

Amodiaquine-**as a Healing Medicine for the Corrosion of Mild Steel in Acid Medium****Dr. (Mrs.) S.Subhashini, Dr. (Mrs.) R.Rajalakshmi****R.Geethanjali, S.Leelavathi*****Department of chemistry, Avinashilingam University for Women,
Coimbatore******subhashini_adu@yahoo.com******raji_adu@yahoo.com*****Abstract**

The inhibitive effect of Amodiaquine, an organic medicinal compound on the corrosion of mild steel in sulphuric acid has been investigated using weight loss, polarization and impedance studies. The weight loss measurements were conducted for mild steel in 0.5M H₂SO₄ with and without the investigated inhibitor for various concentrations, time intervals and temperature ranges. From the calculated weight loss, the inhibition efficiency and surface coverage were calculated. The adsorption of the inhibitor molecules on the metal surface was found to be monolayer obeying Langmuir adsorption isotherm. Potentiodynamic polarization studies have shown that the compound studied is a of mixed type of inhibitor. Electrochemical impedance studies are also conducted. The inhibitor was found to give 75% efficiency.

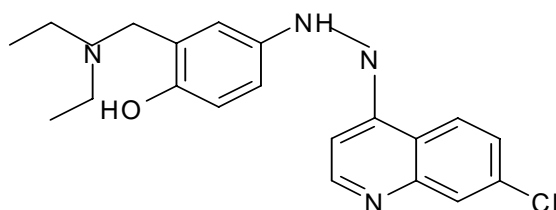
Key words : Mild steel Corrosion, H₂SO₄, Amodiaquine.

Introduction

Sulphuric acid is extensively used in pickling, descaling and oil well acidizing of metallic materials. The dissolution of metal in such process while subjecting to aggressive acids is obvious. The study of the organic corrosion inhibitors in the acid medium is an attractive field of research due to its usefulness in several industries like construction, agricultural equipment, oil and gas, petrochemical, medical services, process and allied industries⁽¹⁾. It has been speculated that organic inhibitors are more effective with iron and that polar organic compounds containing hetero atoms like such

as O, N, S and multiple bonds in their molecules are of particular interest as they give better efficiency than those containing N and S atom alone^(2,3). According to adsorption theory of corrosion inhibition, the primary step in the action of inhibitors is chemisorption onto the metal surface. Chemisorption usually occurs through donation of electrons from a functional atom. The adsorption process is a general one occurring on both cathodic and anodic types of electrochemical sites. Most organic compounds that act for corrosion prevention are mixed inhibitors. Chemisorption of an inhibitor depends on some factors like molecular structure, coverage area and electron donating ability of the inhibitor. Although the inhibitive action of these additives is commonly known, the true mechanism for their beneficiary action is only little known. This necessity is the mother of invention of new acid corrosion inhibitors in which a measurable role is done by organic compounds⁽⁴⁾. In the presence of two or more adsorbed species, lateral interaction between the inhibitor molecules can significantly affect the inhibitor performance. If the interaction is attractive, a synergistic effect arises i.e., the degree of inhibition of both the inhibitors is higher than the sum of the individual effects⁽⁵⁾. Based on this, an organic medicinal compound Amodiaquine was selected for the corrosion of mild steel in 0.5M H₂SO₄. An attempt has been made to study its effect using weight loss, potentiodynamic polarization and impedance measurements.

Structure of AMQ



Methodology

Sample preparation

A rectangular mild steel bar of composition was cut into pieces of area 5x1 cm². The specimens were polished mechanically, degreased, cleaned successively in

deionized water, dried, stored in a dessicator and used for all studies. For electrochemical polarization and impedance experiments mild steel strips with an exposed area of 1cm² were used.

Experimental

Weight loss

The MS coupons were weighed in Denvar balance. Weighed samples in triplicate were immersed in 100 ml of acid solution (with and without inhibitor) for a fixed duration. The specimens were removed and washed with saturated sodium bi carbonate solution and water, dried and reweighed. The average weight loss of the coupons was recorded. Using a thermostat temperature studies were conducted by varying the temperature from 313K-363K for a fixed immersion period of half an hour.

- The rate of corrosion was calculated using the formula.

$$\text{C.R. (mpy)} = \frac{534 W}{\text{DAT}}$$

Where, W is the weight loss in g, D is the density of specimen in g/cm, A is the area of the specimen in cm², T is the exposure time in hr.

WL method:

- The inhibitor efficiency was obtained from the following formula.

$$\text{IE} = \frac{W_0 - W}{W_0} \times 100$$

Where, IE – Inhibitor efficiency in percentage, W₀ – weight loss without inhibitor
W – Weight loss with inhibitor.

The corrosion monitoring techniques like Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods have been used. For both the techniques, **Solartron Electrochemical Measurement Unit** (1280B) model was used with a software package of **Z plot and Corrware**. The system includes a potentiostat, personal computer and Frequency Response Analyser.

The cell assembly for the electrochemical measurements consisted of a mild steel working electrode, platinum foil as a counter electrode and saturated calomel electrode as reference. All the experiments were performed at room temperature. For potentiodynamic polarization studies, the experiments were carried out over a potential range of -200mV to +200mV with respect to reference electrode and its current response was measured at a scan rate of 5mVsec⁻¹.

Impedance measurements were carried out at corrosion potential. The A.C. amplitude of 10mV was applied and the frequency was varied from 10 kHz to 10 MHz. The real and imaginary parts of the impedance were plotted in Nyquist plot. From the Nyquist plots and Bode plots, the Charge Transfer Resistance (R_{ct}) and Double Layer Capacitance (C_{dl}) values were calculated.

Values of corrosion current were obtained by Tafel extrapolation method. A extrapolation of linear portion to the corrosion potential gave the corrosion current and the slope of the linear portion of the anodic and cathodic curves gave b_a and b_c respectively. R_p was obtained from the slope of linear polarization resistant curves.

TI method:

The inhibitor efficiency was obtained from these equations,

$$IE = \frac{I_{corr(b)} - I_{corr(i)}}{I_{corr(b)}} \times 100$$

$I_{corr(b)}$ - Corrosion current in the absence of inhibitor,

$I_{corr(i)}$ - corrosion current in the presence of inhibitor

LPR method:

$$IE = \frac{R_p(\text{inhibited}) - R_p(\text{blank})}{R_p(\text{inhibited})} \times 100$$

$R_p(\text{blank})$ - linear polarization resistance in the absence of inhibitor

$R_p(\text{inhibited})$ - linear polarization resistance in the presence of inhibitor

$$IE = \frac{R_{ct}(\text{inhibited}) - R_{ct}(\text{blank})}{R_{ct}(\text{inhibited})} \times 100$$

$R_{ct}(\text{blank})$ - charge transfer resistance in the absence of inhibitor

$R_{ct}(\text{inhibited})$ - charge transfer resistance in the presence of inhibitor

The surface coverage θ is calculated using the following equation

$$\theta = \frac{C_{dl}(\text{blank}) - C_{dl}(\text{inhibited})}{C_{dl}(\text{blank})} \times 100$$

$C_{dl}(\text{blank})$ - double layer capacitance in the absence of inhibitor

$C_{dl}(\text{inhibited})$ - double layer capacitance in the presence of inhibitor

Results and discussion

Weight loss method

1. Effect of concentration and time

The effect of AMQ dosage on the corrosion of MS in 0.5M H_2SO_4 has been investigated and the results are presented in Table-1. The inhibition efficiency increased with increase in inhibitor dose until a maximum efficiency was obtained. Maximum inhibition efficiency was found to be 76% with 10^{-2} M inhibitor at 3 hrs immersion period. It was due to the increase in the surface area of the inhibitor molecules on the metal surface. The results are pictorially represented in the Fig1. IE increases with the increase in concentration for all the periods of immersion. As the time of immersion increases from $\frac{1}{2}$ hr to 3hr the IE increased and reached 75% for 10^{-2} M concentration of AMQ. After 3hrs the immersion, results indicates a decrease in IE. This may be explained as the time of immersion increases the adsorbed molecules on MS may undergo desorption resulting in decrease in IE. Corrosion rate with increase in the time of immersion may be ascribed to changes occurring in the inhibitor and to the built up of metal salts in solution.

2. Effect of temperature

From the table 2, and fig 2 for each temperature the corrosion rate decreased and inhibitor efficiency increased with increase in the concentration of AMQ. IE increases up to 313 K

and after that there is a decline in IE at 323K. Maximum IE was found to be 67.6% with 10^{-2} M concentration of AMQ. This may be explained as adsorption and desorption of inhibitor molecules continuously occurs at the metal surface and an equilibrium exists between these two processes at a particular temperature. With the increase of temperature, the equilibrium between adsorption and desorption processes is shifted leading to a higher desorption rate than adsorption until equilibrium is again established at a different value of equilibrium constant⁽¹⁶⁾. It explains the lower inhibitor efficiency at higher temperature.

3. Langmuir Adsorption Isotherm

A plot of $\log(\theta / 1 - \theta)$ Vs $\log C$ gave a straight line fig.3. showing that the adsorption of these inhibitors can be fitted to Langmuir adsorption isotherm. These results demonstrated that the inhibition of MS by AMQ was attributed to adsorption of the Amodiaquine on the MS surface. It also confirms the monolayer adsorption.

4. Activation energy and thermodynamic parameters

The activation energy at different concentrations of the inhibitor at various temperature was determined by plotting $\log CR$ Vs $1/T$. From the slope the values of activation energy (E_a) was calculated using Arrhenius equation. Thermodynamic parameters were evaluated from temperature studies results. Activation energy decreased in the presence of AMQ. This indicates that the inhibitor molecules are firmly held on the metal surface. The values of change in free energy of adsorption can be calculated using standard equation⁽¹⁷⁾. The negative values of free energy of adsorption infer that the strong interaction between the MS and the inhibitor molecules. A plot of $-\Delta G$ Vs $1/T$ gives a straight line. From that ΔH and ΔS values are evaluated and confirm that the process is enthalpic and entropic controlled.

5. Potentiodynamic polarization studies

The values of I_{corr} , E_{corr} and Tafel slope constants obtained from potentiodynamic polarization curves for MS in 0.5M H_2SO_4 and in the presence of different concentrations of AMQ are given in Table.3. The cathodic and anodic polarization curves of MS in the presence of AMQ are represented in the Fig .4.

It is evident that the values of I_{corr} decreased with the increase in inhibitor concentration and a maximum decrease is observed at high inhibitor concentration. Both cathodic and anodic polarization curves are affected by inhibition which proved that the inhibitor behave as mixed type. E_{corr} values obtained also infer that the inhibitor AMQ functions as mixed type inhibitor. This finding indicates that the corrosion of MS is strongly inhibited in the presence of AMQ. Linear polarization resistance R_p is obtained from potentiodynamic curves. The values of R_p increases with the increase in concentration of AMQ. This infers that AMQ is acting as an adsorption inhibitor on MS surface.

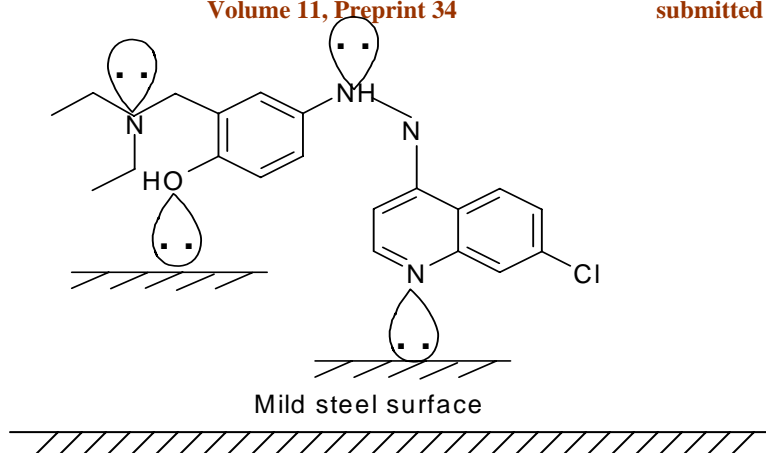
6. Electrochemical impedance spectroscopy

Impedance diagram obtained for the frequency range 100 MHz to 100 KHz at the open circuit potential for MS in 0.5 M H_2SO_4 , in the presence and absence of different concentration of AMQ is presented in the Table.5. Impedance diagrams for MS in the presence and absence of 10^{-3} M AMQ are given in the Fig.5. The values of R_{ct} and C_{dl} with corresponding IE and θ are listed in the table 4. It can be seen that the impedance diagrams are not perfect semicircles and it is due to frequency dispersion. Increasing R_{ct} values and decreasing C_{dl} values indicate that at 10^{-2} M of AMQ.

Mechanism

In the current investigation AMQ was selected as the potential inhibitor for MS acid corrosion.

- * A skeletal representation of the proposed mode of adsorption of the AMQ clearly indicates the active adsorption centers. Most probably the adsorption takes place through the secondary amine nitrogen and the OH group present in AMQ. The phenyl rings are in the plane and lie flat on the surface.



- * The inhibition of corrosion caused can be due to interaction between π electrons of benzene ring and lone pair of electrons present on Nitrogen and Oxygen atoms with the positively charged metal surface.
- * Presence of imido group (N-H) also plays a major role in increasing inhibition efficiency. The variation in the inhibitive performance mainly depends on the nature of the inhibitor molecule. This can be explained on the basis of presence of an additional π bond between C atoms (C=C) in conjugation with C=N group. These extensively delocalize π electrons and favor a greater adsorption on the metal surface. All the observation mentioned confirm the efficiency of AMQ and adsorption on the metal surface.

Conclusion

In the present investigation AMQ was proved as an excellent inhibitor for MS acid corrosion. It is found that IE increases with the increasing concentrations of AMQ and the maximum efficiency is 75% inhibition is taking place through the process of adsorption. Optimum time of immersion is found to be $\frac{1}{2}$ an hour for maximum efficiency. AMQ was proved to be a promising inhibitor at room temperature. Langmuir adsorption isotherm was obeyed. Electrochemical measurement confirmed that AMQ act as a mixed type of inhibitor, furnishing 75% of IE.

Table 1. IE of AMQ at different Concentration and period of immersion

| S.No. | Conc in (M) | ½ hr | 3 hrs | 6 hrs | 12 | 24 hrs |
|-------|--------------------|---------|---------|---------|---------|---------|
| | | IE % | IE % | IE % | IE % | IE % |
| 1. | Blank | - | - | - | - | - |
| 2. | 10^{-4} | 1.7 | 13 | 9.75 | 17.4 | 10.52 |
| 3. | 5×10^{-4} | 35.52 | 20 | 15.68 | 21.5 | 10.69 |
| 4. | 10^{-3} | 43.36 | 49 | 26.4 | 25.2 | 16.06 |
| 5. | 5×10^{-3} | 63.21 | 60 | 53.19 | 44.76 | 25.72 |
| 6. | 10^{-2} | 75.59 | 75 | 64.57 | 60 | 46 |

Table 2 IE of AMQ at different temperatures

| S. No. | Conc. | 303 K | 313 K | 323 K | 333 K | 343 K | 353 K |
|--------|--------------------|-------|-------|-------|-------|-------|-------|
| | | IE % | IE % | IE % | IE % | IE % | IE % |
| 1. | Blank | - | - | - | - | | - |
| 2. | 10^{-4} | 1.7 | 1.7 | 4.7 | 4.0 | 13 | 13.8 |
| 3. | 5×10^{-4} | 35.52 | 3.2 | 10.8 | 4.9 | 18 | 17 |
| 4. | 10^{-3} | 43.36 | 8.3 | 12.42 | 12.85 | 25 | 18 |
| 5. | 5×10^{-3} | 63.21 | 30.59 | 20 | 32.73 | 40 | 43 |
| 6. | 10^{-2} | 75.59 | 67.66 | 63 | 45.53 | 50 | 53 |

Table 3

Potentiodynamic Polarization results for the Adsorption of AMQ on MS in 0.5M H_2SO_4

| S.No. | Conc. of inhibitor (M) | b_a mV/dec | b_c mV/dec | I_{corr} (Amp/cm ²) | E_{corr} mV/sec | IE(%) | R_p Ohm/cm ² | IE(%) |
|-------|------------------------|-----------------|-----------------|--------------------------------------|----------------------|-------|------------------------------|-------|
| 1 | Blank | 182.61 | 166.45 | .0064887 | 517.9 | - | 4.2634 | - |
| 2 | 10^{-4} | 110.75 | 104.22 | 0.0064797 | 512.5 | 0.13 | 4.2789 | 0.36 |
| 3 | 5×10^{-4} | 224.2 | 211.14 | 0.0054556 | 507.7 | 15.91 | 5.5334 | 22.95 |
| 4 | 10^{-3} | 87.866 | 83.295 | 0.0050709 | 513.0 | 21.8 | 6.1644 | 30.83 |
| 5 | 5×10^{-3} | 92.52 | 87.56 | 0.0018476 | 519.7 | 71 | 6.302 | 32.34 |
| 6 | 10^{-2} | 114.47 | 106.13 | 0.0016762 | 504.9 | 74.6 | 6.556 | 35 |

Fig 1 I.E as a function of concentration and time

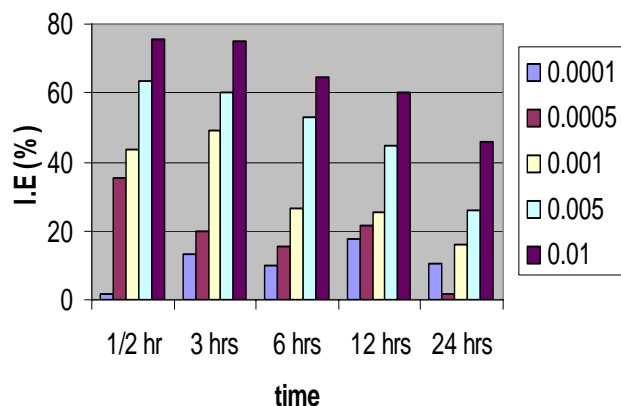


Fig.2 Variation of I.E for different temperatures at different concentrations

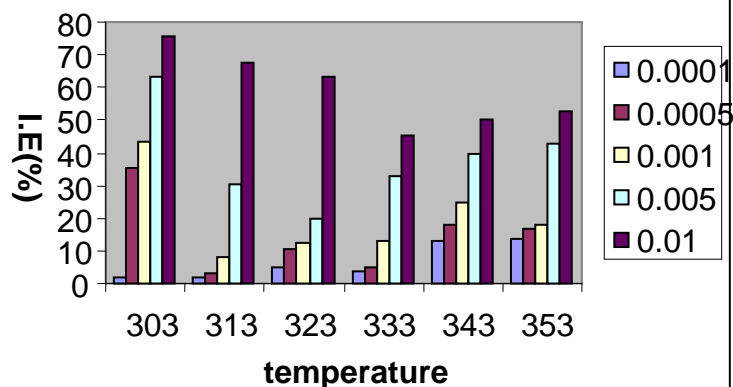
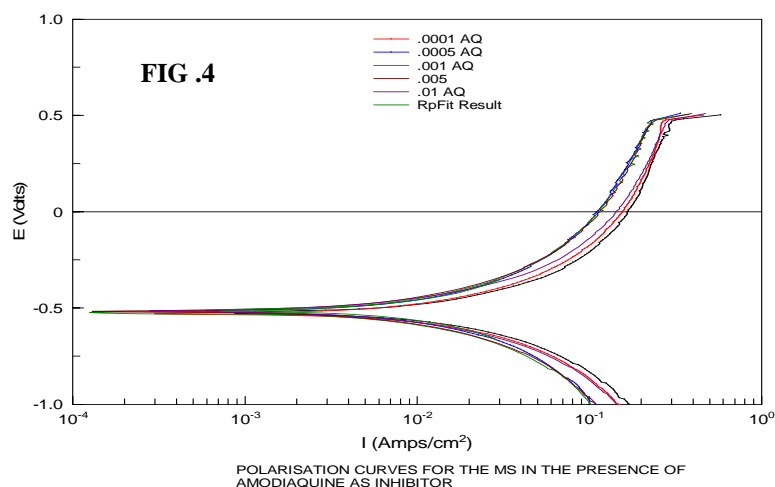
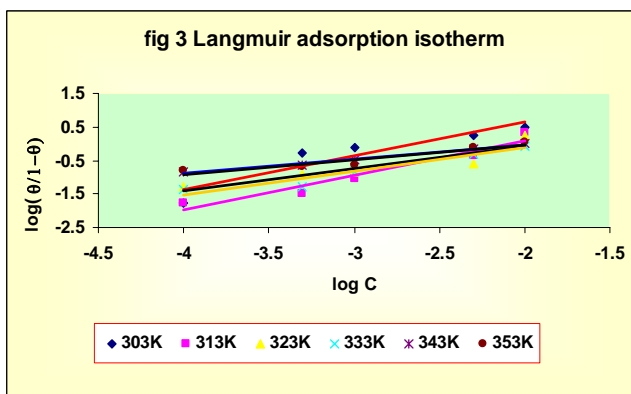


fig 3 Langmuir adsorption isotherm



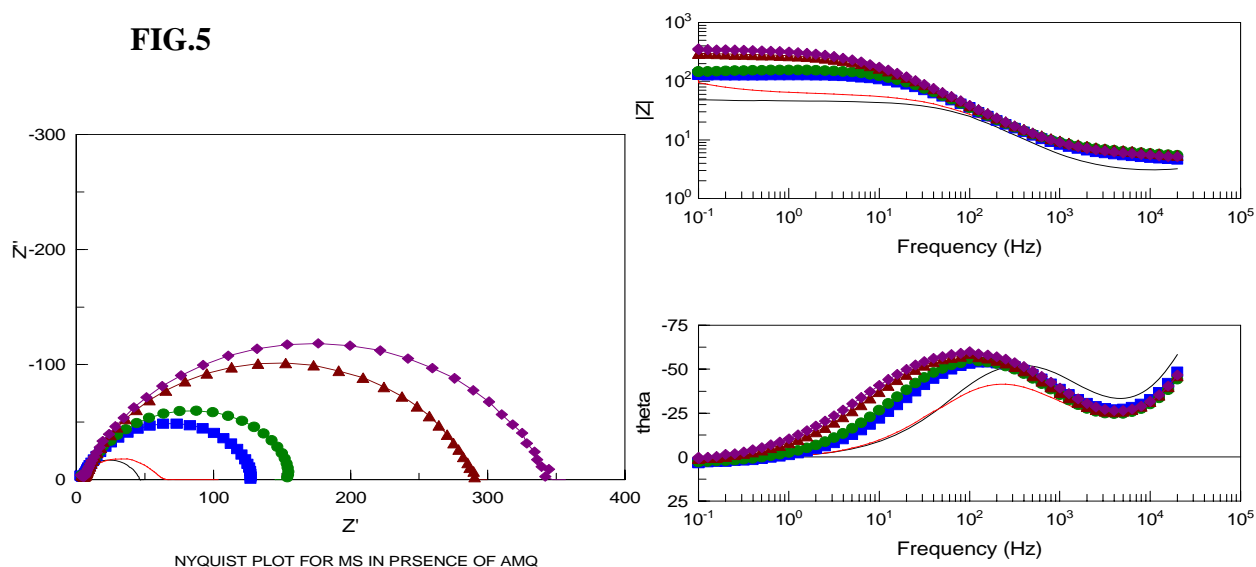


Table 4
Values Of R_{ct} And C_{dl} for the Adsorption of
AMQ on MS in 0.5M H_2SO_4

| S.NO | Conc. (M) | R_{ct} (ohms) | IE(%) | $C_{dl} \times 10^{-5}$ (μ farads) | θ |
|------|--------------------|-----------------|-------|--|----------|
| 1 | Blank | 44.271 | - | 7.9482 | |
| 2 | 10^{-4} | 59.761 | 25.91 | 6.3586 | 0.20 |
| 3 | 5×10^{-4} | 125.07 | 64.60 | 3.17928 | 0.60 |
| 4 | 10^{-3} | 153.21 | 71.10 | 2.7817 | 0.65 |
| 5 | 5×10^{-3} | 286.08 | 84.52 | 1.78774 | 0.80 |
| 6 | 10^{-2} | 339.87 | 86.97 | 1.4704 | 0.81 |

1. G.Trabanelli, corrosion, 47 410. (1991)
2. J.M.Sykes, Br. Corros.J. 25 175. (1990)
3. P.Chatterjee, M.K.Banerjee, K.P.Mukherjee, Indian J.Technol. 29 191. (1991)
4. Vetter, K.J. electrochemische kinetic. Spjringer. Verlag, Berlin 588 -641. (1961),
5. R.M.Hudson, Q.L.Loony & G.J.Warning Br.Corros.J., 2, 81,(1967).
6. A.A.El Hosary & R.M. Salaeh, Int.Symp.Recent Aspects of Electroanal.Chem. & Electrochem. Tech., Chandigash, India, Dec,1982.
7. R.M.Saleh & A.A.El Hosary, Int.Conf.Corros. Inhibitors, Dallas Texas, May 1983.
8. Jha.G.S.Chardhry.B.P & Sanyl.S,2006, Transaction os the SAEST, "Inhibition by Benzoate on corrosion of Mild steel in binary mixture & aggressive ions", 41, 18- 22.
9. K.Aramaki & J.Hackerman, J.Electrochem, SOC.116. 568 (1969).
10. S.Syed Azim, S.Muralidharan & S.Venkatakrishna Iyer.J.Appl.Electrochem. 25, 495 (1995)
11. S.Syed Azim , S.Muralidharas, L.Berjjchmans & S.Venkatakrisna Iyer, Anticorr. Methods & Materials 44 ,30 (1997)
12. S.Syed Azim, S.Muralidharan & S.Venkatakrisna Iyer, Ind.J.Chem.Tech. 5,167 (1998).
13. Ashassi-Sorkhabi.H, Majidi.M.R and Seyvedi.K ,Applied surface science, 225,(1-4) (2002)
14. Abdel-Gaber A.M,Abd-El-Nabey.,B.A., Sidahmed.I.M,El-Zayady. A.M. and. Saadawy M, CorrosionScience .,48 ,9 (2005)
15. Keny S.J., Kumbhar A.G,Thinaharan., C. and Venkateswaran G,Corrosion Science, 50 ,2(2007)
16. N.S.Rawat and A.K.Singh, Bull.Eletro chem, 3, 7(1987)
17. M.El.Achouri,M.S.Hajji,M.Salem J.Aiida and E.Essassi,Corrosion 52 ,103 (1996)