.79	70.7
	90	1.10	1.96	393	0.69	68.9
	120	1.10	1.49	557	0.80	60
	180	1.11	1.42	906	0.79	61.5
0.050	30	1.50	8.20	219	0.77	91
	60	1.69	6.38	225	0.75	89.6
	90	1.90	3.62	299	0.82	82.9
	120	1.33	2.67	346	0.80	78
	180	1.30	1.98	450	0.87	72.5



Figure 3: Nyquist plots of mild steel electrodes in 0.5M HCl solutions containing (a) 0.001M, (b) 0.005M, (c) 0.01M and (d) 0.05M thiophene for different immersion time.



Figure 4: Nyquist plots of mild steel electrodes in 0.5M HCl solutions in absence and presence of different concentrations of thiophene (180 min).

3.4. Surface Morphology and Analysis:

Figs. 6(a, b) - 10(a,b) represent the photomicrographs obtained for mild steel electrodes in 0.5M of HCl, HClO₄, H₃PO₄, H₂C₂O₄ and HNO₃ solutions inhibited with two different concentrations

(a) MS/HCl (after 24h immersion)

of thiophene (0.001M and 0.05M) after 24hrs immersion time at room temperature. Comparison of Figs. 5(a-e) of mild steel in plain acids after immersion of 24hrs by Figs. 6(a, b) - 10(a,b) of mild steel electrodes in inhibiting HCl at the same condition, show that the attack of mild steel in inhibiting acids with 0.001M were much less and the surfaces showed superficial etching with minute scattered pits. SEM micrographs of mild steel in inhibiting acid with 0.05M thiophene. Figs. 6b -10b show homogeneous, smooth and more adherent films than that of 0.001M thiophene.Figs. 6a - 10a and this prove that the increase of thiophene concentrations, increase the corrosion protection.

From the potentiodynamic polarization, electrochemical impedance spectroscopy results and the microscopical examination, it may be generalized that the thiophene is an excellent inhibitor for mild steel in 0.5M oxalic and phosphoric acids, good inhibitor for MS in 0.5M hydrochroric and perchloric acids and medium inhibitor for mild steel in 0.5M HNO₃.

(b) MS/HClO₄ (after 24h immersion)



(c) MS/ H₃PO₄ (after 24h immersion)





(e) MS/HNO3 (after 24h immersion)



Figure 5(a-e): Micrograph of MS in (a)HCl,(b) HClO₄, (c) H₃PO₄, (d) H₂C₂O₄ and (e) HNO₃after 24h immersion.

 (a) MS/0.05M thiophene/HCl (after 24h immersion)
 (b) MS/0.001M thiophene/HCl (after 24h immersion)

 Image: Constraint of the second s

Figure 6(a-b): Micrograph of mild steel in (a) 0.05M and (b) 0.001M thiophene/HCl solution after 24h immersion.

(a) MS/0.05M thiophene/HClO₄ (after 24h (b) MS/0.001M thiophene/HClO₄ (after 24h immersion) immersion)



Figure 7(a-b): Micrograph of mild steel in (a) 0.05M and (b) 0.001M thiophene/HClO₄ solution after 24h immersion.

(a) MS/0.05M thiophene/ H_3PO_4 (after 24h (b) MS/0.001M thiophene/ H_3PO_4 (after 24h immersion)

immersion)



Figure 8(a-b): Micrograph of mild steel in (a) 0.05M and (b) 0.001M thiophene/H₃PO₄ solution after 24h immersion.

(a) MS/0.05M thiophene/ $H_2C_2O_4$ (after 24h (b) MS/0.001M thiophene/ $H_2C_2O_4$ (after 24h immersion)

immersion)



Figure 9(a-b): Micrograph of mild steel in (a) 0.05M and (b) 0.001M thiophene/H2C₂O₄ solution after 24h immersion.

- (a) MS/0.05M thiophene/ HNO₃ (after 24h immersion)
- (b) MS/0.001M thiophene/ HNO₃(after 24h immersion)



Figure 10(a-b): Micrograph of mild steel in (a) 0.05M and (b) 0.001M thiophene/HNO₃ solution after 24h immersion.

Conclusion

The thiophene acts as effective corrosion inhibitor for mild steel in 0.5 M of different acid solutions (HCl, HClO₄, H₃PO₄, H₂C₂O₄ and HNO₃). The inhibition efficiencies, increase with increasing the concentration of thiophene in all acids solutions.

The lowest inhibition efficiency is obtained by immersing the mild steel electrodes in nitric acid solutions, even in the presence of high concentration of thiophene, due to its oxidizing properties. Oxalic acid increases the corrosion protection of thiophene for mild steel because of the inhibiting character of it. The inhibition efficiency of thiophene increases with increasing the immersion time in HCl, HClO₄ and H₃PO₄ acid solutions. The corrosion inhibition of thiophene comes from its adsorption on the metal surface due to the presence of an electron pair on sulpher atom and the π -electrons in the double bonds. The higher concentration of thiophene shows homogeneous, smooth and more adherent films than that of the lower concentration.

References

- Chatterjee P., M. K. Benerjee, and K. P. Mukherjee: 'Synergistic inhibition of inorganic anions with pyridine-derivatives for steel in hydrochloric-acid', *Ind. J. Technol.*, 1991, 29, 191-199.
- 2. Bentiss F., M. Traisnel, and M. Lagrenee: 'The substituted 1,3,4-oxadiazoles: a new class of corrosion inhibitors of mild steel in acidic media', *Corr. Sci.*, 2000, 42, 127-146.
- Al-sarawy A. A., A. S. Fouda, and W. A. Shehab El-Dien: 'Some thiazole derivatives as corrosion inhibitors fo C-steel in acidic medium', J Desalination, 2008, 229, 279-293.
- 4. Amar H., T. Braisaz, D. Villemin, and B. J. Moreau: 'Thiomorpholin-4-ylmethyl-phosphonic acid and morpholin-4-methyl-phosphonic acid as corrosion inhibitors for carbon steel in natural seawater', J Mater Chem Phy., 2008, 110, 1-6.
- Fouda A. S., S. Abd El-Wanees, A. A. Atia, and A. M. Negm: 'Corrosion Inhibition of Carbon Steel in Hydrochloric Acid Solutions using some Thiophene Derivatives', J Adv Chem., 2013, 4, 351-367.
- Villar R., I. Encio, M. Migliaccio, M. J. Gil, and V. Martinez-Merino: 'Synthesis and cytotoxic activity of lipophilic sulphonamide derivatives of the benzo[b]thiophene 1,1-dioxide', *Bioorg Med Chem.*, 2004, 12, 963-968.
- Kalinin A. V., M. A. Reed, B. H. Norman, and V. Snieckus: 'Synthesis of Constrained Raloxifene Analogues by Complementary Use of Friedel–Crafts and Directed Remote Metalation Reactions', *J Org Chem.*, 2003, 68, 5992-5999.
- Russell R. K., J. B. Press, R. A. Rampulla, J. J. McNally, R. Falotico, J.A. Keiser, D. A. Bright, and A. Tobia: 'Thiophene System 9. Thienopyrimidinedione derivatives as potential antihypertensive agents', *J Med Chem.*, 1988, 31, 1786-1793.
- 9. McCormick W. C., and I. B. Abrass: 'Shifting thinking about memory impairment', Lancet, 1998, 352Supl. IV, 6.
- Khaled K. F., and N. A. Al-Mobarak: 'A predictive model for corrosion inhibition of mild steel by thiophene and its derivatives using artificial neural network', *Int J Electrochem Sci.*, 2012, 7, 1045-1059.
- 8/16/2015

- Kaminski M. and Z. Szklarska-Smialowska: 'Adsorption of thiophene derivatives on steel in sulfuric acid solutions', Corros Sci., 1973, 13, 557-565.
- Abou-Romia M. M., and M. M. Hefny: 'Electrochemical behaviour of iron in H2SO4 containing thiophene', J Electroanal Chem., 1982, 136, 339-344.
- Abd El-Rehim S. S., S. A. M. Refawy, F. Taha, M. B. Saleh, and R. A. Ahmed: 'Corrosion inhibition of mild steel in acidic medium using 2-amino thiophenol and 2-cyanomethyl benzothiazole', J Appl Electrochem., 2001, 31, 429-435.
- 14. Bouklah M., B. Hammouti, A. Aouniti, and T. Benhadda: 'Thiophene derivatives as effective inhibitors for the corrosion of steel in 0.5M H2SO4', *Prog Org Coat.*, 2004, 49, 225-228.
- Bouklah M., B. Hammouti, M. Benkaddour, and T. Benhadda: 'Thiophene derivatives as effective inhibitors for the corrosion of steel in 0.5M H2SO4', J Appl Electrochem., 2005, 35, 1095-1101.
- Galal A., N. F. Atta, and M. H. S. Al-Hassan: Effect of some thiophene derivatives on the electrochemical behavior of AISI 316austenitic stainless steel in acidic solutions containing chloride ions II, Effect of temperature and surface studies', *Mat Chem and Phys.*, 2005, 89, 28-37.
- 17. Sürme Y. I., and A. A. Gürten: 'The role of the Polyethylene glycol tert-octylphenyl ether on the corrosion behavior of mild steel in acidic solution', Corros Eng Sci Technol., 2009, 44, 304-314.
- Ameer M. A., A. M. Fekry, A. A. Ghoneim, and F. A. Attaby: 'Electrochemical Corrosion Inhibition of Steel in Alkaline Chloride Solution', *Int J Electrochem Sci.*, 2010, 5, 1847-1861.
- Abo Dief H. A., E. A. Eissa, S. T. Keera, and A. R. Taman: 'Study of Carbon Steel Corrosion in Sulphur Media', J Appl Sci., 2010, 6, 1325-1333.
- Fouda A. S., G. Y. Elewady, and M. G. Salama: 'Corrosion inhibition of Al-Si alloy in sulphuric solution using some thiophene derivative', *Protection Materials*, 2010, 51, 133-141.
- 21. MacDonald J. R.: 'Impedance spectroscopy emphasizing solid materials and systems', 1987, Wiley Interscience, New York.
- 22. Mueller W. A.: 'A Model of the Mechanism of Electrochemical Conversion from Active to Passive States', *J Electrochem Soc.*, 1960, 107, 157-164.
- 23. Fontana M. G. and N. D. Greene: 'Corrosion Engineering', 2ndedn., 1987, McGraw-Hill, New York.
- Wiersma B. J. and K. H. Subramanian: 'Corrosion Testing of Carbon Steel in Acid Cleaning Solution', WSRC-TR-2002-00427.
- Szklarska Smialowska Z.: 'Electrochemical and Optical Techniques for the study of Metallic Corrosion', 1991, PP 545, Kluwer Academic Publishers, Dordrecht.