JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 5 submitted 16 January 2014

The influence of Sulfalene drug (SFL) on the Corrosion and hydrogen permeation through Stainless steel 304 in 5% NaCl-Part I

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Abstract

The influence of Sulfalene (SFL) on corrosion and hydrogen permeation through Stainless steel 304 in 5% NaCl has been studied using weight loss measurements and various electrochemical techniques. The inhibitor is found to be more effective in retarding the metal corrosion saline medium. Potentiodynamic polarization studies clearly indicate that SFL behaves as a mixed inhibitor. Hydrogen permeation studies and AC impedance measurements also proved an excellent performance of the compound in 5% NaCl. The adsorption of this compound on the mild steel surface obeys Temkin's adsorption isotherm which is further validated by Quantum chemical calculations.

Keywords: Corrosion inhibitor, Sulfalene, hydrogen permeation

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ISSN 1466-8858 Volume 17, Preprint 5 submitted 16 January 2014

1. Introduction

Antibiotics and allied drugs have been reported in recent years as corrosion inhibitors because of their less toxicity [1-3]. Organic compounds containing sulphur, nitrogen and oxygen atoms are capable of retarding metallic corrosion. While extensive investigations have been carried out on inhibitor properties of antifungal drugs , due attention has not yet been paid to a systematic study on Sulfalene as potential corrosion inhibitors for stainless steel alloys in high corrosive medium, i.e 5% NaCl. However, very few reports are available using Sulfalene as corrosion inhibitors for aluminium in HCl medium [4]. Most of the effective organic inhibitors have hetero atoms such as O, N, S containing multiple bonds in their molecules through which they can adsorb on the metal surface [5-9]. The corrosion inhibiting property of these compounds is attributed to their molecular structure. The lone pair of electrons on nitrogen of amino group attached with benzene ring of SFL , lone pair of electrons of oxygen atoms of sulphoxide group, nitrogen atom , delocalization of π electrons of benzene ring and imidazoline groups of the present drug establish the adsorption of the compound on SS 304 surface. All the above studies expose one common observation that Sulfalene can be regarded as excellent corrosion inhibitors. But studies on the influence of Sulfalene on hydrogen permeation through steel substrate during pickling are very scarce. It belongs to the class of imidazole and sulpho amido derivatives for topical use and utilized in the treatment of fungal infection. A good inhibitor should have the following two important requisites: (1) it should have very good inhibition efficiency and (2) it should bring down the hydrogen permeation

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current to a considerable extent. Some organic compounds offer very high values of inhibition efficiency, but they have a insignificant effect in plummeting the hydrogen permeation current and vice versa. Compounds which come under this class produce hydrogen embrittlement in a later stage by the combination of permeated atomic hydrogen. This delayed failure creates cracking, pitting, breakage, etc., on the metal surface.

2. Experimental

Stainless steel 304 specimens of compositions, C= 0.08% , Si = 0%, Ni = 8%, Cr = 18% and Fe remainder, and of size 4 x 1 x 0.020 cm were used for weight loss and hydrogen permeation studies. A mild steel cylindrical rod of the same composition as above and embedded in araldite resin with an exposed area of 0.283 cm^2 was used for potentio polarisation and AC impedance measurements.

The inhibitor was preliminarily screened by a weight loss method described earlier. [9] Both cathodic and anodic polarisation curves were recorded potentiodynamically (1 mA s^{-1}) using corrosion measurement system BAS Model: 100A computerized electrochemical analyzer (made in West Lafayette, Indiana) and PL-10 digital plotter (DMP-40 series, Houston Instruments Division). A platinum foil, $Hg/Hg_2Cl_2/KCl$ (satd) were used as auxiliary and reference electrodes, respectively. The hydrogen permeation study was carried out using an adaptation of the modified Devanathan and Stachurski's two compartment cell, as described earlier [4]. Double layer capacitance (Cdl) and charge transfer resistance values (R,) were obtained using AC impedance measurements as described in an earlier publication." The surfaces of

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 5 submitted 16 January 2014

corroded and corrosion inhibited mild steel specimens were examined by diffuse reflectance studies in the region 200- 700 nm using U-3400 spectrometer (UV-VIS-NIR Spectrometer, Hitachi, Japan).

3. RESULTS AND DISCUSSION

3.1 Weight loss and Gasometric measurements

Table 1 gives the values of inhibition efficiency for different concentrations of Sulfalene for the corrosion of SS 304 in 5% NaCl obtained from weight loss and gasometric measurements. It is found that the compound inhibits the corrosion of stainless steel in saline medium effectively. The structure of the compound is given in Figure 1.

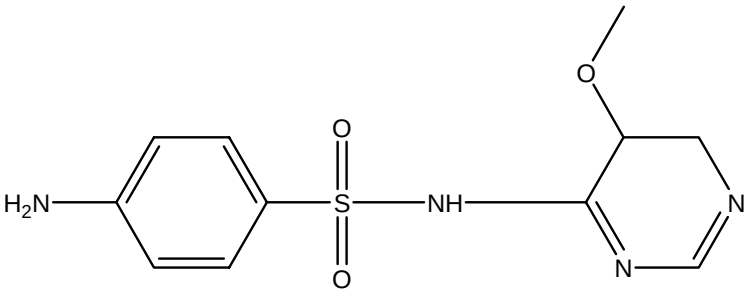

Figure 1. Structure of Sulfalene

The inhibition of corrosion of brought about by Sulfalene can be due to the following interactions:

1.The interaction between the lone pairs of electrons of the nitrogen atoms of the imidazole ring and the positively charged metal surface [10].

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ISSN 1466-8858 Volume 17, Preprint 5 submitted 16 January 2014

2.The interactions between delocalized electrons of the benzene groups and the positively charged metal surface [11].

It is found that there is very good conformity between the values of inhibition efficiency obtained by weight loss and gasometric methods.

3.2 Potentiodynamic polarization studies

Table 2 indicates values of corrosion kinetic parameters such as Tafel slopes (b_a and b_c), corrosion current (I_{corr}) , corrosion potential (E_{corr}) and inhibition efficiency obtained from potentiodynamic polarization plots for SS 304 in NaCl in the presence of different concentrations of inhibitor. It can be visualized from this table that values of Tafel slopes and I_{corr} are very much similar to those reported earlier [12-13]. Further it is confirmed that enhancing the concentrations of Sulfalene alters the values of both b_a and b_c in irregular fashion justifying that the inhibition of corrosion of SS 304 in saline medium is under mixed control. Values of E_{corr} is shifted to less negative values in the presence of different concentrations of SFL. This can be attributed to the formation of strongly adherent adsorbed film on the metal surface. The presence of increasing concentrations of Sulfalene retards I_{corr} values in 5% NaCl. It can also be seen that most of the values of inhibition efficiency obtained by weight loss measurements and potentiodynamic polarization studies agree very well.

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3.3 Hydrogen permeation measurements

Hydrogen permeation measurements results for the corrosion of SS 304 in the presence and absence of the inhibitor are presented in Table 3. Hydrogen permeation current for stainless steel in 5% NaCl is more, because of the aggressive nature of chloride ions. It can be seen from the table that the presence of Sulfalene in saline medium retards the entry of hydrogen gas and does not influence the ingress of hydrogen gas into SS 304. The reduction in permeation current can be ascribed to the effective adsorption of the compound on the mild steel surface [12-16]. It can be found from the table that the decrement of permeation current is more, if the concentration of Sulfalene is more.

3.4 Impedance studies

Values of charge transfer resistance (R_t)and double layer capacitance (C_{dl}) derived from Nyquist graphs are shown in table 4. It can be seen in table that the values of R_t has begun to increase with enhancement of SFL concentrations in 5% NaCl. Values of double layer capacitance are establishing that steel dissolution is high in 5% NaCl .It is found that values of C_{dl} are decreased by increasing concentrations of Sulfalene in electrolyte. This could be due to the increased adsorption of the SFL molecule on the surface of SS 304 as the concentration of inhibitor increases.

A plot of surface coverage (ø) versus log C gave a straight line illustrating that the adsorption of SFL on SS 304 surface from 5% NaCl follows Temkin's adsorption isotherm. This is major support to corrosion inhibition by this compound, as a result of its adsorption on the metal surface.

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3.5 Quantum chemical studies:

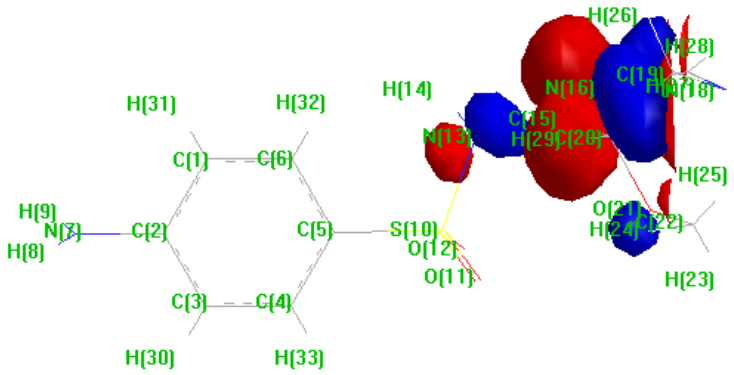

Figure 2. Highly Occupied MO's of inhibitors

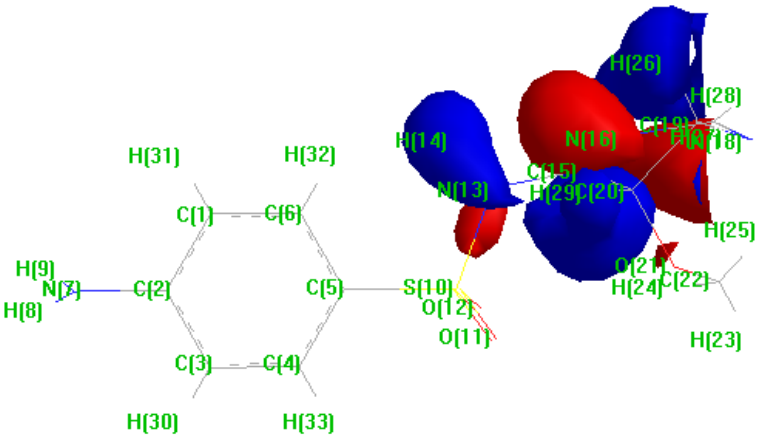

Figure 3. Lowest unoccupied MO's of inhibitors

The computed quantum chemical indices such as energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), LUMO- HOMO, energy gap (ΔE), dipole moment (μ), are summarized in Table 5. From figures 2 and 3, it can be observed that HOMO and LUMO energy orbital's

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were strongly distributed on benzene groups and and imidazole moiety for HOMO structure nitrogen and almost nil, on aniline moiety in the case of HOMO and LUMO establishing that the imidazoline and imino moieties contain good adsorption centres [17-20] and this is in agreement with publications of molecular orbital studies confronting that π electrons and N atoms are liable for inhibition activity[20].

According to karthikeyan et al. [21], when a molecule possess similar frontier orbitals, its inhibition effectiveness can be allied to the energy levels of HOMO and LUMO and the distinction between them. It has been widely investigated that, higher the value of E_{HOMO}, better will be the adsorption of an inhibitor by virtue of releasing electrons to vacant d orbital of metal atom and higher is the inhibition efficiency. Also, lower E_{LUMO} values, associated with the acceptance of electrons from metal atom to make feedback bonds. Hence the gap between HOMO-LUMO energy levels of molecules was calculated as a vital data. Smaller value of ΔE of an inhibitor, signify the effective inhibition efficiency of organic compound. It has been reported that, large values of dipole moment will considerably enhance the corrosion inhibition[22-24].

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4. Conclusions

1. **Sulfalene** inhibits the corrosion of SS 304 in 5% NaCl effectively.

2. The inhibition of corrosion of stainless steel in salt water, by the inhibitor is under mixed control.

3. The presence of inhibitor molecule in salt water is found to reduce the extent of entry of hydrogen through steel surface.

4. R_t and C_{dl} values studied from impedance measurements confirm the improved performance of the compound.

5. The adsorption of the inhibitor on SS 304 surface follows Temkin's adsorption isotherm which is further validated from quantum chemical calculations.

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Table 1. Values of inhibition efficiency for the corrosion of stainless steel 304 in 5% NaCl in the presence of different concentrations of Sulfalene obtained from weight loss and gasometric measurements.

Concentration of Inhibitor (mM)	5% NaCl (Inhibition efficiency)	
	Weight loss Studies	Gasometric measurements
20	47	46.8
40	60	60.2
60	72	71.9
80	24.2	24.1

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Table 2. Corrosion kinetic parameters of SS 304 in 2N HCl in the presence of different concentrations of Sulfalene obtained from potentiodynamic polarization studies.

Concentration of Inhibitor (mM)	E_{corr} (mV)	Tafel slopes in mV in dec^{-1}		I_{corr} A cm^{-2}	Inhibition efficiency (%)
		b_a	b_c		
Blank	-320	87	135	19.42	---
20	-295	68.2	126	10.26	47
40	-292	65.5	119.8	7.8	60.2
60	-280	67	124.5	6.7	72

Table 3. Values of permeation current for the corrosion of stainless steel in 5%NaCl in the presence of different concentrations of Sulfalene .

Concentration of Inhibitor (mM)	5% NaCl
Blank	20.5
20	18.3
40	10.5
60	7.2

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Table 4.Impedance parameters for the corrosion of Stainless steel 304 in NaCl in the presence of different concentrations of Sulfalene .

Concentration of Inhibitor (mM)	5% NaCl	
	Charge Transfer resistance (R_t) Ohm.cm^2	Double layer capacitance (C_{dl}) µF.cm^{-2}
Blank	3.4	5.9
20	5.4	2.68
40	6.28	3.2
60	7.63	4.1

Table 5: Quantum chemical parameters for Sulfalene

Compound	LUMO (eV)	HOMO (eV)	ΔE (Cal.Mol^{-1})	Dipole moment (Debye)
Sulfalene	-1.953	-8.343	6.39	5.1