Comparative inhibition study of mild steel corrosion in hydrochloric acid by new class synthesised quinoxaline derivatives: part I

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Abstract 7-Cchloro-3-(4-methoxystyryl)quinoxalin-2(1H)-one (CMOSQ) and 7-chloro-2-(4-methoxyphenyl)thieno(3.2-b)quinoxaline (CMOPTQ) have been investigated for mild steel corrosion in 1 M HCl at different concentrations using weight loss measurements, potentiodynamic polarization curves and electrochemical impedance spectroscopy methods. Generally, inhibition efficiency of the investigated compounds was found to depend on inhibitor concentration and their structures. Comparitive results showed that CMOPTQ was the best inhibitor and the inhibition efficiency increased with increasing the concentration and attained 86 and 87 % at 10^{-3} M of CMOPTQ and 10^{-3} M of CMOSQ, respectively. Potentiodynamic polarization studies clearly reveal that these inhibitors act essentially as cathodic-type inhibitors. The inhibition efficiency increases with immersion time and reaches 95 % CMOPTQ at 24 h. The electrochemical impedance spectroscopy result showed that these compounds act by formation of film.

Keywords Synthesised quinoxaline derivatives · Mild steel · Hydrochloric acid · Corrosion inhibition

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Scheme 1 Synthesis of, 7-chloro-3-(4-methoxystyryl) quinoxalin-2-one (CMOSQ)

Introduction

Corrosion problems have received a considerable amount of attention because of their attack on materials. Due to its prominent properties, hydrochloric acid is widely used in industry, for example in acid pickling, acid cleaning and acid descaling. The use of inhibitors is one of the most practical methods for protection against corrosion. The corrosion inhibition of metals in acids by organic additives has been studied in considerable detail [1-4].

Most of the efficient inhibitors used in industry are organic compounds which mainly contain oxygen, sulphur, nitrogen atoms and multiple bonds in the molecule through which they are adsorbed on the metal surface [5–12]. Moreover, many N-heterocyclic compounds have been proved to be effective inhibitors for the corrosion of metals and alloys in aqueous media [13–21].

A perusal of the literature reveals that 7-chloro-3-(4-methoxystyryl)quinoxalin-2(1H)-one (CMOSQ) and 7-chloro-2-(4-methoxyphenyl)thieno(3.2-b)quinoxaline (CMOPTQ) have not been investigated as corrosion inhibitors. Accordingly, this work deals with the study of the corrosion inhibition properties of these compounds. The choice of these products was based on the consideration that these compounds contain π -electrons and heteroatoms such as N, O and S, which induce greater adsorption of the inhibitor molecule onto the metallic surface compared with compounds containing only nitrogen, oxygen or sulphur. The inhibition of these compounds always depends upon the number of active adsorption centres that an inhibitor molecule may have, as well as the charge density, molecular size, adsorption mode, and its capability to form metallic complexes.

This paper aims to determine the inhibition efficiency of quinoxaline derivatives via mild steel corrosion in 1 M HCl solution at different concentrations in order to compare the effect of molecular structure. The effects of immersion time and temperature were evaluated and discussed.

Experimental details

Synthesis and characterisation of quinoxalines derivatives

Quinoxalines derivatives have been prepared by a new method developed in our laboratory. The synthesised compounds have been obtained with good yield (80 %) and their synthesised schemas are presented in schemas 1 and 2:



Scheme 2 Synthesis of, 7-chloro-2-(4-methoxyphenyl)thieno[2,3-b]quinoxaline (CMOPTQ)

- 6.25 mmol of 7-chloro-3-methylquinoxaline-2-one is merged with 12.5 mmol of the appropriate aldehyde for 2 h at the boiling temperature of the latter. At the end of the reaction, the solid was allowed to cool and then heated to 100 °C for 10 min in 50 ml of acetone. The product was filtered hot and washed with acetone (Scheme 1).
- 4 mmol of 7-chloro-3-styrylquinoxalin-2-one undergoes sulfuration by Lawesson's reagent 4 mmol, for 30 min at reflux of toluene. After evaporating the solvent to dryness, the product is recrystallized in ethanol (Scheme 2).

These products have been purified and characterised by NMR ¹H and NMR ¹³C analysis using a Brucker AMWB 300 spectrometer:

• 7-chloro-3-(4-methoxystyryl)quinoxalin-2-one: (CMOSQ)

RMN ¹H (300 MHz, DMSO-d6) δ (ppm): 7.45 (s, 1H), 7.50 (d, 2H, H Cl, 3J = 8.4 Hz), 7.60 (d, 1H, CH ethylenique, 3J = 16.2 Hz), 7.78 (d, 2H, H Cl, 3J = 8.4 Hz), 8.00 (s, 1H), 8.06 (d, 1H, CH ethylenique, 3J = 16.2 Hz), 12.64 (s, 1H, NH).

RMN 13 C (75.5 MHz, DMSO-d6) δ (ppm) 112.55 (2xC), 115.56, 116.63, 123.82, 124.05, 128.29, 129.27, 129.69 (2xC), 131.73, 133.09, 138.25, 151.59, 153.96, 155.36.

• 7-chloro-2-(4-methoxyphenyl)thieno (2,3-b)quinoxaline: (CMOPTQ)

RMN¹H (300 MHz, TFA) δ (ppm): 7.52 (d, 2H, 3J = 8.7 Hz), 7.86 (d, 2H, 3J = 8.7 Hz), 7.96 (s, 1H), 8.32 (s, 1H), 8.52 (s, 1H)

¹³C RMN (63 MHz, TFA) δ (ppm): 108.91, 119.7, 126.5, 128.8 (2xC), 129.4, 123.0 (2xC), 137.9, 138.6, 140.7, 141.8, 141.9, 159.5, 169.1

Methods and experimental electrochemical conditions

Corrosion tests were performed on mild steel of the following percentage composition: 0.09 % P; 0.38 % Si; 0.01 % Al; 0.05 % Mn; 0.21 % C; 0.05 % S and the remainder iron. Mild steel rods were mounted in teflon (surface area 1 cm²). The specimens' surface was prepared by grinding with emery paper of different grit sizes, rinsing with distilled water, degreasing in ethanol, and drying before use. Solutions of 1 M HCl were prepared by dilution of analytical grade 37 % HCl with distilled water.

For weight loss measurements, rectangular mild steel specimens of size $(4 \times 1 \times 0.05 \text{ cm})$ were used as samples for corrosion tests. After having been successively polished with emery paper (400–1,200 grade) and weighed, the

samples were immersed for 24 h in 100 ml of uninhibited and inhibited solutions at room temperature in the air. At the end of immersion, the specimens were cleaned according to ASTM G-81 and reweighed to 10^{-4} g for determining the corrosion rate [22]. The inhibition efficiency (IE%) is defined as follows:

$$IE\% = \frac{\omega_0 - \omega}{\omega_0} \times 100 \tag{1}$$

where ω_0 and ω are the corrosion rate values after immersion in solution without and with inhibitor, respectively.

For electrochemical measurements, a conventional three-electrode glass cell with a platinum counter electrode and a saturated calomel electrode (SCE) as reference was used. A mild steel cylindrical rod of the same composition as the working electrode was pressure-fitted into a polytetrafluoroethylene holder (PTFE) exposing only 1 cm² surface to the solution. All potentials were measured against SCE.

The potentiodynamic polarization curves were recorded by changing the electrode potential automatically with a potentiostat type PGZ 100, at a scan rate of 1 mV/s. Before each experiment, the working electrode was immersed in the test cell for 30 min until reaching steady state.

The evaluation of corrosion kinetics parameters was obtained using a fitting by Stern–Geary equation such as mentioned in our previous work [23]. The inhibition efficiency was evaluated from the measured i_{corr} values using the relationship:

$$\mathrm{IE\%} = \frac{i_{\mathrm{corr}}^0 - i_{\mathrm{corr}}}{i_{\mathrm{corr}}^0} \times 100 \tag{2}$$

where i_{corr}^0 and i_{corr} are the corrosion current densities values without and with inhibitor, respectively.

The electrochemical impedance spectroscopy measurements were carried out using a transfer function analyser (VoltaLab PGZ 100), with a small amplitude AC signal (10 mV rms), over a frequency domain from 100 kHz to 10 mHz at room temperature and in air atmosphere. The results were then analysed in terms of equivalent electrical circuit using the Bouckamp program [24]. The inhibition efficiency of the inhibitor was found from the relationship:

$$IE\% = \frac{R_{\rm ct} - R_{\rm ct}^0}{R_{\rm ct}} \times 100$$
(3)

where R_{ct}^0 and R_{ct} are the charge transfer resistance values in the absence and the presence of inhibitor, respectively.

Results and discussion

Corrosion weight loss tests

The addition of quinoxaline derivatives effect on mild steel corrosion in 1 M HCl solution was studied using weight loss measurement at 24 h of immersion. Table 1 represents the corrosion rate and the inhibition efficiency values. It is noted that

Table 1 Corrosion rate and inhibition efficiencies for mild steel in 1 M HCl at various concentrations of quinoxaline derivatives	Compounds	Conc. (M)	Corrosion rate (mg cm ^{-2} h ^{-1})	IE%
	Blank solution	00	0.0574	_
	СМОРТQ	10^{-5}	0.0205	64
		5×10^{-4}	0.0164	71
		10^{-4}	0.0136	76
		10^{-3}	0.0125	78
	CMOSQ	5×10^{-4}	0.0211	63
		10^{-4}	0.0165	71
		10^{-3}	0.0145	75
		10^{-2}	0.0138	76

CMOPTQ and CMOPTQ are good corrosion inhibitors for mild steel in acidic media. As the corrosion rate decreased, inhibition efficiency increased with increasing concentration and reached a maximum at 10^{-3} M of CMOPTQ and at 10^{-2} M of CMOSQ.

The presence of CMOPTQ gives high inhibiting efficiencies and CMOSQ somewhat lower efficiency. This is probably due to the presence of sulphur and nitrogen atoms in the CMOPTQ molecule. According to Every and Riggs [25], the organic compound containing the nitrogen and sulphur has better inhibition efficiency in acidic media compared to the organic compound containing nitrogen or sulphur.

Potentiodynamic polarization curves

The corrosion behaviour of mild steel in 1 M HCl solution in the presence of quinoxaline derivatives was investigated by potentiodynamic polarization curves at room temperature after 30 min of immersion. Figures 1 and 2 show the results obtained. It is shown that all inhibitors suppressed the cathodic and anodic reactions. It is clear that the increase of concentration gave rise to a consistent decrease in anodic and cathodic current densities, indicating that these inhibitors act as a mixed type inhibitor [26].

Table 2 represents the various electrochemical parameters such as corrosion potential, E_{corr} , corrosion current density, i_{corr} , Tafel slopes, b_c and b_a and the inhibition efficiencies values, %IE. It can be seen that all compounds decreased i_{corr} significantly at all the studied concentrations. The almost unchanged corrosion potential and Tafel slopes in the presence of inhibitors indicate that the inhibition effect is caused by geometrical blocking of the reaction sites of the metal surface by adsorbed molecule species without changing the anodic and cathodic reaction mechanisms [27]. Values of corrosion inhibition efficiency obtained for CMOPTQ are greater than obtained for CMOSQ. The lesser value of inhibition efficiency for CMOSQ as compared to CMOPTQ can be attributed to the lower electron densities around the chemisorption center. Compounds can produce protonated species in HCl medium by the reaction of the amino group with HCl. This reaction is easer in



Fig. 1 Potentiodynamic polarization curves for mild steel in 1 M HCl containing different concentrations of CMOPTQ



Fig. 2 Potentiodynamic polarization curves for mild steel in 1 M HCl containing different concentrations of CMOSQ

the case of the presence of sulphur. The better performance of CMOPTQ over CMOSQ is also due to the greater surface area which leads to more adsorption on the metal surface, thereby exhibiting a better inhibitory effect. This result is a good match with the results obtained from weight loss tests.

Compounds	Conc. (M)	$E_{\rm corr}$ (mV sce ⁻¹)	$i_{\rm corr}$ ($\mu A \ {\rm cm}^{-2}$)	$b_{\rm a}$ (mV dec ⁻¹)	$b_{\rm c}$ (mV dec ⁻¹)	IE%
Blank solution	00	-456	289.5	65.5	-146.4	-
CMOPTQ	10^{-5}	-437	78.57	228	-124	73
	5×10^{-4}	-429	52.54	453	-123	82
	10^{-4}	-452	40.99	367	-129	86
	10^{-3}	-455	39.45	447	-120	87
CMOSQ	5×10^{-4}	-429	75.96	357	-129	74
	10^{-4}	-510	63.16	442	-124	78
	10^{-3}	-446	42.26	328	-162	85
	10^{-2}	-467	40.50	245	-204	86

 Table 2
 Electrochemical parameters and inhibition efficiencies for mild steel in 1 M HCl containing different concentrations of inhibitors



Fig. 3 Nyquist diagrams for mild steel in 1 M HCl at $E_{\rm corr}$ containing different concentrations of CMOPTQ

Electrochemical impedance spectroscopy (EIS) measurements

Figures 3 and 4 show Nyquist plots for mild steel in 1 M HCl solution in the presence of different concentrations of quinoxaline derivatives. It is clear that all of the impedance spectra obtained in the absence and in the presence of inhibitors consist of one depressed capacitive loop corresponding to one time constant. It is obvious that the addition of the inhibitors results in an increase in the semicircular capacitive loop diameter. These observations clearly bring out the fact that the mild steel corrosion in 1 M HCl is controlled by a charge transfer process and the corrosion inhibition occurs through the adsorption of the inhibitors on mild steel



Fig. 4 Nyquist diagrams for mild steel in 1 M HCl at $E_{\rm corr}$ containing different concentrations of CMOSQ

Fig. 5 Equivalent circuit model represents the metal/solution interface



surface. The impedance diagrams obtained are not perfect semicircles and this difference has been attributed to frequency dispersion [28].

In order to obtain accurate results, the analysis of complex plane plots was done by fitting the experimental results to the equivalent circuit given in Fig. 5, which has been used previously to model the mild steel/acid interface [29–32]. The circuit consists of solution resistance, R_s , in series with the parallel combination of charge transfer resistance, R_{ct} , and a constant phase element, CPE, used in place of double layer capacitance, C_{ct} , to represent the not ideal capacitive behaviour of the double layer more clearly. Various parameters obtained from these complex plane plots are given in Table 3.

It is apparent that the charge transfer resistance value of mild steel in uninhibited 1 M HCl solution changes significantly after the addition of the inhibitors. The inhibition efficiency of CMOSQ is lower than that of CMOPTQ which is somewhat expected when considering the presence of the C=S group in CMOPTQ. This result is a agreement with that obtained by Muzaffer Ozcan et al. [33] in the case of mild steel corrosion inhibition in phosphoric acid.

Compounds	Conc. (M)	$E_{\rm corr} ({\rm mV} {\rm sce}^{-1})$	$R_{ct} (\Omega \ cm^2)$	$C_{\rm ct} \ (\mu \rm F \ cm^{-2})$	IE%
Blank solution	00	-490	60	912	_
CMOPTQ	10^{-5}	-464	280	39	79
	5×10^{-4}	-471	387	40	85
	10^{-4}	-478	499	36	88
	10^{-3}	-480	520	26	89
CMOSQ	10^{-4}	-422	255	197	77
	5×10^{-4}	-473	309	51.53	81
	10^{-3}	-485	450	35.40	87
	10^{-2}	-509	499	35.38	87

 Table 3
 Impedance data and inhibition efficiencies for mild steel in 1 M HCl at different concentration of inhibitors

Immersion time effect

Figures 6 and 7 show the impedance spectra obtained for mild steel after different immersion times at $E_{\rm corr}$ in aerated 1 M HCl solution in the presence of 10^{-3} M of CMOPTQ or 10^{-2} M of CMOSQ, respectively. It is clear that all impedance spectra obtained consist of one depressed capacitive loop and that its diameter is significantly changed with immersion time. In addition, the presence of inhibitors increases the impedance but does not change other aspects of the behaviour. The characteristic evolution of the parameters with time is summarized in Table 4. It is noted that that R_{ct} values increased when C_{ct} values decreased with increasing of immersion time. The decrease in the C_{ct} which can result from a decrease in local dielectric constant and/or an increase in the thickness of the double layer was attributed to the inhibitor molecules adsorption on the metal surface [34]. However, it is known that, in acidic media, the halide ions facilitate the adsorption of organic inhibitors through intermediate bridges between the metal surface and the positively charged inhibitor. Thus, if the inhibiting effect is due to the protonated species, a synergistic increase in inhibition efficiency should be observed in the presence of the halide ions [35]. In our case, more ions (Cl⁻ ions) adsorbed when the immersion time increased.

Temperature effect

The temperature influence on the corrosion kinetic process in free acid and in the presence of adsorbed inhibitor leads to the obtaining of more information on the electrochemical behaviour of metallic materials in aggressive media.

Table 5 presentzx the corrosion rate values for mild steel in 1 M HCl in the presence of 10^{-3} M of CMOPTQ and 10^{-2} M of CMOSQ determined by potentiodynamic polarization curves at various temperatures ranges (303–333 K). It is well known that the corrosion rate increases with increasing of temperature in acidic media. Apparently, the results obtained postulate that the inhibitor function through adsorption on a metallic surface by blocking their active sites to form a



Fig. 6 Nyquist diagrams for mild steel in 1 M HCl containing 10^{-3} M of CMOPTQ at various immersion times



Fig. 7 Nyquist diagrams for mild steel in 1 M HCl containing 10^{-2} M of CMOSQ at various immersion times

screen onto the mild steel surface from the acidic solution. As the temperature increases, the desorption rate manifests parallel to the adsorption rate; the surface becomes less protected and then the inhibitors gradually lose their effectiveness.

Compounds	Immersion time (h)	$E (\mathrm{mV sce}^{-1})$	$R_{\rm ct}~(\Omega~{\rm cm}^2)$	$C_{\rm ct} ~(\mu {\rm F~cm^{-2}})$	IE%
Blank solution	1/2	-490	60	912	_
10 ⁻² M of CMOSQ	1	-490	520	56.10	88
	2	-499	524.15	33.89	89
	4	-519	709.55	32.72	91
	6	-526	742.26	30.37	92
	12	-549	768.77	26	92
	24	-562	815	19.54	93
10 ⁻³ M of CMOPTQ	1	-495	499	36.38	88
	2	-501	802.31	27.55	93
	4	-518	912.99	27.48	93
	6	-560	989.31	25.43	94
	12	-569	1,244.71	20.21	95
	24	-576	1,295.66	12.28	95

Table 4 Electrochemical impedance parameters for mild steel in 1 M HCl solution with 10^{-2} M of CMOSQ and 10^{-3} M of CMOPTQ, separately at different immersion times

Table 5Electrochemicalparameters for mild steel in 1 MHCl containing 10^{-3} M ofCMOPTQ and 10^{-2} M ofCMOSQ at various temperatures	Compounds	Temperature (K)	$i_{\rm corr}~(\mu {\rm A~cm}^{-2})$
	Blank solution	303	392
		313	639
		323	1,628
		333	3,293
	10^{-2} M of CMOSQ	303	40.50
		313	76.93
		323	144.56
		333	215.03
	10 ⁻³ M of CMOPTQ	303	39.45
		313	60.27
		323	168.49
		333	225.57

However, the corrosion reaction of mild steel in 1 M HCl depends on temperature. The dependence of the chemical reaction rate constant K on the temperature T is expressed by the Arrhenius law:

$$i_{\rm corr} = K \exp\left(-\frac{E_{\rm a}}{RT}\right) \tag{4}$$

where i_{corr} is the corrosion current density, K the Arrhenius pre-exponential factor, T the absolute temperature and R is the universal gas constant.

The logarithm plots of corrosion current density versus reciprocal temperature T^{-1} are given in Fig. 8. The plots obtained are straight lines and the slope of each



Fig. 8 Arrhenius plots for mild steel in acidic medium containing 10^{-3} M of CMOPTQ and 10^{-2} M of CMOSQ

one gives its activation energy E_a . The calculated activation energy values E_a are 61.31, 52.62 and 47.48 kJ/mol in the absence and the presence of 10^{-3} M of CMOPTQ and 10^{-2} M of CMOSQ, respectively. The change in the apparent activation energy values may be explained by the modification of the corrosion process mechanism in the presence of adsorbed inhibitor molecules [36].

The literature [36–38] mentions that the apparent activation energy E_a values in the presence are higher than these in the absence of an inhibitor. Other studies [39, 40] showed that in the presence of inhibitor the apparent activation energy values were lower than those in the absence of the inhibitor. However, in our study, E_a decreases in the presence of CMOPTQ and CMOSQ concentration indicating their chemisorptions on a metallic surface.

Conclusion

Quinoxalines derivatives, namely, 7-chloro-3-(4-methoxystyryl)quinoxalin-2(1H)one (CMOSQ) and 7-chloro-2-(4-methoxyphenyl)thieno(3.2-b)quinoxaline (CMO PTQ), have proved to be good inhibitors for the mild steel corrosion in 1 M HCl. These inhibitors act as cathodic-type inhibitors. The inhibition efficiencies were found to increase with an increase in inhibitor concentration and with immersion times. The electrochemical parameters obtained calculated from EIS show the same trend as those estimated from potentiondynamic polarization and weight loss measurements. The decrease in activate energy values E_a in the presence of inhibitors indicate their chemisorptions on a metallic surface.

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