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Retardation of Stainless steel 314 dissolution in acidic medium

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Abstract

The significance of an antihistamine drug viz., Cetrizine [CZN] on corrosion of Stainless steel 314 in 2N Sulphuric acid was studies using mass loss measurements, Tafel polarization studies and impedance measurements. The results indicated that CZN is a good inhibitor for SS 314 in 2N H_2S0_4 and maximum efficiency obtained was 94 % at 450ppm concentration of CZN . Potentiostatic Polarization analyses showed that CZN acts as a mixed type of inhibitor. Quantum chemical studies were done for Cetrizine and its various quantum chemical parameters were calculated and discussed.

Keywords: Corrosion, Cetrizine, SS 314, Quantum Studies

1. Introduction

The Stainless steel is widely used in aerospace /Auomobile industries because of its ideal Massto strength ratio. The high strength of the SS 314 is owing to the presence of alloying element predominantly chromium and Nickel and these make alloy more disposed to to restricted corrosion due to sensitivity of the intermetallic particles in grain boundaries [1-2].Generally Sulphuric acid is used for removing scales , chemical and electrochemical etching of SS 314. Numerous methods are used to EXPLAIN the corrosion rate of metals in acids, and in the among of different methods practice of inhibitor is highest one. Many organic compounds were used as corrosion inhibitor [3-7]. But currently use of antibiotics as corrosion inhibitors is increased tremendously because of less toxicity and eco-friendly nature. Heterocyclic compounds holding hetro atoms such as sulphur, nitrogen and oxygen atoms comprising multiple bonds adsorb on the metal surface and thus act as active corrosion inhibitor for Stainless steel 314 in acid medium [8-13]. A scrupulous examination was used to find the inhibition properties of Cetrizine. The corrosion inhibiting capability of Cetrizine might be due to its arrangement of atoms. Various studies demonstrate that Cetrizine is prospective corrosion inhibitor. Cetirizine is an antihistamine that reduces the natural chemical histamine in the body. Histamine can produce symptoms of sneezing, itching, watery eyes, and runny nose. It is used to treat cold or allergy symptoms such as sneezing, itching, watery eyes, or runny nose.

2. Experimental Details

2.1Materials and methods

Materials employed for the analyses were SS 314 sheet of compositions (wt. %), Cr (4.3), Mn (2), Ni(21) and appreciable amount of Si, C,P in addition to Fe balance. The sheet was then cut into number of sample of each 4 x 1 x 2 cm dimensions were used for Mass loss and electrochemical studies. Each sample was mechanically polished followed by degreasing with acetone then washed with double distilled water and finally dried. Electrochemical experiments were performed in three electrode cell assembly with SS 314 as working electrode. Platinum wire as counter and Ag/Agcl/kcl (sat) as reference electrode.AR grade Hydrochloric acid and double distilled water are used to make 0.1N HCl for all experimentations.

2.2 Inhibitor

The antibiotic namely Citrizine was purchased from corresponding manufacturer and used without further purification. The structure of Cetrizine is shown in fig 1.CZN contains nitrogen atoms incorporated into the lactone ring, thus making the lactone ring 5 membered. With this structure it is likely to act as good inhibitor.

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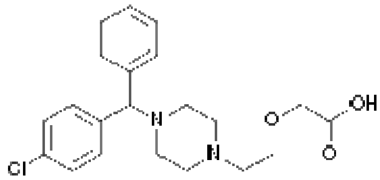

FIG 1 Structure of Cetrizine

2.3 Mass loss studies

The inhibitor was initially screened by a Massloss method [12].various samples Al were submerged in 0.1 N HCl solution comprising diverse concentrations of inhibitors (CZN).Samples were weighed before and after immersion and Massloss was estimated. The surface coverage (Θ) and inhibition efficiency were determined by means of following equations. Surface coverage (Θ) $= W_o - W / W_o$

Inhibition efficiency (%) $= W_o - W / W_o \times 100$

Where, W_o – Massloss without inhibitor

W – Massloss using varied concentrations of inhibitors

2.4 Tafel polarization studies

Tafel Polarization studies were carried out in a conventional three – electrode cylindrical glass cell, using BAS-100 A electrochemical analyzer Before to computing the polarization graphs the solution was deaerated for 20 min. and the working electrode was sustained at its corrosion potential for 10 min for attaining a steady state. The Al 2024 surface was bare to different concentrations of Cetrizine in 100mL of 2N sulphuric acid at room temperature. The inhibition efficiency (IE %) was estimated using the equation

Inhibition Efficiency (IE %) $= (I_0 - I / I_0) \times 100$

Where I_0 and I are the corrosion current density in absence and presence of inhibitor respectively.

The current-potential curves were documented by altering the electrode potential from -750mV to +150mV versus the open circuit potential. The resultant corrosion current (I corr) was recorded. Tafel plots were made by plotting E versus log I. Corrosion Potential (E corr), corrosion current density (I corr) and cathodic (βc) and anodic slopes (βa) were intended from known procedures.

2.5. Impedance studies

Impedance studies were carried out in the frequency range from 0.1 to 10000 Hz using amplitude of 20 mV and 10 mV peak to peak with an AC signal at the open-circuit potential .The impedance graphs were schemed in the nyquist representation. Charge transfer resistance (R_{ct}) values were acquired by subtracting the high-frequency impedance. The inhibition efficiency was obtained from the equation:

Inhibition Efficiency (IE %) = $(R_{ct} - R_{ct} / R_{ct}) \times 100$

Where R'_{ct} and R_{ct} are the corrosion current of Aluminum 2024 with and without treatment of inhibitor respectively.

2.7 Theoretical Analysis

Quantum studies were done using MOPAC 2000 program of CS Chemoffice packet program. The highest occupied molecular orbital (HOMO)energy, lowest unoccupied molecular orbital (LUMO) energy, Dipole moment (μ), hardness(η), absolute softness(σ) and total energy of the molecule were intended with the above given software package.

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3. RESULTS AND DISCUSSION

3.1 Massloss Studies

The values of inhibition efficiency (IE %) and the rate of corrosion from Massloss studies at diverse concentrations of Cetrizine are presented in table-1. It showed that the compound successfully inhibits the corrosion of SS 314 in 2N H_2SO_4 medium. Extreme inhibition efficiency and declined corrosion rate is due to the influence of firm adsorption and enlarged coverage of cetirizine on SS 314 with growth in the dosage of inhibitor.

The corrosion inhibition by cetirizine may possibly be due to the following interactions:

1. The interaction between the lone pairs of electrons of the nitrogen atoms of the CZN and the positively charged Fe surface.

2. The interactions between the +M effect of -Cl atom in inhibitor ring structure and the positively charged metal surface.

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3.2 Potentiodynamic polarization studies

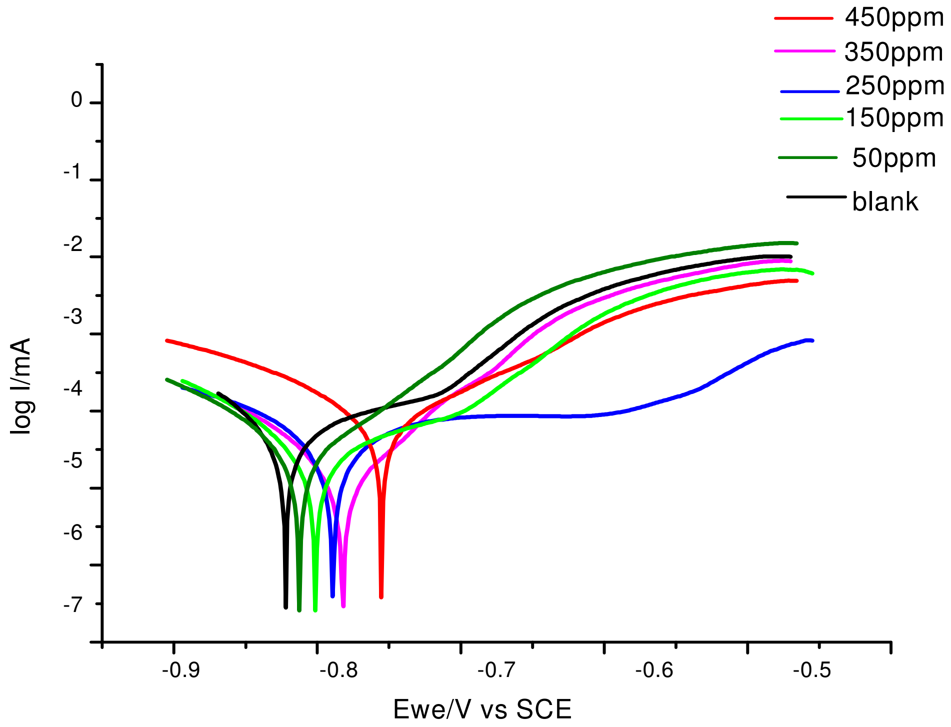

FIG 2 Tafel curves of SS 314 alloy in 2N H_2SO_4 at various concentrations of Cetrizine

Tafel curves for Stainless steel 314 in H_2SO_4 medium at various concentrations of Cetrizine are presented in figure-2. The parameters such as corrosion potential (E_{corr}), current densities (I_{corr}), anodic tafel slopes (β_a) and cathodic tafel slopes (β_c) and inhibition efficiency were studied from Tafel polarization curves as a function Cetrizine concentration are displayed in table- 2. It can be realized from the table that values of Tafel slopes and I_{corr} are very much diminished in contrast to the metal surface without inhibitor. It is also revealed that growing the concentrations of Cetrizine amplifies the β_a and β_c in imbalanced fashion approving that the inhibition of corrosion of Al alloy in

HCl medium is in mixed control [14-16]. Values of E_{corr} are progressed to less negative values in the existence of different concentrations of CZN. This might be the cause for developing resolutely adherent adsorbed film of CZN on the Aluminum alloy. It marked that most of the values of inhibition efficiency found by Massloss procedures and Tafel polarization method are with virtuous agreement.

3.4 Impedance studies

The Nyquist illustrations of impedance performance of SS 314 alloy 2024 in acidic medium with and without Cetrizine is used to compute charge transfer resistance (R_t)and double layer capacitance (C_{dl}) values which are tabularized in table-3. From the table, it is found that values of R_{ct} increases at the expenditure of double layer capacitance with growth in CZN concentration [17]. This contributes to the improved adsorption of the CZN antibiotic on the Al alloy surface with intensification of drug concentration.

A plot of surface coverage (ø) against log C exhibited a straight line plot endorsing that the adsorption of CZN on Al alloy surface from HCl medium followed Temkins adsorption isotherm. This is main confirmation to corrosion inhibition of Cetrizine, as a consequence of its adsorption on the aluminum surface.

3.5 Quantum chemical studies:

The quantum chemical aspects such as highest occupied molecular orbital (E_{HOMO}) energy, lowest unoccupied molecular orbital (E_{LUMO}) energy, LUMO- HOMO, energy gap (ΔE), dipole moment (μ), [18-21] are summarized in table -4.

CZN revealed greater inhibition efficiency due to its improved softness values by unshared electron pairs on nitrogen .The ionization potential (I) and electron affinity (A) were resulting from Koopmans theorem

$$A = -E_{LUMO} \quad I = -E_{HOMO}$$

The absolute hardness (η) and absolute electronegativity (x) of the inhibitor molecules were studied from the following equations

$$X = \frac{I + A}{2}$$

$$\eta = \frac{I - A}{2}$$

The softness (σ) can also be specified as

$$\sigma = \frac{1}{\eta}$$

Where, hardness and softness are the features of an inhibitor to define its stability and reactivity. A hard molecule reveals large energy gap and a small gap prevailing in soft molecule. Soft inhibitors are highly reactive than hard molecule because of its electron donor nature to metal is high for prior. For the modest transfer of electrons, adsorption might occur at the fragment of the molecule where (σ) which is a local property, has the uppermost value.

4. Conclusions

1. Cetrizine performs as worthy inhibitor for corrosion inhibition of SS 314 alloy 2024 in acidic environment.
2. Tafel polarization investigation confirms that Cetrizine is a mixed kind of inhibitor.
3. The Cetrizine act as good inhibitor which is demonstrated from improved R_{ct} and diminished C_{dl} values.
5. The values of HOMO, LUMO, ΔE and μ resultant from quantum chemical studies validated the outcomes of chemical and electrochemical studies.

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Table 1. Inhibition efficiency, corrosion rate and surface coverage for the corrosion of SS 314 alloy in 2N H_2SO_4 with different measures of Cetrizine gained from Mass loss studies

Concentration (ppm)	Inhibition efficiency (IE %)	Surface coverage (ϴ)
Blank	–	–
50	62	0.62
150	69	0.69
250	76	0.76
350	88	0.88
450	96	0.96

Table 2. Electrochemical parameters of SS 314 alloy in 2N H_2SO_4 with different concentrations of Cetrizine from Tafel polarization studies.

Concentration of Inhibitor (ppm)	E_{corr} (mV)	Tafel slopes in mV in dec^{-1}		I_{corr} μA cm^{-1}	Inhibition efficiency (%)
		β_a	β_c		
Blank	−0.827	71	124	850	–
50	−0.809	78	108	327.4	61.8
150	−0.799	71	117	264.35	68.9
250	−0.791	75	123	204.0	76.0
350	−0.782	77	129	102.85	87.9
450	−0.751	72	123	37.4	95.6

Table 3.Electrochemical impedance parameters and its inhibition efficiency for the corrosion of SS 314 alloy in 2N H_2SO_4 with different dosages of Cetrizine.

Concentration of Inhibitor (ppm)	Charge Transfer resistance (R_{ct}) K.Ohm.cm^2	Double layer capacitance (C_{dl}) μF.cm^{-2}	Inhibition efficiency (%)
Blank	1.30	2.4	–
50	2.53	0.912	62
150	3.11	0.7488	68.8
250	4.28	0.5832	75.7
350	6.79	0.288	88.0
450	11.8	0.0984	95.9

Table 4: Quantum chemical data of Cetrizine

Compound	LUMO (eV)	HOMO (eV)	ΔE (Cal.Mol^{-1})	Dipole moment (Debye)	Hardness (η)	Softness (σ)
Cetrizine	3.1	0.2	2.9	4.5	5.5	0.1818