Research Article

STUDY OF NATURALLY OCCURRING BIOCIDE AS CORROSION INHIBITOR FOR STAINLESS STEEL IN ACIDIC MEDIUM

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ABSTRACT

The present study was carried out with 1,3,5 Tri Methyl Xanthine(TMX) is also called caffeine a naturally occurring substance found in the extracts of leafs of Green tea and Beans of coffee Arabica as corrosion inhibitor for the corrosion of stainless steel in acid medium. Caffeine is found to have biocidal efficiency and prevents microbial corrosion. The corrosion behaviour of stainless steel in 1.0 M HCl solution by weight loss (at 30o C and 40o C), and electrochemical techniques were carried out. Experimental results reveal that inhibition efficiency increases with increasing inhibitor concentration up to a maximum of 83% and it decreases with increase of temperature. The best fit adsorption isotherm for the experimental data was Langmuir adsorption isotherm. Tafel polarization analysis reveals that the studied compound is a mixed type inhibitor.

Keywords: Corrosion Inhibitor, Stainless Steel, Adsorption, Polarization.

INTRODUCTION

Pitting Corrosion of 430 Stainless Steel is of great practical interest. It can be a destructive form of corrosion in engineering structures if it causes perforation of equipment. Most equipment failures in Stainless Steel are caused by pitting corrosion [1-3]. Acidic solutions are extensively used within industry for industrial-equipment cleaning, and the pre treatments of compositions [4–6]. Hydrochloric acid is widely- used in pickling solutions. The addition of an inhibitor is necessary to prevent corrosion i.e. to reduce the dissolution of metals within these acidic environments. The usage of chemical corrosion-inhibitors is common during production and processing operations. The addition of high molecular weight organic compounds, such as surface active agents, to acid solutions has been proved to be an effective method to reduce the rate of corrosion of metals. Moreover, ionic and non-ionic surfactants have been reported to be corrosion inhibitors for metals like copper, aluminium and mild steel [7-16]. The development of new chemicals is particularly challenging, as they would need to maintain good protection of the materials under a variety of conditions, whilst being environmentally acceptable. There is increasing concern about the toxicity of corrosion-inhibitors used in industry. Any toxic effects not only affect living organisms but also poison the earth. Therefore, over recent years, the traditional approach regarding corrosion inhibitors has gradually changed, owing to the increasing interest and attention of the world towards environmental problems, towards protecting the environment and the hazardous effects of the usage of chemicals on the ecological balance. It is believed that toxic inhibitors, widely-used within industrial processes should be replaced by new environmentally friendly inhibitor. Caffeine

a naturally available organic substance is used in the present study to explore the possibility of usage as green inhibitor to control the corrosion of stainless steel in acid medium. Pawar pruthiviraj et. al. have reported antibacterial activity of caffeine at different concentration against most tested bacteria [18]. For any industrial applications in order to prevent microbial growth biocides are added, caffeine itself is reported as a good biocide its corrosion inhibition effect on stainless steel in HCl solution is undertaken. Organic compounds containing electronegative functional groups act as good inhibitors. One possible mechanism is the adsorption of the inhibitor due to their specific interaction between functional groups and the metal surface which blocks the metal surface and thus do not permit the corrosion process to take place. Heteroatoms like N, O and S [19-22] play an important role in inhibition due to the free electron pairs they possess. When both these features combine, increased inhibition can be observed [23-27].

MATERIALS AND METHODS

Preparation of inhibitor

Commercially available 1,3,5 Tri Methyl Xanthine compound with molecular formula $C_8H_{10}N_4O_2$ is used as such. All the solutions were prepared from doubly distilled water.
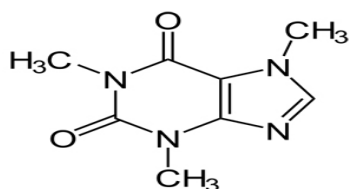
1,3,5 Tri Methyl Xanthine

Specimen preparation

Stainless steel 430 grade having composition of 0.12% C,1.00% Si,1.00% Mn, 16.00% Cr,0.75% Ni,.04% P,.03% S and the remainder Fe, specimens used in the weight loss experiments were mechanically cut from commercially available stainless steel samples into coupons of 4.0cm×1.5 cm×0.0457 cm dimensions, polished with soft 3M 1500 sand paper to a metallic shine, washed with acetone and double distilled water, dried to room temperature and stored in a moisture free desiccators before use in corrosion studies. The stainless steel specimens for the electro chemical measurements were machine cut from stainless steel sample into test electrodes of dimensions,8.0cm×1.0cm×0.0457cm and coated with epoxy resin (araldite)leaving a surface area of 1cm2. The corrosive medium,1.0 M HCl solution was prepared from analytical grade 37% HCl by diluting with double-distilled water.

Weight loss method

The weight loss (WL) measurements were carried out by weighing the prepared specimens before and after immersion for 1 h in 100 mL test solution in the presence and absence of various concentrations of the 1, 3, 5, tri methyl xanthine. From the weight loss data, percent inhibition efficiency (IE %) was calculated at different concentration at 30⁰Cand 40⁰C.

Electrochemical measurements

The stainless steel coupons, were prepared as detailed above, was used as working electrode. Before each experiment, the exposed area of the working electrode was polished with soft 3M 1500 sand paper, to a metallic shine. Then it was washed with distilled water, degreased with ethanol, and finally dried with soft paper. The electrochemical measurements were performed in a conventional three electrode glass cell which consist of stainless steel as working electrode (WE),Calomel as reference electrode, platinum as counter electrode. Potential was allowed to stabilize 60 min before starting the measurements. Measurements were performed using Princeton Applied Research Electrochemical Analyzer (model K0264 micro cell kit).Electrochemical analyzer software was used for plotting, graphing and fitting data. Tafel polarization curves were obtained by changing the potential from -440mV to -470mV around open circuit potential with scan rate of 10mV/sec. Impedance measurements were carried out in frequency range from100kHz to 10 Hz using ac signals with an amplitude of 60mV peak to peak at open circuit potential.

Scanning electron microscopy (SEM)

The surface of stainless steel specimens immersed in 1 M HCl in the presence and absence of the TMX was studied by using scanning electron microscopy.

RESULT AND DISCUSSION

Weight loss measurement and adsorption

The inhibition efficiencies,(IE%)were calculated by the following equation.

$$CR=W_0/t\times A$$

Where W0 weight difference, t immersion time, A area of metal surface.

$$IE\% = \frac{CR_0-CR_t}{CR_0} \times 100 \quad (1)$$

Where,CR_0 and CR_t are the Corrosion rate in the absence and the presence of the inhibitor respectively. The inhibition efficiency increases with increasing concentration of the inhibitor and decreased with increase of temperature (table 1).

Adsorption studies

Adsorption of TMX can be explained on the basis that adsorption of the inhibitor was mainly via heteroatoms (viz,N,O) present in TMX [28].The establishment of isotherms that describe the adsorptive behaviour of a corrosion inhibitor is an important part of its study ,as they can provide important clues to the nature of the metal-inhibitor interaction. The values of surface coverage(θ) are obtained from weight loss measurements at 300 and 400c.The θ values were tested for several adsorption isotherms and the best fit was found to obey Langmuir adsorption isotherm[29,30],which is expressed by

$$C/\theta = 1/K_{ads} + C$$

where θ is the surface coverage, C is the inhibitor concentration and K_{ads} is the equilibrium constant of adorption process. The regression coefficient, R^2 was found to be 0.968 (30°C) and 0.941 (40°C). Plot of c/θ versus C is shown (fig.1).

The slope deviates from unity indicates that there is attraction or repulsion in the adsorbed layer of inhibitor on the stainless steel.[31,32].

The standard free energy of adsorption (ΔG^0_{ads}) is related to equilibrium constant of (K_{ads}) according to the following equation [33]

$$K_{ads} = 1/C \text{ (solvent) exp } (\Delta G^0_{ads}/RT)$$

where $C_{solvent} = C_{H_2O} = 55.55$ mol dm^{-3}, R(J mol^{-1} K^{-1}) is the gas constant and T (K) is the temperature.

The negative values of (ΔG^0_{ads}) suggest that the adsorption of inhibitor molecules on to stainless steel surface is a spontaneous process [34]. It is seen that the maximum inhibition efficiency was found to slightly decrease from 83% to 50.0% with the increase of temperature from 30° to 40°C and it is indicative of physical adsorption of the TMX on the stainless steel in1.0 M HCl [35]. In addition the values of ΔG^0_{ads} around -20 kJmol^{-1} are consistent with physisorption. The value around – 40 kJmol^{-1} or higher correspond to chemisorptions [36,37].

Thus in examining the effect of temperature on the corrosion process, the apparent activation energies (Ea) was calculated using equation [38]:

$$\text{Log } r2/ r1 = Ea/2.303(1/ r1-1/ r2) \quad (4)$$

where r2 and r1 are the corrosion rates at temperatures T1 and T2,respectively. An estimate of heat of adsorption , Q ads, was obtained from the trend of surface coverage with temperature as follows [39]:

$$Q_{ads}=2.303 R[\log \theta 2/1- \theta 2-\log \theta 1/1-\theta 1]\times[T1 \times T2/T2-T1] \text{ kJ mol}^{-1} \quad (5)$$

where $\theta 2$ and $\theta 1$ are the degrees of surface coverage at temperature T1 and T2,respectively.The calculated values for Ea and Q ads are given (table 3)

Increased activation energy, Ea in inhibited solutions compared to the blank suggest that the inhibitor is physically adsorbed on the corroding metal surface, either unchanged or lower (Ea) in the presence of inhibitor suggest chemisorptions[40].It is seen (table 3) that Ea values increases with increase in the concentration of the inhibitor. This shows that the inhibitor retards corrosion at ordinary temperature and its corrosion retarding efficiency is considerably diminished at higher temperatures [41]. The low and negative Q ads values are indicative of less surface coverage with rise in temperature.

Table1 Inhibition of corrosion of stainless steel in 1M HCl by TMX at 30±0.5 and 40±0.5ºC

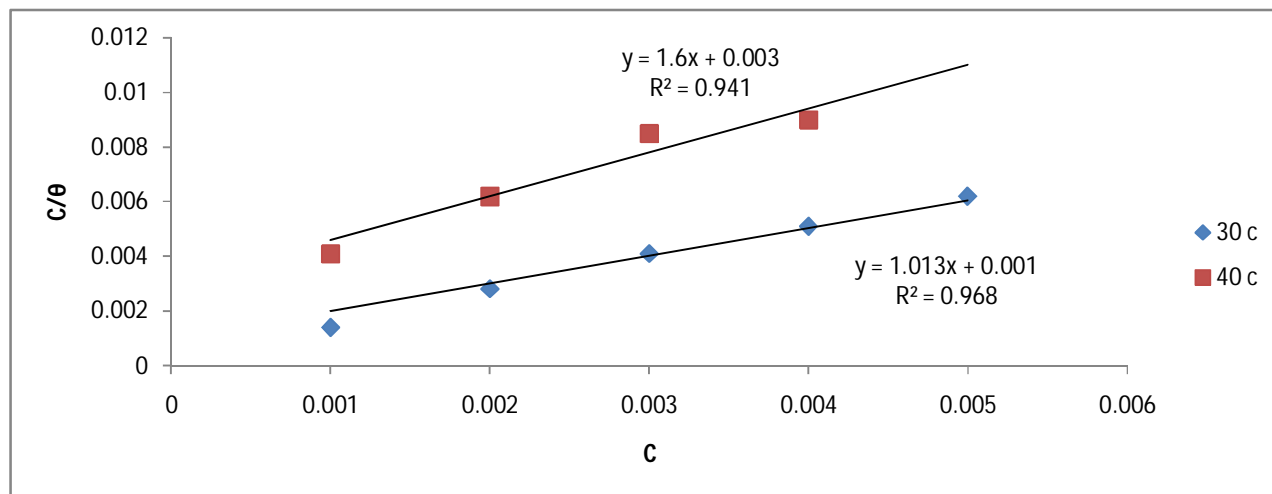| [Concentration] ×10^{-3},M	30ºc		40ºc	
	CR_0-CR_t / CR_0	% IE	CR_0-CR_t / CR_0	% IE
1.00	0.67	67	0.24	24
2.00	0.71	71	0.32	32
3.00	0.73	73	0.35	35
4.00	0.78	78	0.44	44
5.00	0.83	83	0.50	50

figure1

Table2 The standard Gibbs free energy of adsorption of TMX on the stainless steel surface in 1.0 M HCl

[Inhibitor],10^{-3}M	30ºC		40ºc	
	θ	ΔG^0_{ads} kJ mol^{-1}	θ	ΔG^0_{ads} kJ mol^{-1}
1.00	0.67	-25.36	0.24	-25.43
2.00	0.71	-24.56	0.32	-24.67
3.00	0.73	-24.14	0.35	-23.96
4.00	0.78	-23.77	0.44	-24.39
5.00	0.83	-23.85	0.50	-24.25

Table 3.Calculated values of Ea and Q ads for stainless steel in 1.0 M HCl without and with TMX

[Inhibitor],10^{-3}M	E_a, kJ mol^{-1}	$Q_{ads.}$ kJ mol^{-1}
Blank	45.857	--------
1.00	106.722	-146.752
2.00	111.929	-130.046
3.00	127.171	-127.249
4.00	119.381	-118.813
5.00	134.275	-125.046

Table 4 Electrochemical polarisation for stainless steel in 1.0 M HCl in the absence and presence of different concentrations of TMX

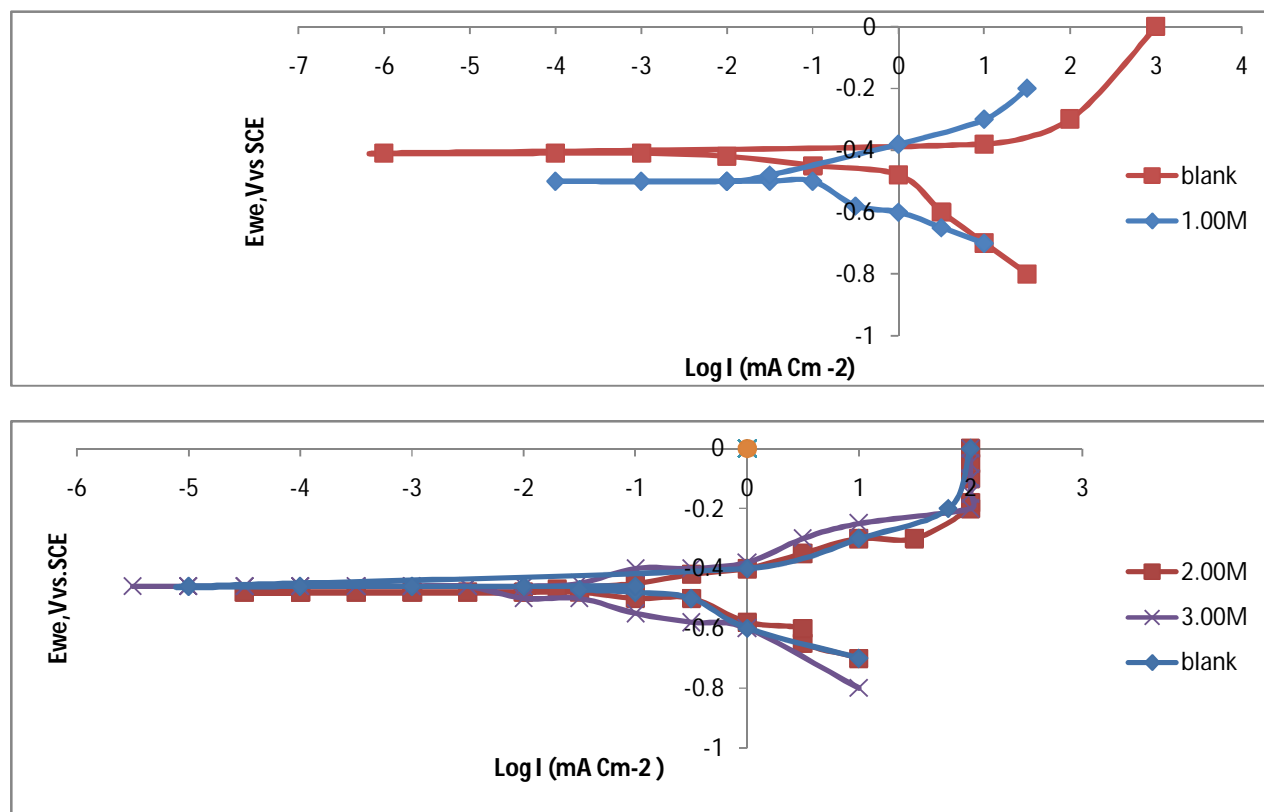| [Concentration], M 10^-3	E_{corr},V	I_{corr},µA	β_c,Mv	β_a,mV
Blank	-464.930	220.020	148.2	80.4
1.00	-455.617	109.081	147.2	83.0
2.00	-461.508	118.907	133.8	77.7
3.00	-463.983	81.291	137.9	81.3

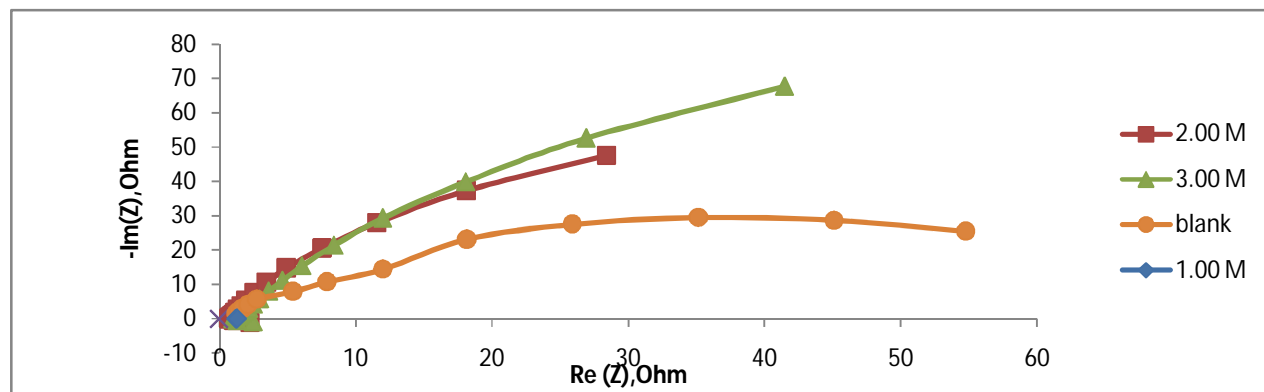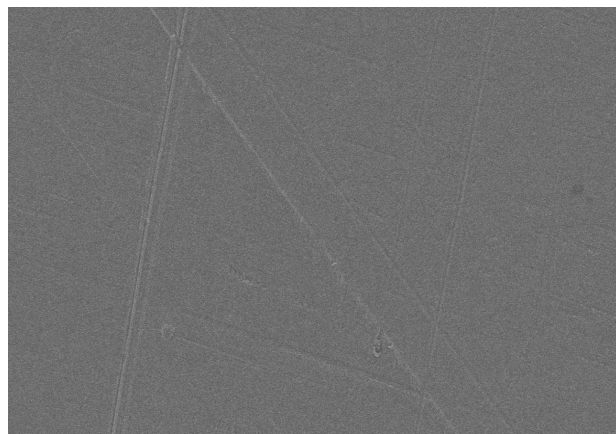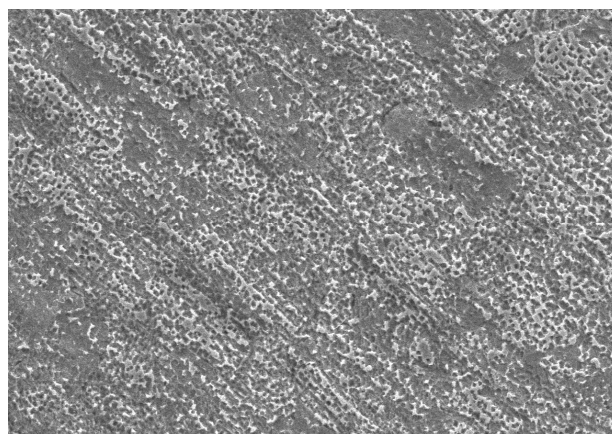**Figure 2** Electrochemical polarisation study

Figure 3 Electrochemical impedance measurements

Table 5 Impedance parameter for the corrosion of stainless steel in 1.0 M HCl in the absence and presence of different concentrations of TMX at $30\pm0.5\,^{0}C$

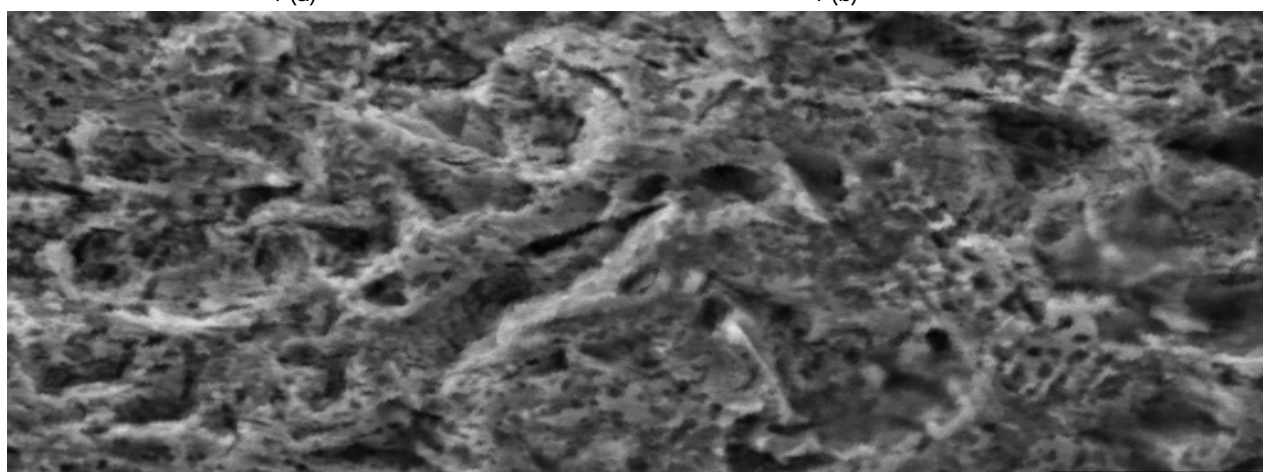| Concentrations, M 10^{-3}	R_{ct},Ohm	C_{dl},µF
Blank	74.56	0.944
1.00	110.52	0.104
2.00	148.5	0.107
3.00	252	0.063

4 (a)

4 (b)

4 (c)

Figure 4 SEM analysis of metal surface

Potentiodynamic polarisation method

The Tafle polarisation curves of stainless steel in 1.0 M HCl solution without and with different concentrations of TMX are shown (fig 2) and the polarisation parameters such as Ecorr, Icorr, anodic Cathodic Tafel slopes (βa , βc) are summarised in table4. Literature survey reveals that only when the open circuit potential (OCP) displacement is at least ±85 mV in relation to the blank solution, a compound can be recognized as an anodic or cathodic inhibitor [42].However it is seen (table 4) that the corrosion potential, Ecorr, was shifted at the most 12 mV with respect to the blank solution and therefore, TMX might act as a mixed type inhibitor.

Electrochemical impedance measurements

Nyquist plots of stainless steel in 1.0 M HCl solution in the absence and presence of different concentrations of TMX are given in Fig.3.

It can be seen from the Nyquist plots that the curve are almost semicircular appearance followed by an inductive loop at the low frequency region. The semicircular nature of the Nyquist plot due to charge transfer process, which mainly

controls the corrosion of stainless steel in 1M HCl solution. Deviation from perfect circular shape is often inferred as the frequency dispersion of interfacial impedance and it may be attributed to the in homogeneity of the electrode surface arising from surface Roughness or interfacial phenomenon. The addition of TMX to HCl leads to increase in the resistance, Rct, and decrease of double layer capacitance, C_{dl}, (Table5).

SEM analysis of metal surface

SEM provides pictorial representation of the metal surface.To understand the nature of the surface film in the absence and presence of inhibitors and extent of corrosion of stainless steel, the SEM micrographs of the surface were examined. The SEM images of stainless steel specimen immersed in 1 M HCl for 1 hr in the absence and presence of inhibitor are shown in figure 4.The SEM micrographs of polished stainless steel surface in figure 4(a) shows the smooth surface of the metal. This shows the absence of any corrosion products or inhibitor film formed on the metal surface. The SEM micrographs of stainless steel surface immersed in 1 M HCl figure 4(b) shows the pits and shows the roughness of the metal surface which indicates the corroded area of the stainless steel. However Figure 4(c) indicates the rate of corrosion is suppered. The metal surface is almost free from corrosion due to the formation of thin layer of inhibitor(TMX),which effectively controls the dissolution of Stainless steel[43]

CONCLUSION

The inhibition efficiency of TMX increases with increase in inhibitor concentration. The TMX controls both anodic and the cathodic reactions by blocking the stainless steel surface and thus the inhibitor are a mixed type inhibitor. The adsorption of TMX on stainless steel follows the Langmuir adsorption isotherm model. The values of $\Delta G0ads$ are suggestive of spontaneous physisorption of the inhibitor.The SEM micrographs confirm the formation of protective film on the metal surface.

Acknowledgement

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