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Synthesis and Application of Isatin Schiff Base as Corrosion Inhibitor

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Isatin Schiff base, 3-(4-hydroxyphenylimino)indolin-2-one, was synthesized and analyzed by NMR and MS. The inhibition and the mechanism of the title compound on the corrosion of high protective Q235A steel in HCl solution were screened and discussed. The results indicated that it can inhibit the corrosion with moderate inhibition efficiency in different conditions and the inhibition mechanism of the corrosion inhibiting may be mainly contributed to the adsorption. While the isatin Schiff base was companied with hexamethylenetetramine (HMTA) and 1,4-dihydroxy-2-butyne (BOZ), the inhibition efficiency was enhanced effectively.

Keywords: Isatin, Schiff base, Synthesis, Corrosion inhibition, Adsorption, Synergist.

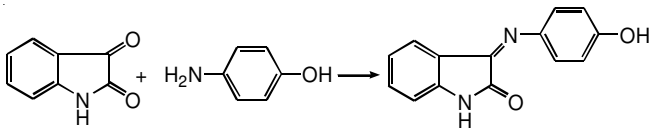
INTRODUCTION

About one third of the world production of crude oil from carbonate reservoirs, most of which have natural permeabilities below 10 mD and the stimulation of the production is achieved through acidification and/or fracturing operations. During the acidification operation, hydrochloric acidic fluid is pumped into wells, which etches the fracture walls irregularly to create highly conductive channels[1]. So it is a challenge for the metal instruments involved. Q235A (A3) steel is a basic material for its resistance properties against corrosion in the gas and oil field. However, there is a need to prolong their lifetime, because the steel is susceptible to pitting corrosion in the presence of in acidic media, especially in high concentration of HCl under high temperature[2,3]. Great attentions have been drawn to 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* and/or π-electron in triple or conjugated double bonds, are found to be efficient as inhibitors against metal corrosion[7,8]. It has been commonly recognized that an organic inhibitor usually promotes formation of a chelate on a metal surface, by transferring *p* and/or π-electrons from the organic compounds to the metal and forming a coordinate covalent bond during the chemical adsorption[9-11]. Organic compounds, containing heteroatoms, such as sulfur, phosphorus, nitrogen and oxygen, together with aromatic rings in their structure are the major adsorption centers and the Schiff bases, a condensation product of an amine and a ketone/aldehyde, are such typical molecules[3-8,12-14]. Some polydentate Schiff base compounds have been reported as effective corrosion inhibitors for various metals in acid media[13,15-17].

Several isatin derivatives have been reported as inhibitors in 1M HCl[18-20], the aim of this work is to screen the inhibitory action of an isatin Schiff base [3-(4-hydroxyphenylimino) indolin-2-one] for the corrosion of mild steel in high concentrated HCl solution. Effects of concentration and the additives on the inhibition efficiencies will also be studied systematically.

EXPERIMENTAL

Synthesis of isatin Schiff bases: 3-(4-hydroxyphenylimino) indolin-2-one was synthesized according to published methods (**Scheme-I**)[21,22]. Isatin (1 mmol) was dissolved in methanol (20 mL) and a methanol solution of 1.2 mmol 4-aminophenol (10 mL) was added dropwise, until the disappearance of isatin, as 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 v/v), to give the title compound. Red single crystals of the title compound suitable for X-ray analysis were obtained on slow evaporation of a methanol solution (30 mL) of the title compound (30 mg) over a period of 4 *d*. ^{1}H NMR (DMSO-d_6, 400 MHz): 10.92 (1H, s), 9.56 (1H, s), 7.32 (2H, m), 6.86 (4H, m), 6.74 (3H, m); MS (EI) *m/z*: 238 (M^+).



Scheme-I: Synthesis of 3-(4-hydroxyphenylimino)indolin-2-one by condensation reaction

Gravimetric measurements: The corrosion tests were performed on 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 3M HCl, prepared from analytical grade 38 % HCl and distilled water. The concentration range of 3-(4-hydroxyphenylimino)indolin-2-one was employed as 0.05 g/L and 0.10 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.

RESULTS AND DISCUSSION

Inhibitor properties and mechanism: Q235A (A3) steel is a widely used material in the gas and oil field. Although it has been treated by heat and changing chemical composition to improve the corrosion resistance, for the aggressiveness of acidic media, it is also a great challenge especially in high concentration of HCl under high temperature. The use of corrosion inhibitors has been considered as the most effective method for the protection against such acid attack. Some inhibitors, such as imidazoline, Mannich base, Schiff base and some other heterocyclic compounds, have been employed in this process, but the concentration or the price is too high to be acceptable. In the following work, the performance of the isatin Schiff base as an inhibiter with the concentration from 100 to 2000 mg/L in 1M and 2M HCl and the results were summarized in Table-1. It was found that almost all the inhibition efficiency increases along with the concentration of inhibiter, but there is difference in the two concentrations and different temperatures and it reaches to 67.64 % with the concentration of 500 mg/L in 2M HCl solution, further increase of the inhibitor does not increase the inhibition efficiency.

The inhibition mechanism of the corrosion inhibiting may be mainly contributed to the adsorption. The process of adsorption is governed by the chemical structure of these inhibitors. The presence of N, O, S atoms and conjugated bonds in the structures makes the formation of *p-d* bonds resulting form the overlap of *p* electrons to the 3*d* vacant orbital of Fe atoms, which conforms the adsorption of the compounds on the metal surface[23]. The inhibitive performance of 3-(4-hydroxyphenylimino)indolin-2-one can be explained on the presence of polydentate Schiff base in the molecular structure which rises the possibility of transferring the unshared electron of this molecule to iron[24]. The molecules may absorb on the ion surface by the coordinate covalent bonds with the 3*d* vacant orbital of Fe atoms in the manner described in Fig. 1 to form the protective film.

TABLE-1
CORROSION INHIBITION EFFICIENCY OF 3-(4-HYDROXYPHENYLIMINO)INDOLIN-2-ONE

Concentration of inhibition (mg/L)	HCl concentration (M)	Temp. (°C)	Inhibition efficiency (%)
100	1	30	12.23
100	1	45	22.49
100	1	60	17.40
100	2	30	12.74
100	2	45	10.77
100	2	60	19.30
200	1	30	26.18
200	1	45	18.01
200	1	60	16.81
200	2	30	16.51
200	2	45	15.09
200	2	60	18.92
500	1	30	14.81
500	1	45	77.63
500	1	60	62.90
500	2	30	40.12
500	2	45	27.00
500	2	60	67.64
1000	1	30	63.94
1000	1	45	27.24
1000	1	60	23.67
1000	2	30	58.68
1000	2	45	13.94
1000	2	60	30.80
2000	1	30	11.90
2000	1	45	9.88
2000	1	60	36.95
2000	2	30	21.71
2000	2	45	19.96
2000	2	60	28.91

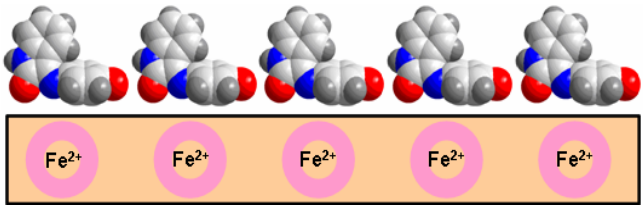
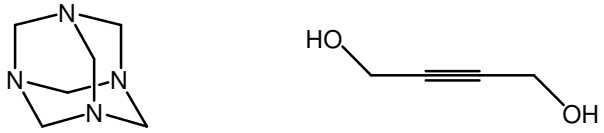


Fig. 1. Absorption of 3-(4-hydroxyphenylimino)indolin-2-one molecules on the ion surface

Optimization of the formulation: Hexamethylenetetramine (HMTA, Fig. 2) is 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 corrosion inhibitor. Beside, 1,4-dihydroxy-2-butyne (BOZ) (Fig. 2) contains hydroxyl groups and *p*-electron in triple bonds, which makes it is suitable used as a corrosion inhibitor in many conditions. But it was found that the inhibition efficiencies are relative poor, or much quantity is needed to obtain higher inhibition efficiency (about 1-3 %), so the two are only used as additives in some corrosion inhibitor formulations[25,26]. In the following work, hexamethylenetetramine (HMTA) and 1,4-dihydroxy-2-butyne (BOZ) were investigated as synergists for the isatin Schiff base (IS) in 2 M HCl and the results were shown in Table-2.



Hexamethylenetetramine 1,4-Dihydroxy-2-butyne

Fig. 2. Structure of hexamethylenetetramine and 1,4-dihydroxy-2-butyne

TABLE-2
CORROSION RATE INHIBITION EFFICIENCY OF ISATIN SCHIFF BASE DERIVATIVES ALONG WITH HMTA OR BOZ

Formulation	Temperature (°C)	Inhibition Efficiency (%)
HMTA	30	23.38
HMTA	45	18.95
HMTA	60	15.32
BOZ	30	19.25
BOZ	45	23.69
BOZ	60	20.18
IS + HMTA	30	60.15
IS + HMTA	45	44.78
IS + HMTA	60	82.56
IS + BOZ	30	55.37
IS + BOZ	45	50.50
IS + BOZ	60	78.26
IS + HMTA + BOZ	30	81.50
IS + HMTA + BOZ	45	75.39
IS + HMTA + BOZ	60	85.33

*All of the concentrations are 1000 mg/L; IS = Isatin Schiff base.

From the table, it was found that HMTA and BOZ are not efficient inhibitors, but they can enhance the inhibvition effi ciency of the isatin Schiff base effectively and the highest inhibvition effi ciency reaches to 85.33 %. The reason might lie on the fruitful *p*-electrons of N, O and 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 conform the protective film on the ion surface.

Conclusion

3-(4-Hydroxyphenylimino)indolin-2-one was synthesized and the its inhibition and the mechanism on the corrosion of high protective Q235A steel in HCl solution were screened. Isatin Schiff base can inhibits the corrosion with moderate inhibition efficiency in different conditions and the highest reaches to 77.63 %, as it was companied with hexamethylenetetramine (HMTA) and 1,4-dihydroxy-2-butyne (BOZ), the inhibition efficiency was enhanced to 85.33 %.

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