Corrosion inhibition of 316 stainless steel in 20%(W/W) HCl solution using dithizone

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Abstract: The inhibiting effect of dithizone (Diphenylthiocarbazone) has been studied regarding the corrosion of 316 stainless steel in 20% w/w HCl at 35°C. The effects of the inhibitor have been demonstrated using weight loss measurements. The increase of the inhibitor concentration leads to a decrease in the corrosion rate. This indicates a good adsorbability of dithizone (Diphenylthiocarbazone) on the metal surface. The value of ΔGad s has been calculated and dithizone has the potent to interact with 316 stainless steel through semi-physiosorption and/or semi-chemisorptions.

Keywords: Corrosion Inhibitor, 316 Stainless Steel, HCl, Dithizone

1. Introduction

Acids are widely used in various technological processes in industry, e.g., in pickling baths, in the extraction and processing oil and gas and in other chemical and petrochemical industries. Also, in the technical cracking of petroleum, acids appear as a result of hydrolysis of salts and may have destructive effect on the equipment. Corrosion due to acids are important and expensive problem in the petroleum refining units and it represents a significant portion of loss as a result of lost production, inefficient operation, high maintenance and the cost of corrosion control chemicals[1]. Corrosion of metals is a major industrial problem that has attracted a lot of investigations in recent year's .Most metals are inherently unstable and have the natural tendency to react with their environments to obtain lower energy by forming a chemical compound in a more stable state. Steel materials which are very susceptible to attack in aggressive media are the commonly exposed metals in industrial environments [2].

The damage by corrosion generates not only high cost for inspection, repairing and replacement, but in addition these constitutea public risk, thus the necessity of developing novel substances that behave like corrosion inhibitors[3].

Inhibitors are compounds that control, reduce, or prevent reactions between a metal and its surroundings when added to the medium in small quantities. Inhibitors should be effective in low concentrations for economy [1,4]. The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media. Hydrochloric acid is widely used in industry, for example, acid pickling, acid cleaning and acid descaling[5].

The dissolution rate of the metal is quite high and the inhibition of these solutions with organic compounds, which may retard the dissolution rate, is favored. Different compounds have been reported to inhibit the corrosion of stainless steel [6]. Most of the well-known acid inhibitors used in industry are organic compounds having multiple bonds in their molecules that mainly contain nitrogen, sulphur, oxygen atoms through which they get adsorbed on the metal surface [7,8].

Adsorbed organic molecules prevent steel corrosion by blocking the active sites on the metal surfaces and the inhibition efficiency (IE %) of an inhibitor depends strongly on the chemical structure or the functional groups on the inhibitor molecule.

Furthermore, the molecular-level structure and composition of materials can dramatically affect their bulk and interfacial properties [9].

There has been a growing interest in the use of organic compounds as inhibitors for the aqueous corrosion of metals. The study of corrosion inhibition processes by organic compounds is a very active field of research [7].
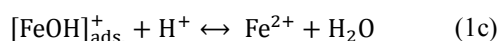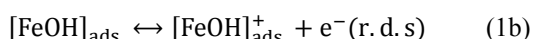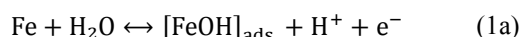
Sulphur-containing compounds are only of minor importance as inhibitor additives in HCl but they are

frequently used in H2SO4. As a rule of thumb it holds that S-containing inhibitors are primarily useful in H2SO4, whilst N-containing inhibitors exert their best efficiencies in HCl [10].
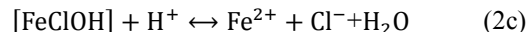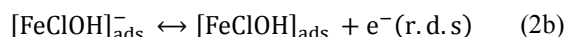
1.1. Corrosion Mechanism of Steel in HCl

If we assume that the electrochemical reaction of iron corrosion involves transfer of two electrons, then there are two steps ($v_s = 2$) each one represents transfer of one electron and one of them may be considered the rate determining step. This result is in good agreement with the mechanisms that are suggested for iron dissolution in:

(i) Aqueous solutions:

$$Fe + H_2O \leftrightarrow [FeOH]_{ads.} + H^+ + e^- \qquad (1a)$$

$$[FeOH]_{ads.} \leftrightarrow [FeOH]^+_{ads.} + e^- (r.d.s) \qquad (1b)$$

$$[FeOH]^+_{ads.} + H^+ \leftrightarrow Fe^{2+} + H_2O \qquad (1c)$$

(ii) Aqueous solutions containing Cl- ions:

$$Fe + H_2O + Cl^- \leftrightarrow [FeClOH]^-_{ads.} + e^- \qquad (2a)$$

$$[FeClOH]^-_{ads.} \leftrightarrow [FeClOH]_{ads.} + e^- (r.d.s) \qquad (2b)$$

$$[FeClOH] + H^+ \leftrightarrow Fe^{2+} + Cl^- + H_2O \qquad (2c)$$

Where [FeOH] and [FeClOH $]^-_{ads.}$ are the adsorbed intermediates which each of them are involved in the rate determining step (Equations 1b and 2b, respectively) of mild steel dissolution according to mechanism (i) and (ii), respectively. It must be pointed out that the presence of Cl- ions does not exclude dissolution through the [FeOH]$_{ads.}$ intermediate in chloride free acid media, as the two mechanisms can proceed simultaneously [11].

In the present work, we investigate the corrosion of steel in 20% HCl by inhibitor.

Weight loss tests have been used to study the effect of addition of this compound on the corrosion of steel in hydrochloric acid solution.

2. Experimental Part

2.1. Materials

The experiments were performed with 316 stainless steel coupons (*39.7 cm^2* area).

Table 1. Chemical composition (in percentage) of commercial 316 stainless steel [10]:

C	Si	Mn	Cr	Ni	Mo	Cu	N	P	S	Fe
0.02	0.50	1.71	16.2	11	2.18	0.35	0.07	0.03	0.023	Bal

2.2. Preparation

The testing solutions were prepared by diluting of analytical grade HCl 37% in distilled water. Different concentrations of the inhibitor prepared by dissolve different amount of the inhibitor in 10 ml of methanol first because it is difficult to dissolve dithizone in HCl solution directly then added to a flask contains 260 ml of 20% HCl. The concentrations of the inhibitor were 250, 500 and 1000 mg/l in the 20% HCl and the blank containing only 260 ml of 20% HCl and 10 ml of methanol. The solutions kept for 19 hours at 35ºC before starting the experiments.

2.3. Corrosion Rates Measurements

Gravimetric methods were employed for corrosion rates calculations. Prior to each experiment, the 316 stainless steel specimens used had a rectangular form (7.43×2.3×0.3 cm) was abraded with a series of emery paper. Then, the specimen was washed several times with de-ionized water then with ethanol and dried using a stream of air. After weighing accurately, it was immersed in 300 ml bottle, which contained 260 ml of 20% HCl and 10 ml methanol in absence and presence of a certain concentration of dithizone (Diphenylthiocarbazone). After 8 days, the specimen was taken out, washed, dried and weighed accurately. Then the tests were repeated at different inhibitor concentrations and at 35ºC.

3. Results and Discussion

3.1. Weight Loss Measurements

The corrosion rate (*C.R*), the inhibition efficiency (% *IE*) and the degree of surface coverage (θ) of 316 stainless steel was calculated using the following equations:

$$C.R \ (g \ .cm^{-1}.day^{-1}) = \frac{m_1 - m_2}{A.t} \qquad (3)$$

Where m_1 and m_2 are the masses of the specimen before and after corrosion, *A* is the total area of the specimen and *t* is the corrosion time.

$$IE = \frac{C.R^0 - C.R}{C.R^0} \times 100 \qquad (4)$$

Where C.R° and C.R are the corrosion rates of 316 stainless steel in absence and presence of certain concentration of dithizone (Diphenylthiocarbazone), respectively. [10,13-17]

$$\theta = \frac{IE}{100} \qquad (5)$$

The inhibition efficiency (*IE*) and the corrosion rate(C.R), and surface coverage (θ), determined by gravimetric methods under the given experimental conditions are presented in Tables 2.

Table 2. *316 steel corrosion rates, the inhibition efficiency (% IE) and the degree of surface coverage (θ) in 20% of HCl in absence and presence of different concentrations of dithizone (Diphenylthiocarbazone).*

$C_{inh.}$ (ppm)	C.R (g.cm⁻¹.day⁻¹)	IE (%)	Θ
0	0.0673	-	-
250	0.0445	33.8	0.338
500	0.024	64.3	0.643
750	0.023	65.8	0.658
1000	0.0224	66.7	0.667

To have more information on the effect of the inhibitor concentrations on the corrosion rate of 316 stainless steel in 20% HCl solution. Assuming that the corrosion rate of 316 stainless steel against the concentration of the studied inhibitor obeys the kinetic relationship given in equation (6) [10,17]:

$$\text{Log C. R} = \text{Log } k + B \text{ Log}_{inh.} \qquad (6)$$

Where *k* is the rate constant and equal to *C.R* at inhibitor concentration of unity, *B* is the reaction constant which in the present case is a measure for the inhibitor effectiveness and $C_{inh.}$ (ppm) is the concentration of the dithizone (Diphenylthiocarbazone). Figure 1 represents the curve of LogC.R versus $\text{LogC}_{inh.}$ at 35ºC. The straight lines show that the kinetic parameters (*k* and *B*) could be calculated by Eq. 6, and listed in Table 3.
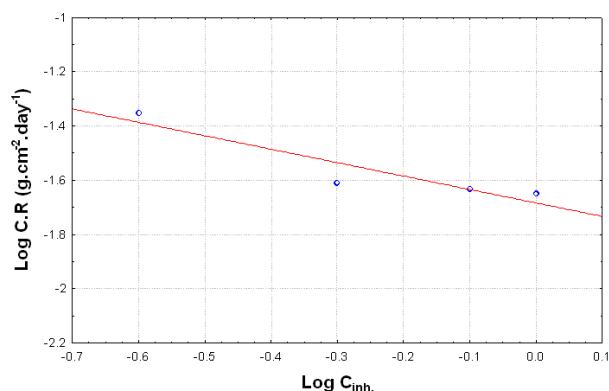
Fig 1. *Variation of LogC.R with log Cinh. for 316 stainless steel corrosion in 20 % HCl*

Table 3. *Kinetic parameters for the corrosion of 316 stainless steelin 20% of HCl containing dithizone (Diphenylthiocarbazone) at 35℃.*

| Temperature (°C)	B	K (g .cm⁻² .day⁻¹)
35	-0.4952	0.0207

The negative sign for the values of reaction constant *B* indicates that the rate of corrosion process is inversely proportional to the inhibitor concentration, meaning that the inhibitor becomes more effective with increasing its concentration. So, when the change of C.R with inhibitor concentration becomes steep (high negative value for constant *B*) it reflects good inhibitive properties for the studied inhibitor [10].

3.2. Adsorption Isotherms

The primary step in action of inhibitors in acid solutions is generally agreed to be adsorption on to the metal surface, which is usually oxide free in acid solutions. The adsorption of an inhibitor species, *Inh.*, on the metal surface in aqueous solutions should be considered a place exchanger reaction [10]:

$$\text{Inh.}_{aq.} + x\text{H}_2\text{O}_{ads.} \longrightarrow \text{Inh.}_{ads.} + x\text{H}_2\text{O}_{ads} \qquad (7)$$

Where *x*, the size ratio, is the number of water molecules displaced by one molecule of organic inhibitor. When the equilibrium of the process described in equation (7) is reached, it is possible to obtain different expressions of the adsorption isotherm plots, and thus the degree of surface coverage can be plotted as a function of the concentration of the inhibitor under test.
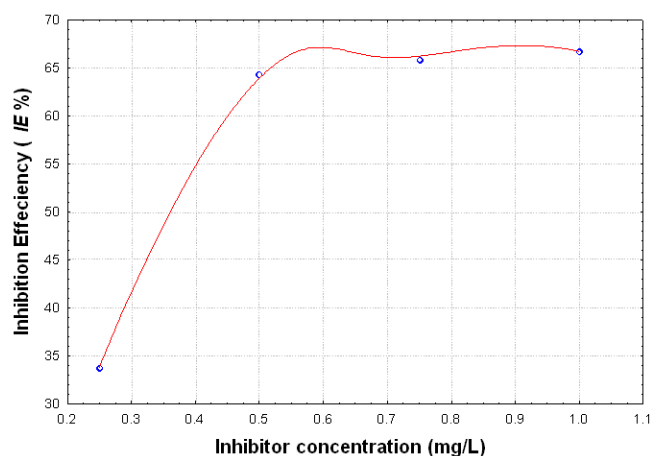
Fig 2. *Variation of the inhibition efficiency with the inhibitor concentration in20%HCl*

As it can be seen from fig.2 that the inhibitor efficiency increases with increasing the inhibitor concentration reaching a limiting value at about 65% where there are no influenced on the inhibition efficiency by further increasing of the inhibitor concentration this can be due to that from 0.5mg/l inhibitor can completely cover the surface of the stainless steel. Popova and al et in 2008 found that the inhibitor efficiency increases with increasing the N-containing Heterocycles concentration reaching up to a limiting concentration where there are no influenced of the inhibitors concentration on the inhibition efficiency for mild steel in 1M of HCl and 1M of H2SO4 [14]

The increase in efficiency may be due to the blocking effect of the surface by both the adsorption and film formation mechanism, which decreases the effective area of attack. The high *IE* exhibited by the compound may be attributed to its adsorption on the metal surface through polar groups as well as through π-electrons of the double bond. This leads to a greater coverage of the metal surface by the compound which results in a higher *IE* [18].

The values of θ increased with increasing inhibitor concentrations. The Langmuir isotherm was applied to

investigate the adsorption mechanism by the following expression [6,9,16,19-22]:

$$\frac{C_{inh}}{\theta} = \frac{1}{k} + C_{inh} \tag{8}$$

Where θ is the degree of surface coverage, C_{inh} the inhibitor concentration and K the equilibrium constant of the adsorption process.

The constant of adsorption, K, is related to the standard free energy of adsorption, $\Delta G_{ads.}$, with the following equation [7,17,18]:

$$K = (1/55.5) \exp(-\Delta G_{ads.} / RT) \tag{9}$$

Where R= ideal gas constant = 8.314 J/mol. K, the value of 55.5 is the concentration of water in the solution in moles and T is temperature in K.
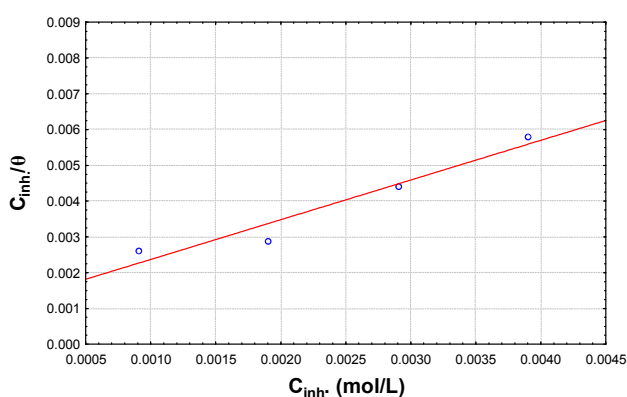
Fig 3. *Langmuir adsorption isotherms plotted as C/ θ versus $C_{inh.}$ for inhibition of 316 stainless steel corrosion in 20% HCl solution by dithizone (Diphenylthiocarbazone).*

C/θ virus inhibitor concentration at 35ºC is shown in Fig.3. The linear regression between C/θ and C was calculated, and K and ΔGads can be calculated according to the above equations. The result was shown in Table 4.

Table 4. *Adsorption parameters of inhibitor on the steel surface at 35°C*

K(mol^{-1}L)	ΔG_{ads} (KJ/mol)	Slop
540.5	-26.41	1.1

Based on Table 4, it was shown that free Gibb adsorption energy value, ΔG_{ads} -26.41(KJ/mol) for the compound is negative, which indicated the spontaneity of adsorption process of the compound on mild steel surface. The value of ΔG_{ads} of the compound according to Langmuir adsorption isotherm is kJ/mol. The more negative of ΔG_{ads} value the more spontaneous its adsorption process on metal surface, therefore the corrosion inhibition activity would increase. The value of ΔG_{ads} up to – 20 kJ/mol is consistent with the physical adsorption (physiosorption), whether the value of ΔG_{ads} which is above – 40 kJ/mol, is consistent with the chemical adsorption (chemisorptions) [15]. Therefore, compound has the potent to interact with 316 stainless steel

through semi-physiosorption and/or semi-chemisorptions because of their ΔG_{ads} values are in between – 20 kJ/mol and – 40 kJ/mol.

4. Conclusions

– Dithizone act as good corrosion inhibitor for 316 stainless steel in 20% HCl solution .
– The inhibitive action of the inhibitor is duo to the adsorption of its molecules on the metal surface.
– The inhibition efficiency of the inhibitor increase with the concentration to attain a maximum value 66.7 at 1000 ppm of the inhibitor.
– The adsorption of the inhibitor on the metal surface is a spontaneous process which follows Langmuir adsorption isotherm.
– The inhibitor has the potent to interact with 316 stainless steel through semi-physiosorption and/or semi-chemisorptions.

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