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Improving Metal Stability in Acidic Environments Through Inhibitor Technology

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Abstract

In this study, a hybrid approach combining fuzzy logic intelligence with conventional corrosion inhibition techniques is proposed to enhance decision-making and performance analysis. The fuzzy logic system is developed to handle the uncertainty and imprecision inherent in corrosion-related parameters such as temperature, inhibitor concentration, and exposure time. By integrating fuzzy rule-based models with experimental data, the system effectively predicts the inhibition efficiency and identifies optimal inhibitor formulations. This intelligent approach offers improved accuracy, flexibility, and adaptability compared to purely mechanistic methods. The results demonstrate that UV,IR and weight loss methods can serve as a powerful tool for optimizing corrosion protection strategies and reducing dependency on exhaustive testing, corrosion management solutions.

Key words: Corrosion, Ethyl Propyl Sulphide , Inhibitor , Weight Loss, Absorption Spectra

1.Introduction

Corrosion is a pervasive issue affecting metals and alloys across a wide range of industries, including oil and gas, marine, chemical processing, and infrastructure. The degradation of materials due to corrosive environments leads to significant economic losses, safety hazards, and operational inefficiencies. To combat this, the use of corrosion inhibitors—chemical substances that reduce the rate of corrosion when added in small quantities—is a widely adopted and cost-effective method. However, the efficiency of these inhibitors is influenced by multiple interdependent factors such as pH, temperature, concentration, and the nature of the corrosive medium[1-4].

Traditional methods for evaluating corrosion inhibitors typically involve experimental testing and empirical modeling, which can be labor-intensive, time-consuming, and sometimes insufficient in capturing the complexity and non-linearity of the corrosion process. In recent years, intelligent systems and soft computing techniques have emerged as promising alternatives for improving prediction accuracy and decision-making in corrosion science[5].

Fuzzy logic, a subset of artificial intelligence, is particularly effective in dealing with uncertain, vague, or imprecise information—conditions often present in corrosion studies. Unlike binary logic, fuzzy logic allows variables to have degrees of truth, enabling more flexible and human-like reasoning. This makes it well-suited for modeling complex systems where exact mathematical relationships are difficult to establish [6-8]In this work, we propose a hybrid approach that integrates fuzzy logic intelligence with conventional corrosion inhibition techniques to enhance the evaluation and optimization of inhibitor performance. The hybrid model combines the strengths of experimental data with the adaptability of fuzzy inference systems, providing a robust framework for analyzing and predicting corrosion inhibition under varying environmental conditions. This approach aims to streamline inhibitor selection, reduce testing efforts, and support the development of more efficient and intelligent corrosion control strategies[9-11].

Materials and Methods

2. Materials

2.1. Preparation of the Copper Specimens

The copper specimens were chosen from the same sheet Copper specimens of the dimensions 1.0 × 4.0 × 0.25 cm were polished to mirror finish, degreased with trichloroethylene and used for weight-loss and surface examination studies.

Copper rod encapsulated in Teflon with an exposed cross section of 1 cm^2 area was used as the working electrode in potentiostatic polarisation studies. The surface of the electrode was polished to mirror finish and degreased with trichloroethylene.

2.2. Chemicals Used

The acid solutions (1M HCl) were prepared by dilution of an analytical grade HNO_3 with double distilled water. The other chemicals used for the study have been of GR grade. All tests were conducted at different temperatures in magnetically stirred solution.

2.3. Preparation of Stock Solutions

Double distilled water was used wherever necessary in the preparation of solutions. Analar grade HCl was taken as such and they were diluted to the required concentration.

The required concentration of the inhibitor stock solution was prepared by dissolving inhibitor in methanol. Then the required volume from the inhibitor stock solution was added in the case of blank, same volume of methanol without the inhibitors were used.

The sulphide sample used in the study were imported Fluka samples. The structure and molecular formulae and molecular weight are given in the table.

Structure and Molecular Formula and Molecular Weight of Organic Sulphide

Sl. No.	Name of Compound	Molecular formula	Structure	Molecular Weight
1.	Ethyl Propyl Sulphide(EPS)	$C_5H_{12}S$	CH_3 - CH_2 –CH_2- S – CH_2–CH_3	104.22

3. Methods

3.1. Weight Loss Measurement

Weight loss measurements were done according to the method EPScribed previously [9-10]. Weight loss measurements were performed at 303 ± 1 for 2h by immersing the copper specimens in 1M HCl acid solutions (100 mL) without and with various amounts of inhibitor (0.000001 – 0.01 M). After the elapsed time, the specimen was taken out, washed, dried, and weighed accurately. All the concentrations of an inhibit for weight loss and electrochemical study were taken in molar concentration (M).The surface coverage (θ) and inhibition efficiency (IE%) were determined by following equations

$$\theta = \frac{W_0 - W_1}{W_0} \qquad (4.1)$$

$$IE(\%) = \frac{W_0 - W_1}{W_0} \times 100 \qquad (4.2)$$

where W_1 and W_0 are the weight loss values in presence and absence of inhibitors respectively.

3.2. Weight Loss Measurement at Different Temperatures

The loss in weight was calculated at different temperatures from 303 K to 333 K. Each experiment was duplicated to get good reproducibility. Weight loss measurements were performed in 1M HCl with and without the addition of the inhibitor at their best inhibiting concentration (0.01M). Percentage inhibition of inhibitor at various temperature was calculated.

3.5. Fourier Transform Infrared (FT-IR) Spectroscopic Studies

Generally a comparison of the infrared spectrum of the ligand and that of its complex will be much helpful to find out the atom or atoms through which the ligand is attached to the metal ion. The percentage transmission is recorded against wave number. The copper specimens were immersed in various test solutions for period of 2h. After 2h the specimens were taken out and dried. The surface film was scratched carefully and its FT-IR spectrum was recorded using Perkin-Elmer model RXI instrument.

3.6. UV-Visible Absorption Spectra of Solutions

The electronic spectra are often very helpful in the evaluation of structural investigation. The UV-visible spectra of the complexes are recorded . Perkin-Elmer model Lambda spectrophotometer. Absorbance values are plotted against the wave length, methanol is employed as a solvent. The electronic spectral measurements can provide valuable information related to bonding and structure.

4. Results and Discussion

4.1. Weight Loss Studies

Weight loss studies for the aliphatic sulphide compound have been carried out in the concentration range 0.0000001 to 0.01M at 303 K ± 1 in $3MHNO_3$ medium and the results have been presented in Tables 4.1.1. The corrosion rate under uninhibited condition has also been given in the same tables.

In 1M HCl medium all the compounds show the performance of greater than 90 % in their best protecting concentration of 0.01M. The efficiencies at the lowest concentration of 0.000001M are greater than 35 % for all the compounds.

The compound EPS has shown a good performance of inhibition of about 94.42 % in its best protecting concentration in 1M HCl medium. The efficiency of more than 90% has been observed at the moderate concentration. *i.e.,*0.0001M concentration. The lowest concentration of the inhibitor has shown an efficiency of about 42.91 %.

Table 4.1.1. Values of corrosion rate, inhibition efficiency and surface coverage calculated from weight loss method for the corrosion of copper in 1M HCl **in the presence of different concentrations of EPS**

Sl.No.	**Concentration of Inhibitor** *(M)*	**Corrosion Rate** *(mpy)*	**Inhibition Efficiency** *(%)*	**Surface Coverage** *(θ)*
1	Blank	2.8899	---	---
2	0.000001	1.7201	42.91	0.4291
3	0.000005	1.5772	49.01	0.4901
4	0.00001	1.1120	57.96	0.5796
5	0.00005	0.9201	68.95	0.6895
6	0.0001	0.9290	78.09	0.7809
7	0.0005	0.7902	81.22	0.8122
8	0.001	0.4025	88.99	0.8899
9	0.005	0.3998	94.09	0.9409
10	0.01	0.1809	94.42	0.9442

5.1. The Effect of Temperature

The effect of temperature on corrosion inhibition is highly complex, because many changes may occur on the metal surface such as rapid etching, rupture, EPSorption of inhibitor and the decomposition and/or rearrangement of inhibitor .

The effect of temperature on the inhibition performance of the compounds at their best protecting concentration of 0.01M were studied and the results are presented in Table 5.1.1. for 1M HCl medium.

The compound EPS is able to maintain an inhibition of about 94.42 % at 313 K in 1M HCl medium. Thereafter, there is a slow decrease in the efficiency and this is observed up to 323 K. This shows an efficiency of 84.42% at 323 K. Thereafter the inhibition declines to 69.02 % at 333 K.

Table 5.1.1. Values of corrosion rate, inhibition efficiency and surface coverage for different temperatures in the presence of 0.01M concentration of EPS in 1M HCl

Sl.No.	**Temperature** *(K)*	**Corrosion Rate** *(mpy)*	**Inhibition Efficiency** *(%)*	**Surface Coverage** *(θ)*
1	303	0.1899	94.42	0.9502
2	308	0.2125	92.21	0.9221
3	313	0.2301	91.67	0.9167
4	318	0.2833	87.47	0.8747
5	323	0.3454	84.42	0.8442
6	328	0.4891	74.28	0.7428
7	333	1.2588	69.02	0.6902

5.2.1a. The Arrhenius Plots for the Effect of Temperature

The Arrhenius Plots for the temperature performance of the compounds in 1M HCl medium. The dependence of corrosion rate at temperature can be expressed by Arrhenius equation

$$\log(CR) = (-E_a / 2.30RT) + \log\lambda \qquad (5.2.1)$$

$$CR = (RT / Nh)\exp(-\Delta H_a^\circ / RT)\exp(\Delta S_a^\circ / R) \qquad (5.2.2)$$

where, E_a is the apparent activation energy, λ is the Arrhenius pre-exponential factor, CR is the corrosion rate, ΔH_a° is the enthalpy of activation, ΔS_a° is the entropy of activation, N is the Avogadro's number, R is the universal constant and T is the absolute temperature.

The apparent activation energies (E_a) at optimum concentration of sulphide compounds were determined by linear regression between log (Rate) and 1/T in acid medium. These are shown in Figures 5.2.1

It is observed that the sulphide barring EPS are found to give poor performance at higher temperature in 3MHNO_3 medium. This may be due to the partial oxidation of sulphid EPS in the oxidising acid at higher temperatures. In the case of EPS such oxidation may be hindered by the bulky groups.

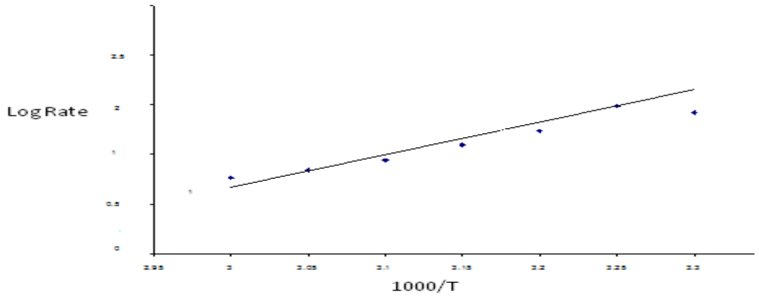

Figure 5.2.1. Arrhenius plot for copper in 1M HCl **in the presence of 0.01M concentration of EPS at different temperatures**

Table 5.2.2 **The Values of activation parameters E$_a$, ΔH°_{a} and ΔS°_{a} for copper in** 1M HCl **in the absence and presence of 0.01M concentration of aliphatic sulphide**

Sl.No.	**Concentration of Inhibitor *(M)***	**E$_a$ *(kJmol^{-1})***	**ΔH°_{a} *(kJmol^{-1})***	**ΔS°_{a} *(KJmol^{-1})***
1	Blank	70.95	70.59	– 251.88
2	EPS	74.01	72.20	– 40.69

The experimental data demonstrate that the decrease of inhibition efficiency value with increase of temperature and the higher value of E$_a$ in presence of inhibitor can be interpreted as an indication for a physical adsorption.

Inspection of these data revealed that activation parameters for dissolution of copper in acid in the presence of all inhibitors are higher than the activation parameters in the absence of inhibitors . The positive signs of ΔH_a°reflect the endothermic nature of the copper dissolution process and suggest that the dissolution of copper is slow in the presence of inhibitors. One can chance that E$_a$ and ΔH_a°values vary in the same way.From the values of the entropy of activation (ΔS_a°)in Table 5.2.2., it is clear that entropy of activation values obtained in the presence of inhibitors are less negative than the uninhibited acids.

5.3. Thermodynamic Parameters

$$\Delta G^{\circ}_{ads} = -2.303\, RT \log\left(55.5\, K_{ads}\right) \qquad (5.3.1)$$

$$K_{ads} = \theta / C_{inh}\,(1 - \theta) \qquad (5.3.2)$$

The above equations were used to calculate the thermodynamic parameters for the adsorption process .

Where θ is the degree of coverage on the metal surface, C_{inh} is the concentration of inhibitor in mol $dm^{-3}$and K_{ads} is the equilibrium constant for adsorption/EPSorption process.

It is known that K_{ads} represents the strength between adsorbate and adsorbent. Large values of K_{ads} imply more efficient adsorption and hence better inhibition efficiency .

The enthalpy of adsorption (ΔH°_{ads})and entropy of adsorption (ΔS°_{ads})were obtained from the Figures 5.3.1.and using the equation

$$\log K = 1/2.303\left(-\Delta H^{\circ}_{ads}/RT + \Delta S^{\circ}_{ads}/R\right) \qquad (5.3.3)$$

The calculated values of K_{ads}, ΔG°_{ads}, ΔH°_{ads} and ΔS°_{ads} over the temperature range 303-333 K are recorded in the Tables 5.3.1. for 1M HCl.

The negative values of ΔG°_{ads} indicate the spontaneous adsorption of sulphide compound on the surface of copper. It is usually accepted that the value of ΔG°_{ads} around –15 kJ mol^{-1}-45 kJ mol^{-1} in the values charge sharing or charge transfer between the metal surface and organic molecules .

In this present study the calculated values of ΔG°_{ads} are greater than –15 KJ mol^{-1} but less than –45 kJ mol^{-1}indicating that the adsorption of sulphide compounds in 1M HCl solutions at studied temperatures may be a combination of both physisorption and chemisorption. However, physisorption is the more contributor while chemisorption is less contributor to the adsorption mechanism.

The negative sign of ΔH°_{ads} indicates that the adsorption of organic sulphide compound is an exothermic process, distinguished between the physisorption and chemisorption by considering the absolute value of ΔH°_{ads}. For physisorption process, the enthalpy of adsorption is lower than 40 kJ mol^{-1}, while that for chemisorption approaches 100 kJ mol^{-1}. In the present study, ΔH°_{ads} values are larger than the common physical adsorption heat, but smaller than the common chemical adsorption heat once again emphasising that both physical and chemical adsorption are involved .

The values of entropy of adsorption are also negative and large because inhibitor molecules freely move in the bulk solution, adsorb in an orderly fashion on the copper metal, resulting the decrease in entropy. More over from thermodynamic principles, since the adsorption is an exothermic process, it must be accompanied by a decrease in entropy

Table 5.3.1 Thermodynamic parameters for adsorption of 0.01M concentration of EPS in 1M HCl **on copper at different temperatures**

Sl.No.	Temperature (K)	K_{ads} (M^{-1})	ΔG°_{ads} (kJ mol^{-1})	ΔH°_{ads} (kJ mol^{-1})	ΔS°_{ads} (J $mol^{-1}K^{-1}$)
1	303	3301.12	–34.51	–59.71 (From graph)	–118.10 (From graph)
2	308	2901.05	–35.72		
3	313	2012.32	–34.79		
4	318	1990.28	–34.80		
5	323	1823.60	–34.32		
6	328	910.17	–34.26		
7	333	574.26	–34.10		

5.3.1a. Fuzzy logic systems

Fuzzy logic systems can analyse this data in a more qualitative and flexible way, which is especially useful when: Relationships are not linear

- Multiple variables interact (temperature, adsorption constant, energy changes)
- Captures nonlinear relationships
- Allows for qualitative assessment where quantitative boundaries are blurry
- Useful for predicting optimal temperature for maximum inhibitior

Table 5.3.1a Thermodynamic parameters for adsorption of 0.01M concentration of EPS in 1M HCl **on copper at different temperatures**

Inhibitor Conc.	Corrosion Rate	Efficiency	Surface Coverage
Low	High	Poor	Low
Medium	Medium	Moderate	Medium
High	Low	Excellent	High
Low	Medium	Moderate	Medium
Medium	Low	Good	Medium–High

5.4. Analysis of FT-IR Spectra

FT-IR Spectra were recorded to understand the interaction of inhibitor molecules with the metal surface. Figures 5.4.1 and Figures 5.4.1a -represent the spectra of the scraped samples obtained from the metal surfaces after corrosion experiments in 1M HCl.

In pure EPS ,the IR bands observed at 644.5cm^{-1}and2965 cm^{-1} have been assigned to CH_2-S and –S– of organic sulphide compounds .In the scraped sample obtained from the copper surface after corrosion experiments in 1M HCl ,the IR bands appeared at 608.09cm^{-1} have been assigned to C–S–C of organic sulphide compounds. All the bands were displayed substantial shifts with fairly low intensity indicating coordination through the sulphur of organic sulphide compounds. Some new bands were found which may be due to Cu-S bonds

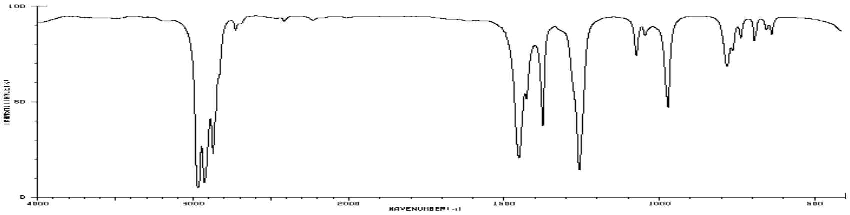

Figure 5.4.1. FT-IR Spectrum of EPS

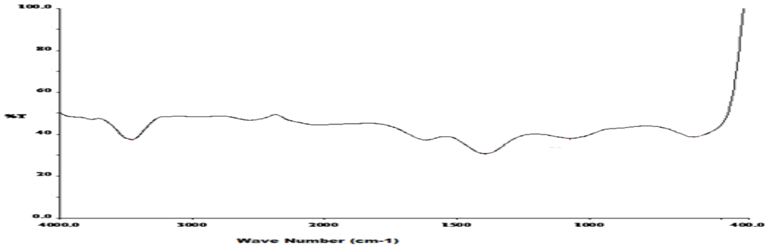

Figure 5.4.1a. FT-IR Spectrum of scraped samples of EPS obtained from the copper surface after corrosion experiment in 1M HCl **at different temperatures**

5.5. Analysis of UV-Visible Spectra

In order to confirm the possibility of the formation of organic sulphide compound copper complex, UV-visible absorption spectra of the pure inhibitor and the scraped sample obtained from the copper surface after immersion in 1M HCl solution containing 0.01M inhibitors for 2h are shown in Figures 5.5.1. for pure samples and 5.5.1a. for the scraped samples in 1M HCl. All the five inhibitors are recorded in methanol medium.

Figure 5.5.1a show the UV-Visible spectrum of pure EPS .Intense absorption peak at 224.13 nm is attributed to n $\rightarrow$Л* transition. This transition indicate the presence of hetero atom in the inhibitor.

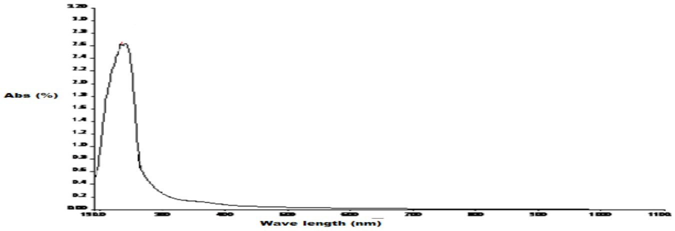

Figure 5.5.1. **UV-Visible Spectrum of EPS**

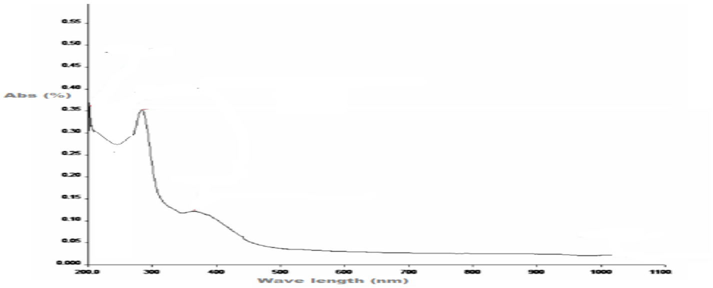

Figure 5.5.1a. **UV-Visible spectrum of scraped samples of EPS obtained from the copper surface after corrosion experiment in** 1M HCl

5.6 Conclusion

The present studies lead to the following conclusion.

- Inhibition efficiency of all the compounds decreases with increase in the temperature.Activation energy Ea value is higher for the inhibited acids than uninhibited acids showing the temperature dependence of Inhibition efficiency. The increase in the apparent activation energy may be interpreted as physical adsorption that occurs in the first stage.The negative values of ΔG°_{ads} indicate the spontaneous and strong adsorption of sulphide compounds on the copper metal surface in acid medium.
- In the present investigation, the calculated values of ΔG°_{ads} are greater than -15 kJ mol^{-1} but less than the -45 KJ mol^{-1}. These values indicate that the adsorption mechanism of all the inhibitors in 1M HCl solution at the studied temperatures may be a combination of both physisorption and chemisorptions.
- In the present investigation ΔH°_{ads} values are larger than the common physical adsorption heat but smaller than the common chemical adsorption heat . This emphasizing that both physical and chemical adsorptions are involved .
- fuzzy systems can interpret certain, linear trends.The results indicate good agreement between the values of corrosion inhibition efficiency from weight loss the adsorption of all the ten sulphide compounds in the acid medium via the bond formation in between copper metal and the inhibitors is confirmed by FT-IR and UV-Visible spectroscopic techniques.

5.7 . References

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