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Synthesis and evaluation of isatin derivatives as corrosion inhibitors for Q235A steel in highly concentrated HCl

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Abstract A series of inhibitors—isatin derivatives aimed at anticorrosion of Q235A steel—was synthesized. The molecule structures were analyzed by NMR and MS. The inhibition on the corrosion in a concentrated HCl solution as high as 3 M was studied by weight loss, molecular simulation, and potentiodynamic polarization. The results indicate that isatin derivatives act as mixed type (cathodic/anodic) inhibitors. Several compounds were investigated in the formulations, during which compound **6** shows 95.5 % inhibition efficiency under the concentration of 100 mg/L accompanied by urotropine and 1,4-dihydroxy-2-butyne.

Keywords Isatin derivatives · Q235A steel · Anticorrosion · Formulation

Introduction

One-third of the world production of crude oil comes from carbonate reservoirs, most of which have natural permeability below 10 mD, and stimulation of the production is achieved through acid and/or fracturing operations. Hydrochloric acidic fluid is pumped into wells, and irregular etching of the fracture walls by the

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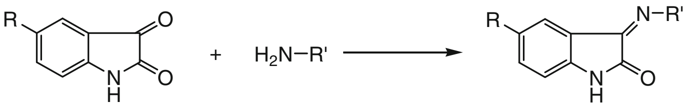
acid is expected to create highly conductive channels [1]. Thus, it is a challenge for the metal instruments involved in the acidification. Q235A (A3) steel is a material frequently used for its resistance properties against corrosion in the gas and oil industry. However, there is a need to prolong their lifetime, because the steel is susceptible to pitting corrosion in the presence of acidic media, especially in highly concentrated HCl under high temperature [2, 3]. Great efforts have been concentrated on heat treatment and changing chemical composition to improve its corrosion resistance. But, for the aggressiveness of acidic media, the use of corrosion inhibitors is considered as the most effective method for the protection of many metals against such acid attack [2–6]. Compounds containing functional electronegative groups and *p*-electrons in triple or conjugated double bonds have been found to be very efficient as inhibitors against metal corrosion in many conditions [7, 8]. It has been commonly recognized that an organic inhibitor usually promotes the formation of a chelate on a metal surface, by transferring electrons from the organic compounds to the metal and forming a coordinate covalent bond during the chemical adsorption, thereby reducing the corrosion in acidic solutions [9–11]. Organic compounds, containing heteroatoms, such as sulfur, phosphorus, nitrogen, and oxygen, together with aromatic rings in their structures, are the major adsorption centers, and many heterocyclic compounds with such polar groups are efficient corrosion inhibitors in acidic solutions [3–8, 12–14]. The planarity and the lonely electron pairs in the heteroatoms are important features that determine the adsorption of these molecules on the metallic surface [14]. Schiff base compounds, a condensation product of an amine and a ketone/aldehyde, are such typical molecules. Some polydentate Schiff base compounds (PSCs) have been reported as effective corrosion inhibitors for various metals in acid media, such as Schiff bases containing thiophene and furoin thiosemicarbazone [13, 15–17].

Several isatin derivatives have been reported as inhibitors in 1 M HCl [18–20], and the aim of this work is to screen the inhibitory action of more isatin Schiff bases for the corrosion of mild steel in 3 M HCl solution. The effects of concentrations and molecular structures on the inhibition efficiencies of the selected Schiff bases have been studied systematically, and the structure activity relationship of these inhibitors are also discussed.

Results and discussion

Molecular structures

Isatin (indole-2,3-dione) is a simple natural product found in many plants, and even in mammalian tissues, with versatile bioactivities. The compound has been produced industrially and the price is acceptable, so it can thus be used for large-scale applications. In this work, we will investigate the application of isatin derivatives in oil field chemistry. The isatin derivatives were synthesized as shown in Scheme 1. All the isatin derivatives were characterized by ^{1}H-NMR (400 MHz) and MS (EI) spectra and the results are summarized in Table 1.



Scheme 1 Synthesis of isatin derivatives by condensation reaction

The entire spectra consist of the anticipated structures. For example, the ^{1}H-NMR spectrum of compound **6** exhibits four peaks from 6.91 to 7.64 ppm, corresponding to the four phenyl protons. The peaks at 8.96, 9.05, and 11.02 ppm are due to the three thiocarbohydrazone protons. The singlet at 12.46 ppm is due to the amide proton. In addition, the MS spectrum shows a peak at 220 (*m*/*z*), which consists of the molecule weight of compound **6**.

Inhibitor properties and mechanism

Q235A (A3) steel is a material widely used in gas and oil fields, and it is easy to corrode in the presence of strong acidic media. It is also a great challenge especially in high concentrations of HCl under high temperature. The use of corrosion inhibitors is considered as the most effective method for protection against such acid attack. Many compounds, such as imidazoline, Mannich base, Schiff base, and some other heterocyclic compounds, have been employed in this process, but the cost is too high to be acceptable [1–5]. In this work, the inhibition efficiency (IE) of isatin as well as its Schiff base derivatives was investigated under the concentrations of 20 and 100 mg/L in 3 M HCl, and the results are displayed in Table 2. From the table, it can be seen that all these compounds can inhibit the corrosion with different efficiencies, compounds **4**, **6**, **7**, **8**, and **10** have an IE of over 60 % with the concentration of 100 mg/L, and compound **6** is the most potent with an IE of 70.4 %.

The mechanism of the inhibition processes of the corrosion inhibitors under consideration is mainly the adsorption. The process of adsorption is governed by the chemical structures. The presence of N, O, and S atoms and conjugated bonds in these molecules leads to the formation of *p*–*d* bonds, resulting in the formation of an overlap of p-electrons to the 3*d* vacant orbital of iron atoms, which enhances the adsorption of the compounds on the metal surface [21].

Among the compounds investigated in this study, compound **6** has been found to display the best performance. This can be explained on the basis of the presence of a polydentate Schiff base in the molecular structure, which increases the possibility of transferring the unshared electron of this molecule to iron, and therefore results in a better adsorption [22]. The steady conformation of compound **6** was simulated by a minimized energy of MM2 in Chem 3D, which is shown in Fig. 1. In the simulation, it was found that the there are two conjugated parts in this molecule, which are connected with a C=N bound. The Schiff base part is almost planar, the dihedral angle of N(11)–N(12)–C(15)–N(16) is −6.428 and that of N(11)–N(12)–C(15)–S(19) is 174.052. Since atoms of O14, N(11), N(12), N(16,) and S(19) almost lie in the same plane, the molecules may absorb on the ion surface by the coordinate

Table 1 The ^{1}H-NMR (400 MHz) and MS (EI) spectra of the isatin derivatives

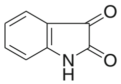
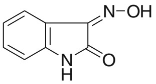
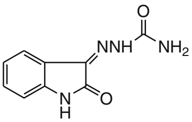
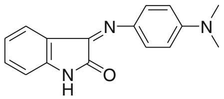
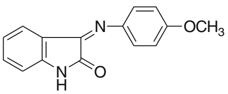
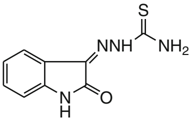
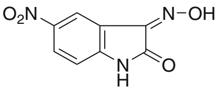
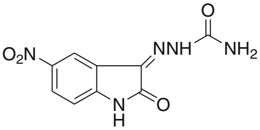
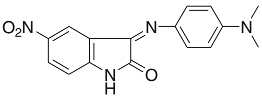
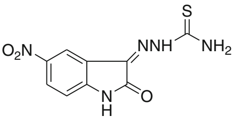
Compound	Structure	^{1}H-NMR (400 MHz) and MS (EI) spectra
1		/
2		^{1}H-NMR (D$_6$-Acetone), δ: 8.05 (1H, d, $J = 7.2$ Hz), 7.36 (1H, t, $J = 7.6$ Hz), 7.04 (1H, t, $J = 7.6$ Hz), 6.95 (1H, d, $J = 7.6$ Hz), 6.84 (1H, d, $J = 7.6$ Hz); MS *m/z*: 162 (M$^+$)
3		^{1}H-NMR (D$_6$-DMSO), δ: 12.40 (1H, s), 11.08 (1H, s), 9.06 (1H, s), 8.95 (1H, s), 7.66 (1H, d, $J = 7.6$ Hz), 7.30 (1H, t, $J = 7.6$), 7.10 (1H, t, $J = 7.6$ Hz), 6.90 (1H, d, $J = 8.0$ Hz); MS *m/z*: 204 (M$^+$)
4		^{1}H-NMR (D$_6$-DMSO, 400 MHz), δ: 10.88 (1H, s), 7.52 (1H, t, $J = 8$ Hz), 7.32 (1H, td, $J = 1.2$, 8 Hz), 7.09 (1H, d, $J = 8$ Hz), 7.02 (2H, d, $J = 7.2$ Hz), 6.89 (1H, d, $J = 7.6$ Hz), 6.81 (2H, d, $J = 7.2$ Hz), 2.97 (6H, s); MS (EI) *m/z*: 265 (M$^+$)
5		^{1}H-NMR (CDCl$_3$), δ: 9.14 (1H, s), 7.32 (1H, d, $J = 7.2$ Hz), 7.08 (2H, d, $J = 8.8$ Hz), 6.99 (3H, m), 6.93 (1H, d, $J = 8.0$ Hz), 6.79 (1H, t, $J = 7.6$ Hz), 3.88 (3H, s); MS *m/z*: 253 (M$^+$)
6		^{1}H-NMR (D$_6$-DMSO), δ: 12.46 (1H, s), 11.02 (1H, s), 9.05 (1H, s), 8.96 (1H, s), 7.64 (1H, d, $J = 7.6$ Hz), 7.34 (1H, t, $J = 7.6$), 7.08 (1H, t, $J = 7.6$ Hz), 6.91 (1H, d, $J = 8.0$ Hz); MS *m/z*: 220 (M$^+$)
7		^{1}H-NMR (D$_6$- DMSO), δ: 11.30 (1H, s), 8.12 (1H, d, $J = 7.2$ Hz), 7.85 (1H, t, $J = 7.6$ Hz), 7.34 (1H, t, $J = 7.6$ Hz), 7.19 (1H, d, $J = 7.6$ Hz); MS *m/z*: 207 (M$^+$)
8		^{1}H-NMR (D$_6$-DMSO), δ: 12.22 (1H, s), 11.57 (1H, s), 10.1 (1H, s), 9.23 (1H, s), 8.02 (1H, d, $J = 7.6$ Hz), 7.83 (1H, t, $J = 7.6$), 7.24 (1H, d, $J = 8.0$ Hz); MS *m/z*: 249 (M$^+$)
9		^{1}H-NMR (D$_6$-DMSO), δ: 11.97 (1H, s), 8.11 (1H, d, $J = 7.2$ Hz), 7.89 (1H, t, $J = 7.6$ Hz), 7.35 (1H, t, $J = 7.6$ Hz), 7.11 (2H, d, $J = 7.2$ Hz), 7.02 (1H, d, $J = 7.6$ Hz), 6.93 (2H, d, $J = 7.2$ Hz), 2.99 (6H, s); MS (EI) *m/z*: 310 (M$^+$)
10		^{1}H-NMR (D$_6$-DMSO), δ: 12.58 (1H, s), 11.22 (1H, s), 9.30 (1H, s), 9.03 (1H, s), 8.31 (1H, d, $J = 7.2$ Hz), 7.88 (1H, t, $J = 7.6$ Hz), 7.33 (1H, t, $J = 7.6$ Hz); MS *m/z*: 265 (M$^+$)

Table 2 The corrosion rate and IE of isatin and the Schiff base derivatives

Extract	Concentration (mg/L)	Corrosion rate (g/m^2 h)	Inhibition efficiency (%)
–	–	168.89	/
1	20	155.71	7.8
1	100	142.03	15.9
2	20	149.46	11.5
2	100	64.36	61.9
3	20	150.64	10.8
3	100	73.30	56.6
4	20	135.45	19.8
4	100	65.87	61.0
5	20	132.91	21.3
5	100	56.07	66.8
6	20	139.20	23.5
6	100	49.99	70.4
7	20	154.53	8.5
7	100	108.60	35.7
8	20	156.22	7.5
8	100	129.20	23.5
9	20	160.44	5.0
9	100	137.98	18.3
10	20	135.11	20.0
10	100	54.55	67.7

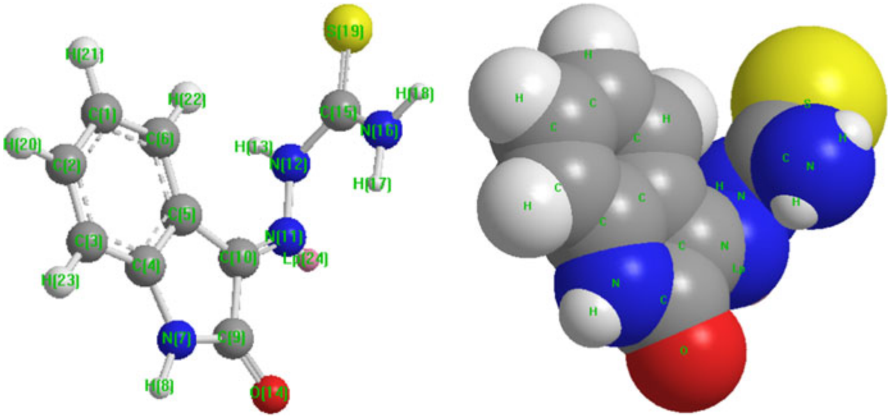


Fig. 1 The steady conformation and the space-filling model of compound **6**

covalent bonds with the 3*d* vacant orbital of iron atoms in the manner described in Fig. 2 to form the protective film. It has also been found that the IE of compound **10** is weaker than that of compound **6**. Comparing the structures of the two compounds,

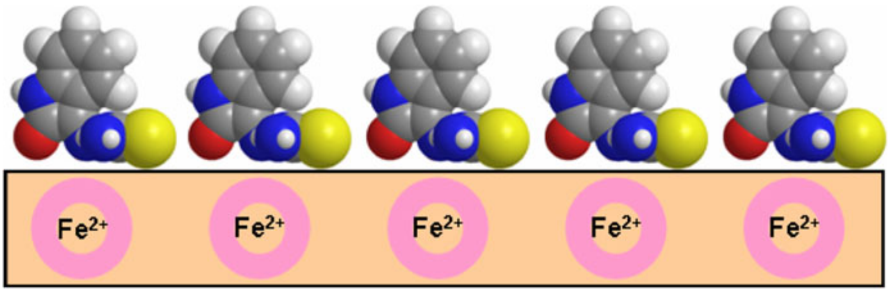


Fig. 2 The absorption of molecules on the ion surface

it can be deduced that the –NO_2 group leads the IE to drop. The reason is that the –NO_2 group is an electro-cloud group which reduces the density of the electron cloud in the oxyindol part and the C=N bond, which weakens the coordinate covalent bonds between the molecules and the ion surface.

Tafel polarisation measurements

Figure 3 shows anodic and cathodic polarisation plots recorded on mild steel electrodes in 3 M HCl in the absence and presence of different concentrations of compound **6**. Table 3 shows the electrochemical corrosion parameters, i.e., corrosion potential (Ecorr), cathodic and anodic Tafel slopes (βa, βc), and corrosion current density (Icorr) obtained from cathodic and anodic curves.

The IE is also calculated from the following equation:

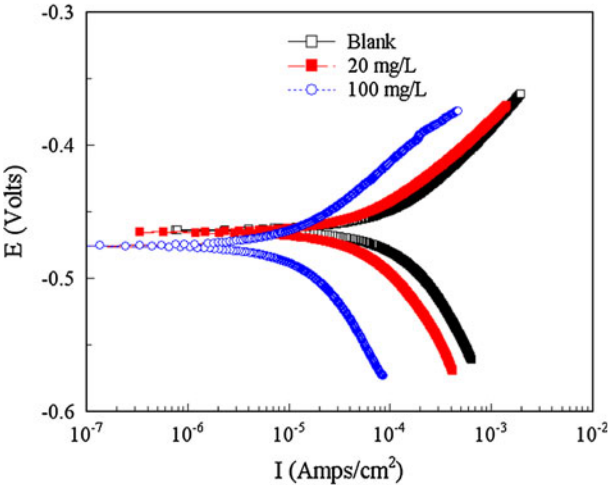


Fig. 3 Typical polarization curves for corrosion of Q235A steel in 3 M HCl in the absence and presence of different concentrations of compound **6**

Table 3 Potentiodynamic polarization parameters for the corrosion of the Q230A steel in 3 M HCl in the absence and presence of different concentrations of compound **6**

Concentration (mg/L)	−Ecorr (mV)	Icorr (μA/cm^2)	βa (mV/dec)	βc (mV/dec)	Corrosion rate (g/m^2 h)	Inhibition efficiency (%)
–	0.46402	159.42	94.273	154.01	1.8775	–
20	0.46551	73.52	73.417	131.3	0.86475	53.9
100	0.47588	17.792	77.925	141.79	0.20927	88.9

$$E(\%) = \frac{I_{\mathrm{corr}} - I_{\mathrm{corr(i)}}}{I_{\mathrm{corr}}} \times 100$$

where Icorr and Icorr(i) are corrosion current densities obtained in the absence and presence of inhibitors, respectively. It can be seen that the corrosion rate is decreased and the IE is increased by increasing the inhibitor concentration [23]. These inhibitors cause changes in the anodic and cathodic Tafel slopes and no definite trend was observed in the shift of Ecorr values in the presence of different concentrations of compound **6**, suggesting that these compounds behave as mixed-type (anodic/cathodic) inhibitors [24].

Optimizing of in the formulation

Hexamethylenetetramine (HMTA) is also known as urotropine. The molecule has a symmetric tetrahedral cage-like structure, similar to adamantane, whose four “corners” are nitrogen atoms and “edges” are methylene groups. The molecule behaves like an amine base, undergoing protonation and *N*-alkylation. With these features, it has been used as a corrosion inhibitor. In addition, 1,4-dihydroxy-2-butyne (BOZ) contains hydroxyl groups and p-electrons in triple bonds, which makes it is suitable for use as a corrosion inhibitor in many conditions. But it was found that the inhibition efficiencies are relative poor, or large quantities are needed to obtain higher IE (about 1–3 %), so the two are only used as additives in some corrosion inhibitor formulations [25, 26]. In the following work, HMTA and BOZ were investigated as synergists for the isatin Schiff base derivatives, and the results are shown in Table 4.

From the table, it was found that HMTA and BOZ are not efficient inhibitors, but they can enhance the IE of these compounds effectively, especially for compounds **6** and **10**, but are less effective for compound **2**. The reason might lie on the fruitful p-electrons of N, O, and the triple bond, which can form covalent bonds between the molecules and the ion surface, capture H^+ to release the acidity, and even join the isatin Schiff base molecules as “bridges” to enhance the protective film on the ion surface. Finally, the IE of the complex of isatin Schiff bases + HMTA + BOZ were investigated, and the results are shown in Table 5. The results show that the IE of Schiff bases can be improved further by using the two additives together. The highest efficiency reaches to 95.5 % by using compound **6** + HMTA + BOZ. Considering the efficiency and the cost, HMTA should be recommended as an effective companion for the isatin Schiff bases.

Table 4 The corrosion rate IE of some Schiff base derivatives companied by HMTA or DHBY

Formulation	Corrosion rate (g/m^2 h)	Inhibition efficiency (%)
–	168.885	/
HMTA	128.690	23.8
BOZ	125.482	25.7
2 + HMTA	31.075	81.6
4 + HMTA	24.488	85.5
5 + HMTA	18.239	89.2
6 + HMTA	10.471	93.8
10 + HMTA	16.044	90.5
2 + BOZ	36.310	78.5
4 + BOZ	33.608	80.1
5 + BOZ	19.422	88.5
6 + BOZ	12.666	92.5
10 + BOZ	14.693	91.3

The concentration is 100 mg/L

Table 5 The corrosion rate IE of some Schiff base derivatives companied by HMTA and DHBY

Formulation	Corrosion rate (g/m^2 h)	Inhibition efficiency (%)
–	168.885	/
HMTA + BOZ	98.291	41.8
2 + HMTA + BOZ	21.111	87.5
4 + HMTA + BOZ	16.382	90.3
5 + HMTA + BOZ	11.315	93.3
6 + HMTA + BOZ	7.5998	95.5
10 + HMTA + BOZ	10.133	94.0

The concentration is 100 mg/L for both HMTA and DHBY

Conclusions

In this work, a series of isatin Schiff bases was synthesized and characterized. Then, the corrosion IE and the mechanism of these isatin Schiff bases were investigated. The results indicate that several compounds, **4**, **6**, **7**, **8** and **10**, show an IE of over 60 % in a high HCl concentration of 3 M under a high temperature of 60 °C. If accompanied by HMTA and/or BOZ, the IEs greatly increase, and the highest efficiency of 95.5 % was obtained by using compound **6** + HMTA + BOZ. Tafel polarization measurements show that these compounds behave as mixed-type (anodic/cathodic) inhibitors.

Experimental section

General remarks

All starting materials and solvents (A.R. grade) are commercially available and were used without further purification. NMR spectra were recorded in the stated solutions, on a Bruker DPX400 spectrometer, operating at 400 MHz for ^{1}H; δ values are reported in ppm and J values in hertz. Mass spectra were recorded on a Micromass Platform II spectrometer, using the direct-inlet system operating in the electron impact (EI) mode.

Synthesis of isatin derivatives

Compounds **2–10** were synthesized according to published methods [27, 28]. Isatin (1 mmol) was dissolved in methanol (20 mL) and a methanol solution of 1.2 mmol amino compound (10 mL) was added dropwise, until the disappearance of isatin was evidenced by thin-layer chromatography. The solvent was removed in vacuo and the residue was separated by column chromatography (silica gel, petroleum ether/ethyl acetate = 1:1–1:3 v/v) to give the product.

Gravimetric measurements

The corrosion tests were performed on a Q235A with a composition (in wt%) C: 0.22; P: 0.045; Si: 0.35; S: 0.05; Mn: 1.40, and Fe balance. The electrolyte solution was 3 M HCl, prepared from analytical grade 38 % HCl and double-distilled water. The concentration range of the isatin Schiff base inhibitor employed was 0.15 g/L. All tests have been performed in deaerated solutions and at 60 ± 0.5 °C. The gravimetric tests were carried out according to the People's Republic of China Standard of Petroleum and Natural Gas Industry (Evaluation method for behavior of corrosion inhibitor for produced water of oilfield, SY/T5273-2000) with a few modifications. Each test was done with three specimens at the same time to give reproducible results.

Electrochemical measurements

The electrodes were mechanically abraded with a series of emery papers (800 and 1,200 grades). Then, they were rinsed in acetone and double-distilled water before their immersion in the experimental solution. Electrochemical measurements were conducted in a conventional three-electrode thermostated cell. The electrode was inserted into a Teflon tube and isolated with polyester so that only its section (0.5 cm^2) was allowed to contact the aggressive solutions. A platinum disk as counter electrode and standard calomel electrode (SCE) as the reference electrode have been used in the electrochemical studies.

The potentiodynamic curves were recorded using a CS350 system connected to a personal computer. The working electrode was first immersed in the test solution for 60 min to establish a steady state open circuit potential. After measuring the open circuit, potential dynamic polarization curves were obtained with a scan rate of 0.5 mV/s. Corrosion rates (corrosion current densities) were obtained from the polarization curves by linear extrapolation of the anodic and cathodic branches of the Tafel plots at points 100 mV more positive and more negative than the Ecorr.

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