ELECTROCHEMICAL AND ADSORPTION STUDIES OF P-TOLYL SULFOXIDE INHIBITOR ON GAS PIPELINE METAL IN NATURAL SEAWATER ENVIRONMENT

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Abstract

Pipelines, the irreplaceable core of energy transmission, are playing a leading role. Energy pipelines, particularly transmission pipelines, are often built of metal and are prone to corrosion by nature. The stifling of energy pipelines is a prominent concern. Corrosion inhibitors are extremely useful, as they are often used to reduce the dissolving behavior of energy pipelines. Because of the simplicity of the process, synthetic chemicals are utilized in corrosion inhibition. In this paper, investigations through potentiodynamic polarization, and electrochemical impedance spectroscopy were used to test new corrosion inhibitors such as P-Tolyl sulfoxide compounds for corrosion on gas pipelines in sea water (EIS).The results indicate that these inhibitors show an protection performance and achieve the corrosion inhibition efficiency values of 82.68%, 79.04% for polarization studies, electrochemical impedance spectroscopy respectively. The surface analysis of gas pipeline was investigated using and energy dispersive X-ray (EDX) methods.

Keywords: P-Tolyl sulfoxide, Gas pipeline, Sea water and Electrochemical studies, EDX.

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1. Introduction

Corrosion is a degradation of material or its properties by chemical reaction with the environment. In oil and gas industries, the corrosion issue has always been of great importance, with consequences. Similar result to those of natural disaster. Since the pipelines play the role of transporting oil and gas from the wellheads to the processing facilities, they are exposed to the continuous threat of corrosion, from the date of commissioning up to decommissioning or abandonment. From the various exposure Pipelines by both coating (1,2,3) and cathodic protection (4,5) and application of first-rate corrosion-resistant alloys (6) that can be implemented to fight against corrosion, yet film-forming inhibitors are still known to be the unrivalled method of defense for mild steel in an acidic environment (7,8). Recently the rise of the "green" chemistry concept in the fields of science, technology and engineering (10, 11) is restraining the application of commercial corrosion inhibitors by implementing certain theories or ideas to minimize the contamination (12) and eco-friendly chemicals (13-15). The application of chemical substances as corrosion inhibitors has received several research attentions (16-17). Most commonly used corrosion inhibitors in oil and gas production and transmission environments are imidazolines, amides, amines, phosphate esters, carboxylic acids and their derivatives, and sulfur-containing organic molecules. Since many of the compounds have to be tested as corrosion inhibitor. In this chapter one of the synthetic inhibitor P-Tolyl sulfoxide tested as a corrosion inhibitor on Gas pipeline metal in natural seawater medium.

2. Materials and methods

2.1 Specimen preparation

Gas Pipeline specimen were mechanically pressed cut to form different coupons, each of dimension exactly 20cm^2 (5x2x2cm), polished with emery wheel of 80 and 120, and degreased with trichloroethylene, then washed with distilled water cleaned, dried and then stored in desiccators for the use of our present investigations.

2.2 Preparation of stock solution/ Inhibitor

1gm of specific synthetic inhibitor is weighed into a digital chemical balance and its dissolved into a specific solvent Dimethyl Sulfoxide (DMSO) then it's made up to a 100ml (SMF) using natural sea water. From this solution in a different concentration from 0 to 1000 ppm using natural seawater and used throughout the experiments.

2.3 Preparation of specimen for electrochemical studies

Electrochemical measurements were conducted by conventional three–electrode system including of Gas Pipeline as working electrode with an exposed area 1cm^2, a platinum electrode as counter electrode and saturated calomel electrode (SCE) as reference electrode. Before testing, the working electrode was immersed in test solution at Open Circuit Potential for 30 min to attain a steady state potential and the potential sweep rate for potentiodynamic polarization (Tafel) curves was 10mVs^{-1}. Corrosion current density (I_{corr}) determined from the intercept of extrapolation of anodic and cathodic Tafel slopes at the corrosion potential (E_{Corr}). The inhibition efficiency (%) was calculated using I_{corr} values both in the presence and absence of inhibitor.

$$IE\% = \frac{I_{Corr}(blank) - I_{Corr}(inh)}{I_{Corr}(blank)}$$

Where I_{corr} (blank) and I_{corr} (inh) are the corrosion current density values of Gas pipeline in the absence and presence of inhibitors.

Electrochemical Impedance Spectroscopy was performed in range of frequency 1Hz to 100KHz with the AC signal of amplitude 5mV using CH660E electrochemical analyzer . The charge transfer resistance obtained from the diameter of the semicircle of the Nyquist plot. The inhibition efficiency (IE%) derived from EIS was calculated using the following equation

$$IE\% = \frac{R_{Ct}(inh) - R_{Ct}(blank)}{R_{Ct}(inh)}$$

Where, R_{ct} (Inh) = charge transfer resistance with inhibitor.

R_{ct} (blank) = charge transfer resistance without inhibitor.

2.4 Adsorption Studies

(a) Langmiur Isotherm:

The Langmuir adsorption isotherm can be expressed by the following Equation is given below.

$$\log C/q = \log C - \log K$$

Where q is the degree of surface coverage, C is the concentration of the inhibitor solution and K is the equilibrium constant of adsorption of inhibitor on the metal surface.

(b) Temkin Isotherm:

Temkin adsorption isotherm, the degree of surface coverage (θ) is related to the inhibitor concentration (c) according to equation

$$\text{Exp}(-2a\,\theta) = KC$$

Rearranging and taking logarithm of both sides of equation the above equation

$$\Theta = (-2.303\log k/2a) - (2.303\log C/2a)$$

(c) Florry-Huggins Isotherm:

Florry- Huggins adsorption isotherm can be expressed according to equation

$$\text{Log}(\theta/C) = \log K + x\log(1-\theta)$$

(d) Frumkin Isotherm

Frumkin adsorption isotherm is given by equation

$$\log\{[C]^*(\theta/1-\theta)\} = 2.303\log K + 2\alpha\theta$$

where k is the adsorption –desorption constant and α is the lateral interaction term describing the interaction in adsorbed layer plots of log { [C]* (θ/1- θ)} versus θ as presented were linear which shows that the applicability of Frumkin isotherm.

(e) Freundlich Isotherm:

The Freundlich adsorption isotherm can be also be applied using equation

$$\Theta = Kc^n$$

Freundlich model equation(6) can be rearranged as,

$$\text{Log}\,\theta = \log K + n\log C$$

This will be drawn through log θ vs log C from the intercept of the values k may be received determined the values of the slopes and intercepts had been taken from the directly line equations.

(f) El-Awady Isotherm:

The El-Awady adsorption isotherm is given by

$$\text{Log}(\theta/1-\theta) = \log K + y\log C$$

kads=k1/y and y represents occupying a given active site value of1/y much less than cohesion implies the formation of multilayer of the inhibitor at the metal floor, while the value of 1/y extra than unity way that a given inhibitor occupy more that one active site.

2.5 Free Energy of Adsorption

The Equilibrium constant of adsorption of dimethyl sulfoxide solution of (PTS) inhibitor on the surface of Gas Pipeline metal is related to the free energy of adsorption (ΔG) according to equation

$$\Delta G= -2.303RT \log (55.5K)$$

Where R is the gas constant, T is the temperature, K is the equilibrium constant of adsorption**.**

2.6 Activation Parameters on the Inhibition Process:

Usually, the temperature plays an important role to understanding the inhibitive mechanism of the corrosion process. To assess the temperature effect, experiments were performed at the range of temperature 303K- 333K in uninhibited and inhibited solutions containing different concentrations of TAA and the corrosion rate was evaluated and the values are presented in Table-1.3. The relationship b/w the corrosion rate (CR) of Gas Pipeline metal in natural seawater medium and temperature (T) is expressed by the Arrhenius equation

$$\text{Log } CR = -Ea/2.303RT + \log \lambda$$

Experimentally the values of corrosion rate evaluated from the weight loss data for Gas Pipeline metal in Natural Seawater in the presence and absence of PTS inhibitor was used to determine the activation of enthalpy (ΔH) and apparent entropy (ΔS) for the formation of the complex in the transition state equation. An alternative formula for the Arrhenius equation is the transition state

$$CR = RT/Nh \exp(\Delta S/R) \exp(-\Delta H/RT)$$

2.7 Corrosion products analysis

After the exposure tests, the surfaces of the exposed specimens were cleaned by an air blast to remove seawater content. The microstructure morphologies of the exposed surface of the samples were characterized by the Quanta 250 SEM–EDS system, and the corrosion products were analyzed by energy dispersive X-ray spectroscopy (EDS). Spot analysis was performed to understand the composition of different features on the surface. The morphology of corrosion surface was also obtained after the corrosion products were removed.

3. Non- Electrochemical Methods

3.1.1 Effect of Temperature.

Dissolution behavior of gas pipeline in natural seawater containing different Concentration of PTS inhibitor solution at temperature range from 303 to 333K and the observed values are listed in Table-1.1. Observed results reveals that the corrosion rate decreased with increase of inhibitor concentrations and also increased with rise in temperature from 303 to 333K. The maximum of 75.56% inhibition efficiency is achieved at 333K. However the effect of inhibition efficiency is increased with rise in temperature may suggests and support the facts that the process of adsorption follows chemisorption. The observed result suggests that the inhibitor may function through adsorption on the Gas pipeline metal surface by blocking the active sites to form a screen onto the metal surface from seawater. The percentage of inhibition efficiency increased with increase of inhibitor concentration and temperature.

Table-1.1 The corrosion parameters of gas pipeline in Natural seawater containing various conc. of P-Tolyl sulfoxide inhibitor at different temp after one hour exposure time.

Conc. (ppm)	**Weight loss (mg)**			**Corrosion rate (mmpy)**			**Inhibition efficiency (%)**		
	303K	**313K**	**333K**	**303K**	**313K**	**333K**	**303K**	**313K**	**333K**
0	595	699	798	167.03	196.22	224.01	----	----	----
10	502	562	625	140.92	157.55	175.45	15.63	19.60	21.67
50	393	455	504	110.32	127.72	141.48	33.94	34.90	36.82
100	322	398	455	90.39	111.72	127.72	45.88	43.06	42.98
500	262	320	394	73.54	89.83	110.60	55.96	54.21	50.62
1000	203	220	195	56.98	61.75	54.74	65.88	68.53	75.56

3.1.2. Adsorption Studies.

Process of adsorption is very important surface phenomenon to determine the corrosion rate of reaction mechanism. The maximumregularly use of isotherms are viz: Langmuir, Temkin, Frumkin, Flory- Huggins, Freund lich, Bockris-Swinkles, Hill-de Boer, Parson's and the El-Awady, thermodynamic-kinetic model.

(a) Langmiur isotherm:

Langmuir adsorption isotherm is expressed according to the below equation

$$\text{Log } C/\theta = \log C - \log K$$

Plotting log (C/θ) against log C gave a linear relationship as shown in fig.1. (a), and the adsorption parameters are presented in Table-3. The average regression value (R^2= 0.9956) is very close to unity shows that the adsorption of Solution of P-Tolyl sulfoxide inhibitor on surface of gas pipeline metal indicated that there is very much interaction between the adsorbate and adsorbent.

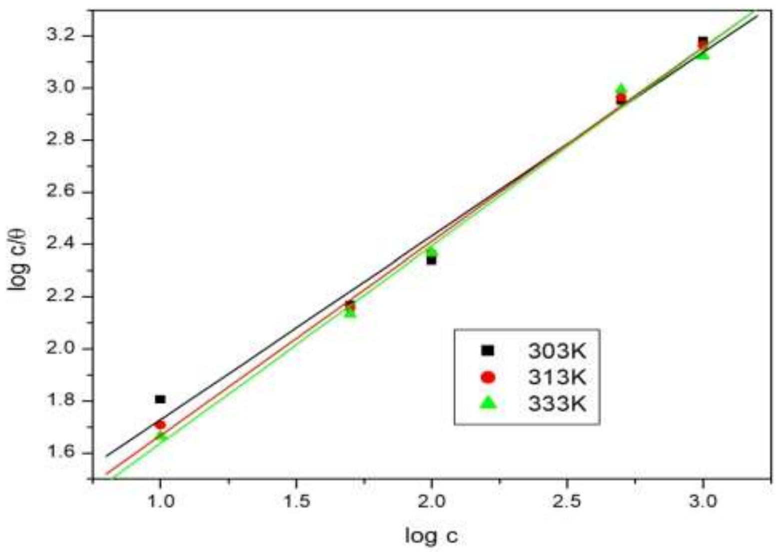


Fig- 1. (a). Langmuir isotherm for adsorption of dimethylsulfoxideSolution of (PTS) inhibitor on gas pipeline metal.

(b). Temkin Isotherm:

Temkin adsorption isotherm, the degree of surface coverage(θ) is related to the inhibitor concentration (c) according to equation

$$\text{Exp } (-2a\, \theta) = KC$$

Rearranging and taking logarithm of both sides of the above equation gives equation

$$\Theta = (-2.303\log k/2a) - (2.303\log C/2a)$$

Plots of θ against log c are presented in fig-1.1(b) gave linear relationship, which shows that the adsorption values fitted with Temkin Adsorption Isotherm. Adsorption parameters obtained from Temkin adsorption isotherm are recorded in Table-1.3. The average regression co-efficient value (R^2 = 0.9758) is also far away from the unity. Howevervalues of attractive parameter (a) are positive in all cases, indicating that there is no repulsion exists within in the adsorption layer.

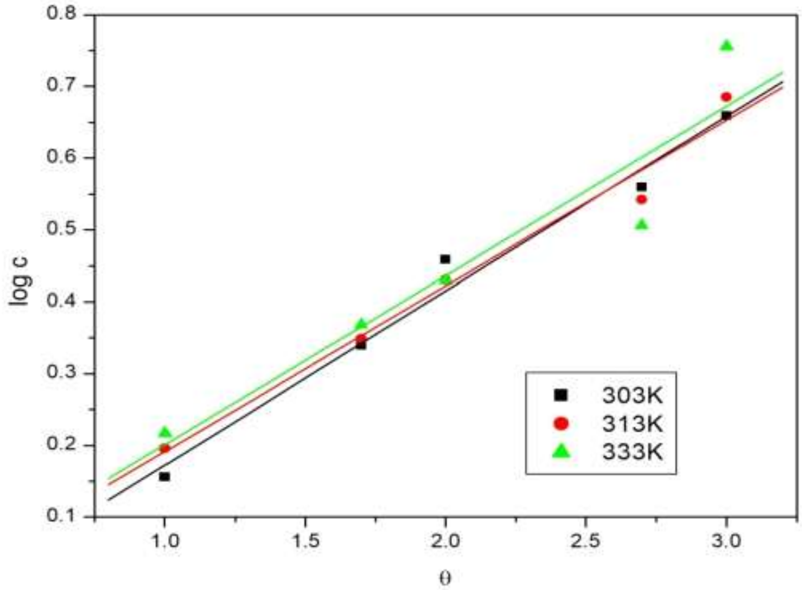


Fig-1.1(b). Temkin isotherm for adsorption of dimethylSulfoxide solutionof (PTS) inhibitor on gas pipeline metal.

(c). Florry-Huggins Isotherm:

Florry- Huggins adsorption isotherm can be expressed according to the below equation

$$\text{Log}\,(\theta/C) = \log K + x\log(1-\theta)$$

The plots of log θ/c against log (1- θ) are shown in fig 1.1(c), and this data conformed to Florry- huggins adsorption isotherm with average regression co-efficient (R^2) value is (0.9367). It is far away from the unity. The values of the size parameter x are positive as shown in Table -1.3. This indicates that the adsorbed species ofdimethyl sulfoxidesolution of P-Tolyl sulfoxide inhibitor is bulky. Since these two hetero atoms are strongly binding on the gas pipeline metal surface.

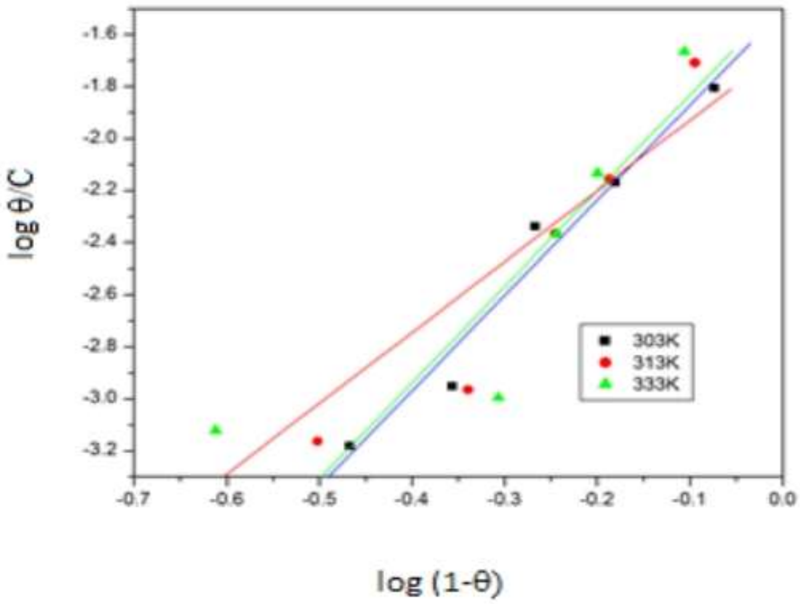


Fig-1.1(c) Florry-Huggins isotherm for adsorption of dimethyl Sulfoxidesolution ofP-tolyl sulfoxide inhibitors on gas pipeline metal

(d). Frumkin Isotherm:

Frumkin adsorption isotherm is given by the equation

log {[C]* (θ/1- θ)} = 2.303 log K +2αθ

where k is the adsorption –desorption constant and α is the lateral interaction term describing the interaction in adsorbed layer plots of log {[C]* (θ/1- θ)} versus θ as presented were linear which shows that the applicability of Frumkin isotherm. The Frumkin adsorption isotherm values were reported in Table-1.3. The average regression co-efficient value (R^2=0.9995) is very close to unity. Also shows that values of the adsorption parameters 'α' are positive suggest that the attractive behavior of the inhibitor on the surface of Gas Pipeline metal.

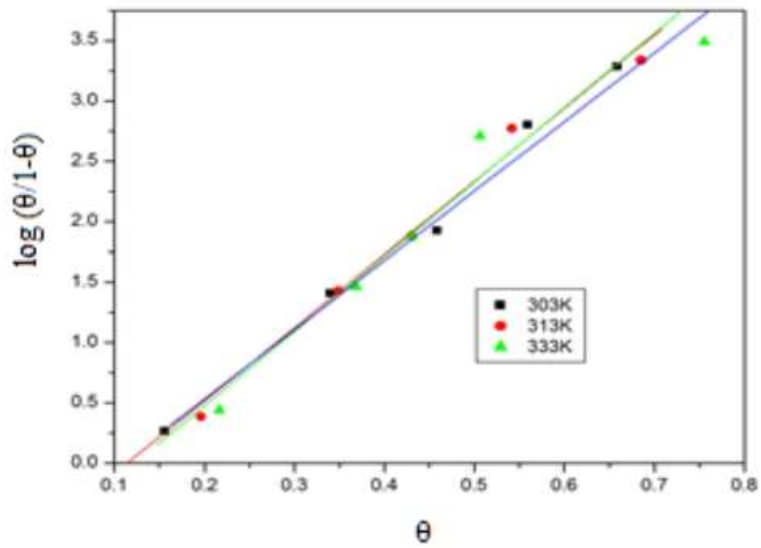


Fig-1.1(d) Frumkin isotherm for adsorption of dimethyl sulfoxidesolution of (PTS) inhibitor on gas pipeline metal

(e). Freundlich Isotherm:

The Freundlich adsorption isotherm can be also be applied using equation

$$\Theta = Kc^n$$

Freundlich model equation(8) can be rearranged as

$$\text{Log } \theta = \log K + n\log C$$

This can be plotted as log θ vs. log C from the intercept values of K can be obtained. Note that the values of the slopes and intercepts were taken from the straight line equations. The higher values of K indicates that the inhibitor is strongly adsorbed on the metal surface. The magnitude of the exponent 'n' gives an indication on the favorability of adsorption. It is generally stated that values of 'n' in the range 2-10 represent good, 1-2 moderately difficult and less than 1 poor adsorption characteristics. Thus P-Tolyl Sulfoxide inhibitor adsorbed on the metal surface by physical process.

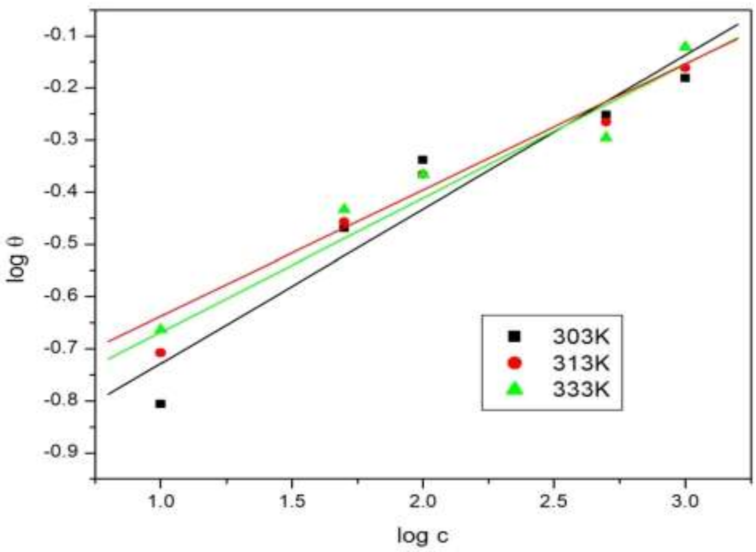


Fig -1.1(e) Freundlich isotherm for adsorption of dimethylSulfoxide solution of (PTS) inhibitor on gas pipeline metal.

(f). El-Awady Isotherm:

The El-Awady adsorption isotherm is given by the equation

$$\text{Log } (\theta/1\text{-}\theta) = \log K + y\log C$$

$k_{ads} = k^{1/y}$ and y represents occupying a given active site. Value of 1/y less than unity implies that the formation of multilayer of the inhibitor on the metal surface, while the value of 1/y greater than unity means that a given inhibitor occupy more than one active site. Curve fitting of the data to the thermodynamic/kinetic model is shown in fig –1.1(f). Plot gives straight lines which show that the experimental data fits the isotherm. The values of k_{ads} and 1/y calculated from the El-Awady et.al isotherm model is listed in Table-1.3.

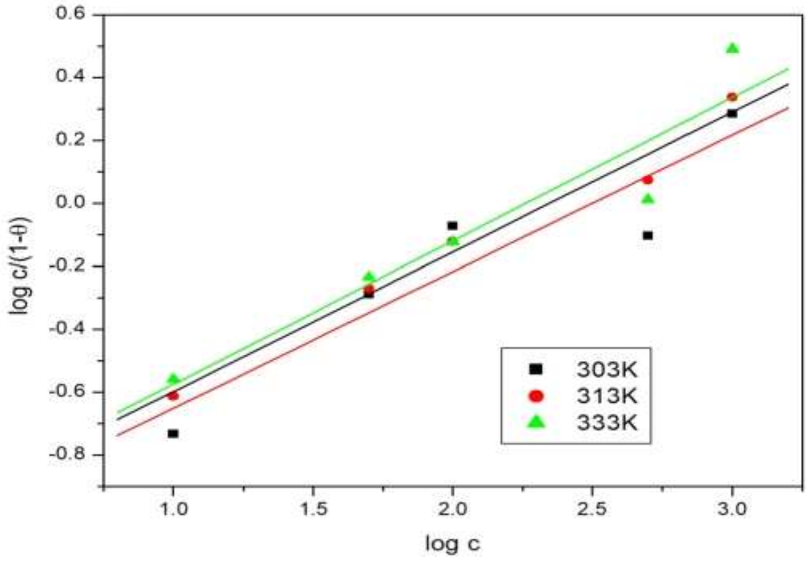


Fig-1.1(f). El-Awady isotherm for adsorption of dimethyl Sulfoxide solution of (PTS) inhibitor on gas Pipeline metal.

(g). Free Energy of Adsorption.

The Equilibrium constant of adsorption of dimethyl sulfoxide solution of (PTS) on the surface of gas Pipeline metal is related to the free energy of adsorption (ΔG) according to equation

$$\Delta G = -2.303RT \log (55.5K)$$

The free energy of adsorption was calculated from values of k obtained from Langmuir, Temkin, Florry –Huggins, Frumkin, Freundlich and El-Awady according to the equation and is recorded in Table-1.3. The results shows that the free energy of adsorption (ΔG) values are negative and less than the threshold value of -40kJ/mol required for chemical adsorption, indicating that the adsorption of dimethyl sulfoxide solution of PTS on gas Pipeline metal surface is spontaneous and the mechanism of physical process. Since phenomenon is attributed to electrostatic interactions between the charged metal and the inhibitor molecules.

Table-1.2. Adsorption parameters for adsorption of dimethyl sulfoxideSolution of P-tolyl sulfoxide inhibitor on gas Pipeline metal.

Isotherm	Temperature	R^2	K	ΔG_{ads} kJ/mol	Slope Values
Langmuir	303K 313K 333K	0.9920 0.9979 0.9971	10.566 1.237 7.575	-16.059 -11.007 -16.725	------
Temkin	303K 313K 333K	0.9907 0.9896 0.9470	0.8504 0.9135 0.9224	-9.710 -10.218 -10.896	a 0.0809 0.0451 0.0403

Florry- Huggins	303K 313K 333K	0.9832 0.9653 0.8615	0.0311 0.0344 0.0219	-1.382 -1.687 -0.545	x 3.6582 3.6904 2.7167
Frumkin	303K 313K 333K	0.9965 0.9945 0.9753	0.2045 0.1755 0.2444	-6.120 -5.924 -7.219	α 3.023 0.082 2.864
Freundlich	303K 313K 333K	0.9572 0.9828 0.9725	0.0946 0.1191 0.1320	-4.178 -4.916 -5.513	n 0.2954 0.2557 0.2418
El-Awady	303K 313K 333k	0.9323 0.9894 0.9474	0.0823 0.0907 0.0932	-3.829 -4.208 4.551	1/y 2.305 2.252 2.195

3.1.3. Thermodynamic/Activation Parameters on the Inhibition Process.

Usually, the temperature plays an important role to understanding the inhibitive mechanism of the corrosion process. To assess the temperature effect, experiments were performed at the range of temperature 303K- 333K in uninhibited and inhibited solutions containing different concentrations of PTS inhibitor and the corrosion rate was evaluated and the values are presented in Table-1.3. The relationship b/w the corrosion rate (CR) of gas Pipeline metal in natural seawater media and temperature (T) is expressed by the Arrhenius equation

$\text{Log CR} = -E_a/2.303RT + \log \lambda$

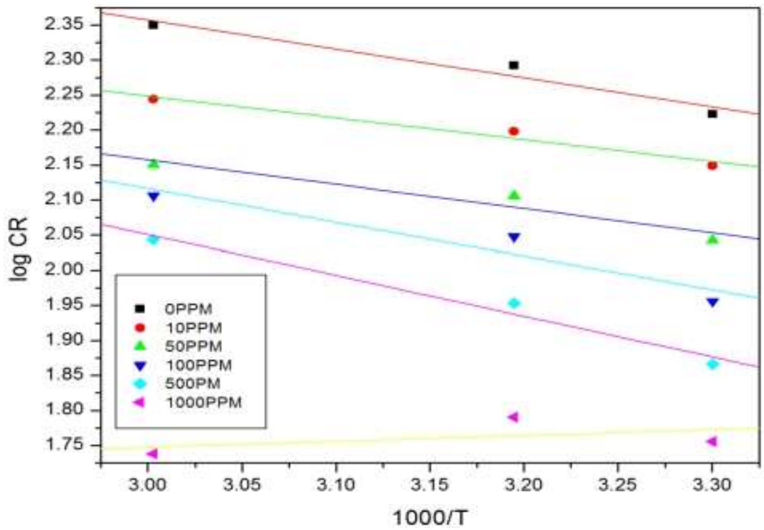


Fig-1.2(g). Arrhenius plot for Gas pipeline metal corrosion natural Seawater in the presence and absence of different conc.of PTS inhibitor.

A plot of log (CR) obtained by weight loss measurement versus 1/T gave straight line with average regression co-efficient (R^2) value close to unity as shown fig-1.2. The values of apparent activation energy (Ea) obtained from the slope (-Ea/2.303R) of the lines and the pre-exponential factor (λ) obtained from the intercept (log λ) are given in Table -1.3. It is evident from the Table-1.3 that the apparent energy of activation decreased on addition of PTS in comparison to the uninhibited solution. These values ranged from 1.6198 to 11.1210 kJ/mol and are lower than the threshold value of 80kJ/mol required for chemical adsorption. This shows that the adsorption of dimethyl sulfoxide solution of PTS solution on Gas pipeline metal surface is Physical adsorption. Decrease in the activation energy is attributed to appreciable increase in the adsorption of inhibitor on Gas pipeline metal surface by increase in the temperature. The increase in adsorption leads to decrease in corrosion rate due to the lesser exposed surface area of the Gas pipeline metal in natural seawater.

Table-1.3 Activation parameters of PTS in Natural seawater.

Inhibitor conc. (ppm)	**E_a kJ/mol**	**λ mg/cm**	**ΔH (kJ/mol)**	**ΔS (J/mol/k)**
Blank	1.6198	3.950	-2.286	85.973
10	5.9467	1.514	-1.432	82.510
50	6.6478	1.581	-1.732	82.668
100	7.9096	3.610	-2.847	85.656
500	1.6198	6.214	-3.679	87.610
1000	11.1210	31.167	-1.854	68.481

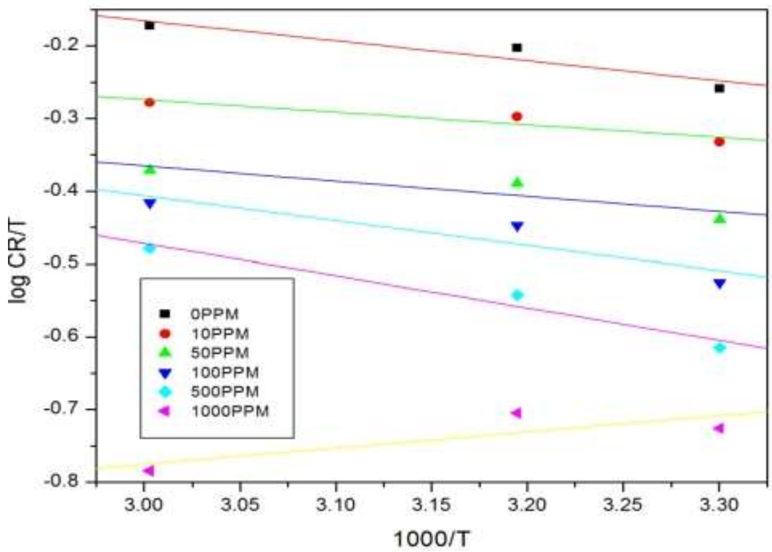


Fig-1.3(h) Transition state plot for Gas pipeline metal corrosion in Natural Seawater in the presence and absence of different conc. of PTS inhibitor.

The value of λ is also lower for inhibited solution than for the uninhibited soln. It is clear from equation (1) that corrosion rate is influenced by both Ea and λ. Moreover increase in concentration of (PTS) inhibitor in leads to an decrease in the value of Ea, indicating that the weak adsorption of the inhibitor molecules on the metal surface.

Experimentally the values of corrosion rate evaluated from the weight loss data for Gas pipeline metal in natural seawater in the presence and absence of PTS inhibitor was used to determine the activation of enthalpy (ΔH) and apparent entropy (ΔS) for the formation of the complex in the transition state equation (2). An alternative formula for the Arrhenius equation is the transition state

$CR = RT/Nh \exp(\Delta S/R) \exp(-\Delta H/RT)$ --------------(2)

A plot of log (CR/T) versus 1/T is shown is fig -1.2(h), a straight lines were obtained with slope (-ΔH/2.303R) and intercept of [log (R/Nh)+(ΔS/2.303R)], from which (ΔH) and (ΔS) were calculated and listed out in Table -1.3. The negative value of enthalpy of activation (ΔH) in the presence and absence of various concentration of inhibitor reflects that the exothermic natures of Gas Pipeline metal. The values of entropy of activation (ΔS) listed in Table-1.4. It is clear that the entropy of activation decreased in the presence of the using inhibitor when compared to free natural seawater. The decrease in the entropy of activation (ΔS) in the presence of inhibitor may decreased in the disordering on going from reactant to activated complex is difficult.

4. Electrochemical Studies

4.1.1. Polarization studies

Polarization experiment has been used to study the protective film formed on the metal surface. The Potentiodynamic polarization curves of gas Pipeline metal in natural seawater environment in the presence and absence of inhibitor are shown in fig-1.4. Other parameters like, corrosion potential (E_{Corr}), Corrosion current density (I_{Corr}), anodic Tafel slope (b_a), cathodic Tafel slope (b_c) and percentage of inhibition efficiency (%IE) are given Table-4. E_{corr} values shifted to negative potential with increase in concentrations of PTS inhibitor solution. The corrosion current densities reduced from 38.64 to 6.69µA with increase in concentrations of the inhibitor. It is evident from Table-1.4 that the addition of PTS inhibitor shows a negative shift in the E_{corr} value shift in corrosion potential exceeds ±85mv with respect to corrosion potential of the uninhibited solution, the inhibitor acts as either anodic (or) Cathodic type. In this present study the maximum displacement in E_{corr} is found to be within ±58mV, which indicates that PTS inhibitor act as mixed type of inhibitor by showing its inhibitory action on both hydrogen evolution and metal dissolution.

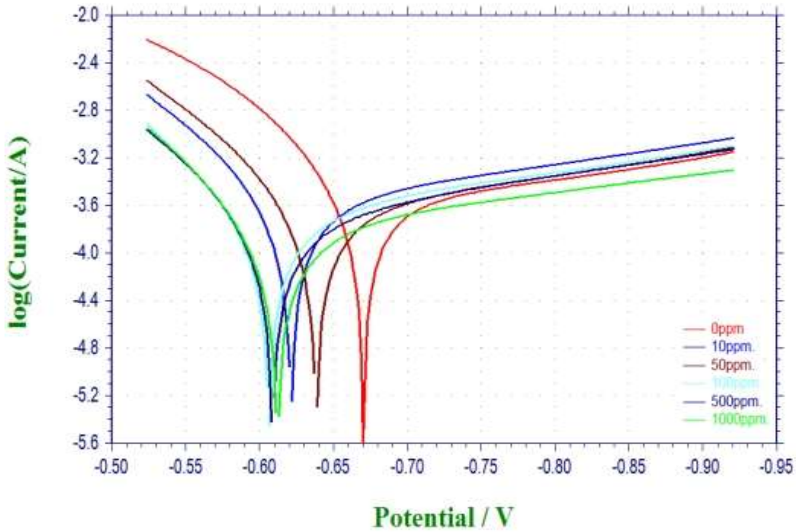


Fig-1.4 Polarization curves for Gas pipeline metal in Natural seawater In the presence and absence of different conc. of PTS inhibitor.

4.1.2. Electrochemical impedance (EIS) studies.

Fig-1.5 shows that typical set of complex planes plot of gas pipeline metal in Natural seawater in the presence and absence of various concentration of PTS inhibitor at room temperature. It was obvious that the addition of inhibitor results in an increase the (R_{ct}) value simultaneous decrease the I_{corr} values.(Fig.1.5(a)), bode impedance plot shows imperfect capacitive loops. (1.5(b)) and the maximum phase angle (Fig.1.5(c)). Careful inspection of this data revealed that the value of charge transfer resistance (R_{ct}) increased from 12.81 to61.07Ωcm^2 of gas pipeline metal in natural seawater with increase of inhibitor concentrations. The inhibition efficiency increased from 10.48to 79.04% with increase of inhibitor concentration. It ensures that the formation of protective film on the metal surface. The double layer capacitance (C_{dl}) decreased as the increase of inhibitor concentration may be due to the adsorption of theactive compounds on the metal surface leading to a film formation. It can be noticed that the corrosion current decreases when increase the inhibitor concentration simultaneously the increase of charge transfer resistance values are indicated its may controlling the dissolution of the metal.

Table-1.4 Parameters derived from electrochemical measurements of Gas pipeline metal in Natural seawater containing various conc. of PTS inhibitor.

Conc.(ppm)	**Polarization studies**					**Impedance studies**		
	$-E_{corr}$ mV	**b_a (mV/ decade)**	**$-b_c$ (mV/ decade)**	**I_{corr} $\mu A\ cm^{-2}$**	**I.E (%)**	**R_{ct} ($\Omega\ cm^2$)**	**C_{dl} x10 $^{-4}$ Fcm^2**	**I.E (%)**
Blank	670	8750	2083	38.64	---	12.812	0.00080	---
10	621	1011	2586	27.70	28.20	14.313	0.00076	10.48
50	638	9714	2651	24.64	36.23	17.722	0.00065	27.7
100	606	3809	2961	8.85	77.09	30.833	0.00050	58.44
500	609	3860	3039	7.60	80.33	31.036	0.00024	58.71
1000	612	3931	2750	6.69	82.68	61.073	0.00022	79.04

Bode impedance plots Fig-1.5 (b) reflected that the value of charge transfer resistance (R_{ct}) increased with increase of inhibitor concentration and suggested that the protective film formed on the metal surface was more stable. Since it was able to with stand the attack of aggressive corrosive environment. In Bode phase plots (Fig.1.5(c)) the phase angle at higher frequencies attributed to anti-corrosion performance. The depression of phase angle at relaxation frequency with the decrease in the inhibitor concentration indicates that the decrease of capacitive response with the decrease of inhibitor concentration. Such a phenomenon reflected that the higher corrosion activity at low concentrations of the inhibitor.

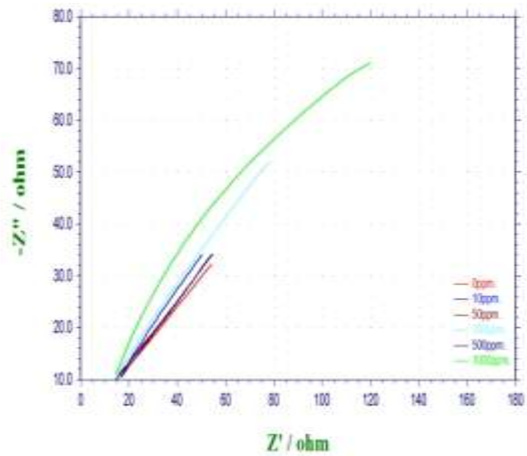


Fig (a)

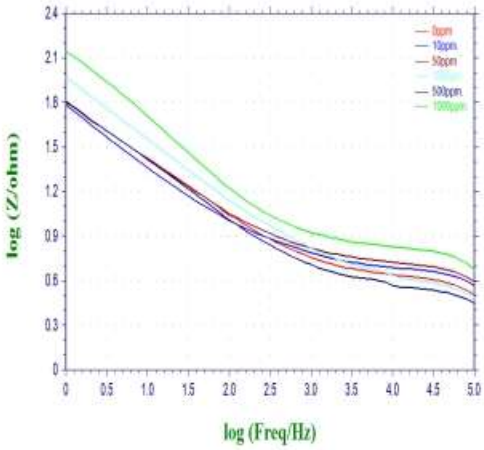


Fig (b)

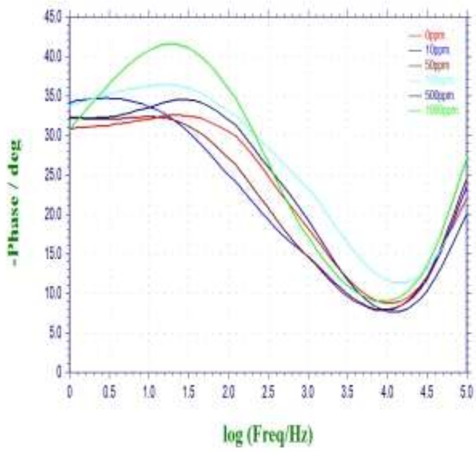


Fig (c)

Fig-1.5 (a-c). Electrochemical impedance plots, (a) Nyquist (b) Bode impedance plot (c) phase angle plot for Gas pipeline metal in Natural seawater containing various conc. of PTS inhibitor.

5. Characterization of Corrosion Composites

5.1.1. EDAX Analysis

EDAX spectroscopy was used to predict the elements present on the Gas pipeline metal surface in the presence and absence of inhibitor. Fig.1.8 (a) and (b) reflects the EDAX spectra for the corrosion product on metal surface in the absence and presence of optimum concentrations of PTS inhibitor solution in Natural seawater medium. In the absence of inhibitor molecules, the spectrum may be confirmed that the percentage of the atoms for iron (49.49%),oxygen (50.07%).However in the presence of the optimum concentrations of the inhibitor percentage level the atoms in oxygen (50.53%), iron (48.94), and sulfur (0.53%). It obviously indicates that the hetero atoms present in the inhibitor molecules may be involved in complex formation with metal ions during the adsorption process and to prevent the further dissolution of metal against corrosion.

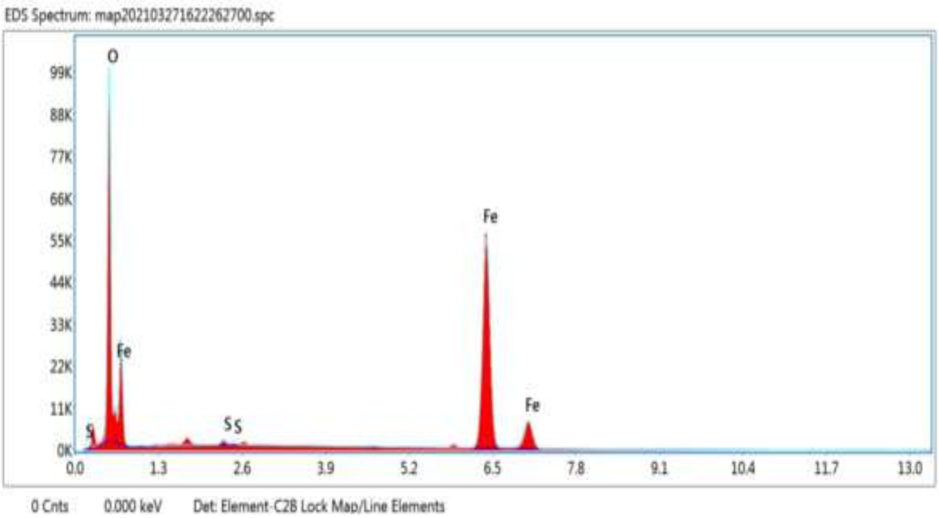


Fig-1.6. (a) EDAX spectrum of the corrosion product on Gas pipeline Metal in natural seawaterin the absence of PTS inhibitor.

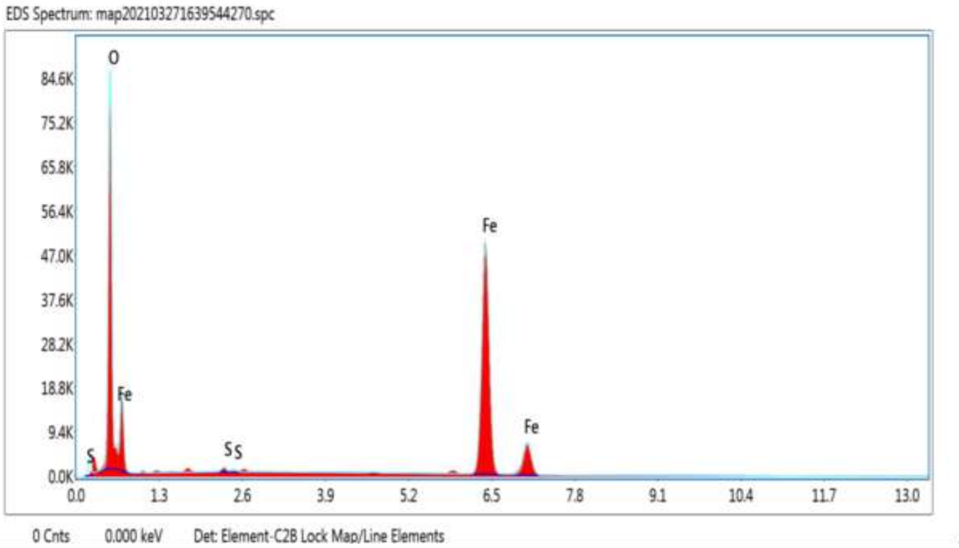
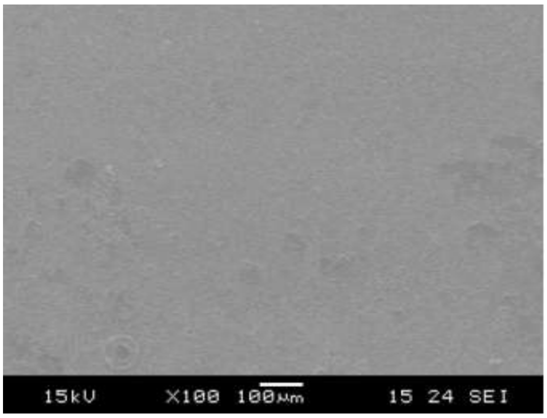
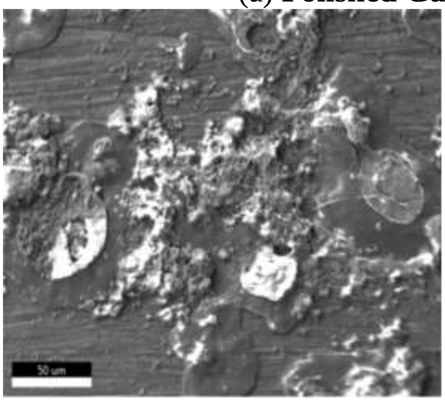


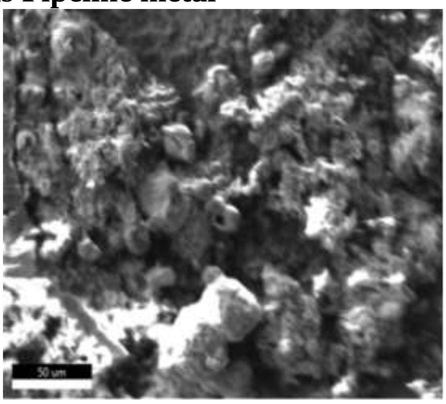
Fig-1.6. (b) EDAX spectrum of the corrosion product on Gas pipeline metal In natural seawater in the presence of PTS inhibitor.

5.1.2 Morphological studies.



(a) **Polished Gas Pipeline metal**

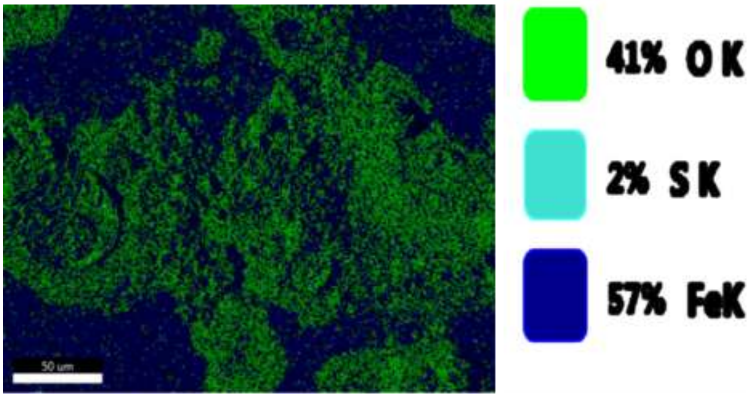




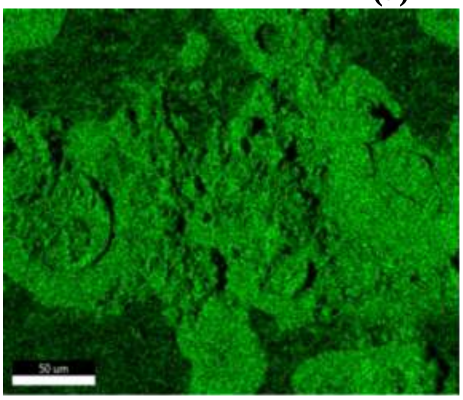
(b)Absence of inhibitor **(c) Presence of inhibitor**

5.1.3 SEM Analysis

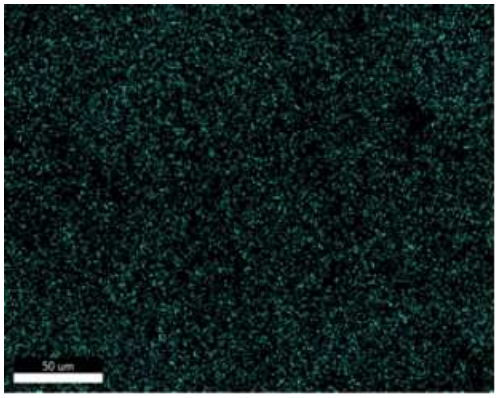
Fig-1.7 (a-c) shows that the surface morphological view of Polished gas pipeline metal in compared the absence and presence of PTS inhibitor solution in natural seawater. In (Fig 1.7(a)) shows the SEM images of polished Gas pipeline metal.(Fig 1.7 (b)) the SEM images shows the morphological studies is Plug type of corrosion in the absence of PTS inhibitor. (Fig 1.7(c)) However after the Gas Pipeline metal is immersion into the PTS inhibitor solution the SEM image reflects which it's may revealed that the surface was spread into spongy mass images.



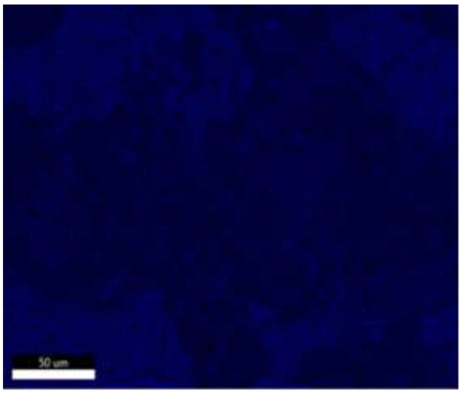
(a)



(b)

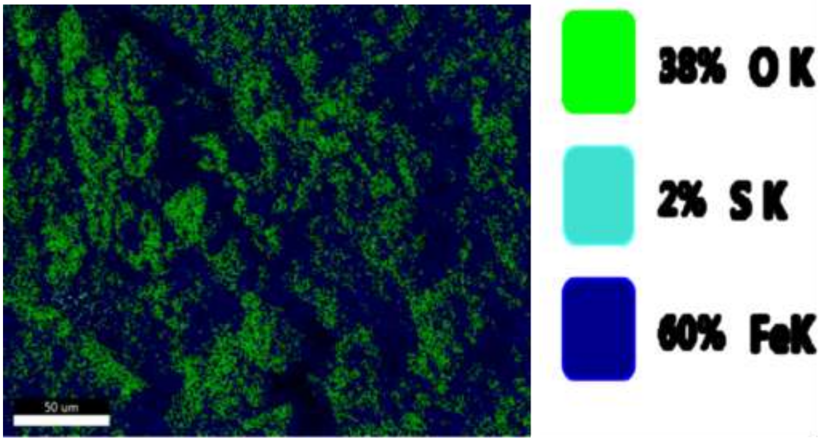


(c)

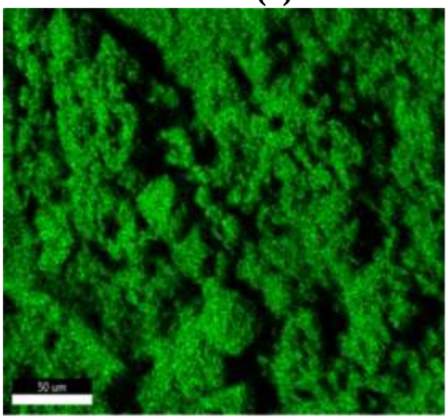


(d)

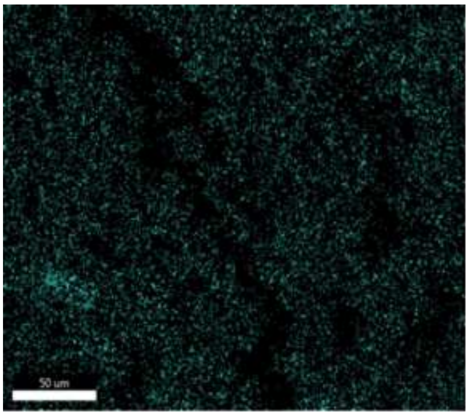
Fig-1.8(a) (a-e). These images show the various percentage level atoms present in the elemental mapping in the absence of inhibitor. (a) Common mapping. (b) Percentage level of Oxygen. (c) Percentage level of Sulfur. (d) Percentage level of iron.



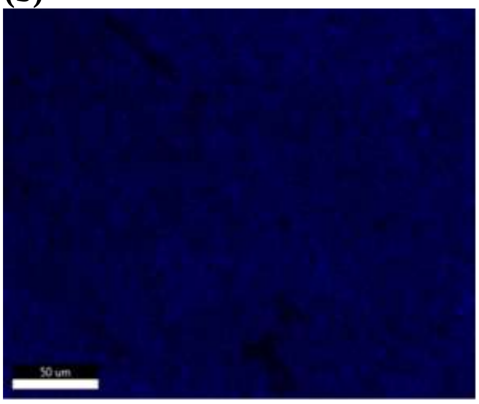
(a)



(b)



(c)



(d)

Fig.1.8 (b) (a-e). These images show the various percentage level atoms present in the elemental mapping in the absence of inhibitor. (a) Common mapping. (b) Percentage level of Oxygen. (c) Percentage level of Sulfur. (d) Percentage level of iron.

6. Conclusion

Dissolution behavior of Gas pipeline metal was increased with the increase of exposure time and decreased with the increase of PTS inhibitor concentration. Maximum of inhibition efficiency for PTS inhibitor was achieved 79.04% in 1000ppm concentration level. In temperature studies, the maximum of 65.88%, 75.56% was attained at 303K and 333K respectively. Values of E_a indicates that the adsorption of PTS inhibitor follows the mechanism of Physical adsorption. Thermodynamic parameters such as ΔAds and ΔG_{ads} represented that the adsorption of PTS solution on metal surface was exothermic and spontaneous process. The inhibitor obeyed Langmuir (R^2=0.9956), adsorption isotherm. In polarization studies the value of I_{corr} decreased from 38.64 to 6.69µA/cm^2 and the maximum of 82.68% I.E was arrived in the presence of inhibitor. The corrosion potential (Ecorr) was shifted to negative direction. i.e. -670 to -612mVand behave as mixed type. The R_{ct} values increased from 12.81 to 61.07Ωcm^2 with increase of inhibitor concentration and the maximum of 82.68% of I.E was attained. The EDAX spectrum shows that the percentage level of the elements in absence and presence of the PTS inhibitor. The SEM image shows that the Plug type of corrosion in metal surface has occurred in the absence of inhibitor but in the presence of inhibitor the covered the Spongy mass occurred on the metal surface.

7. References

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