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Metol as Corrosion Inhibitor for Steel

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The inhibition behavior of metol (N-methyl-p-aminophenol sulphate) on mild steel in HCl and H_2SO_4 containing different concentration of metol at room temperature was investigated by chemical and electrochemical method. It has been observed that corrosion rate decreases and inhibition efficiencies and surface coverage degree increases with increasing in metol concentration. The recorded electrochemical data indicated the basic modification of steel surface as a result in a decrease in the corrosion rate. Corrosion inhibition could be explained by considering an interaction between metal surface and the inhibitor. SEM studies revels the formation of passive film on the metal surface.

Keywords: Corrosion inhibition, Metol, Mild steel, Polarization, Impedance

1. INTRODUCTION

Metals generally tend to move to its original state by corrosion process. Mild steel is an alloy form of iron, which undergoes corrosion easily in acidic medium. Acidic solutions are extensively used in chemical laboratories and in several industrial processes such as acid pickling, acid cleaning, acid descaling and oil wet cleaning etc[1]. Also mild steel is used under different conditions in chemical and allied industries for handling alkaline, acid and salt solutions. Chloride, sulphate and nitrate ions in aqueous media are particularly aggressive and accelerate corrosion. Corrosion products are formed when a metal give its electrons to the oxidizing substances. This can be delayed by painting the metal, or other way of protecting these metals from corrosion is to use corrosion inhibitors. Many of the well-known inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms[1-5]. It has been observed that many of the organic inhibitors act by adsorption on the metal surface[6]. This phenomenon is influenced by the nature and surface charge of metal, type of aggressive medium and chemical structure of inhibitors.

The adsorption of corrosion inhibitor depends mainly on physico-chemical properties of the molecule such as functional groups, steric factor, molecular size, molecular weight, molecular structure, aromaticity, electron density of the donor atoms and π- orbital character of donating electrons[7-11] and also on the electronic structure of the molecules[12-13]. Many studies had been made on the corrosion and the inhibition of mild steel in acid media[14-18].

The aim of the present study is to determine the inhibition efficiency of metol for the corrosion of mild steel in HCl and H_2SO_4 medium containing different concentration of inhibitor.

2. EXPERIMENTAL PART

The inhibitor used in this experiment was AR grade metol (N-methyl-p-amino phenol sulphate) and procured from S.d. fine chemicals, Mumbai, India. The structure is shown in figure 1. All the chemicals used for the preparation of solutions were of AR grade (S.d. fine chemicals, Mumbai, India). The solutions were prepared in bi distilled water by using different concentration of metol in 1M HCl and 0.5 M H_2SO_4 solutions. Mild steel strips with chemical composition (C-0.14%, Si-0.17%, Mn-0.35%, P-0.03%, S-0.025% the remainder being Fe.) were used for Weight-loss and electrochemical measurements. Steel strips having a size 6 cm x 1 cm x 0.1 cm were used. Before weight loss and electrochemical measurements the samples were abraded with 600 grit SiC paper, degreased with trichloroethylene vapors and rinsed with acetone and dried.

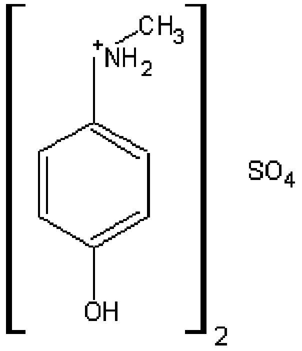

Figure 1. Structural formula of metol

The weight-loss measurements were carried out as described elsewhere [19]. The steel specimens were immersed in 400 cm^3 of HCl and H_2SO_4 in presence and absence of inhibitor with different concentration at 298 K, according to ASTM standards for 2 hour. The inhibition efficiencies (η%) were calculated using the relation:

$$\eta(\%) = \frac{W_u - W_i}{W_u} X\ 100$$

where, W_u and W_i are the average weight-losses of test sample after immersion in corrosive solutions with and without inhibitor respectively.

The potentiodynamic polarization studies were carried out for steel strips having an exposed area of 1 cm^2. The specimens were cleaned using standard procedure. Polarization experiments were performed using different concentration of metol in HCl and H_2SO_4 solutions. A conventional three-electrode compartment, consisting of steel specimen, saturated calomel and platinum as the working, reference and counter electrodes respectively, were selected for the polarization study. The anode and cathode potential values were measured under galvanostatic condition using digital potentiometer (Equiptronics, model EQ- 602). Anodic and cathodic polarization curves were obtained after immersion of the specimens in the aerated solution for 30 minutes. The percentage inhibition efficiency (η%) was calculated using the relationship.

$$\eta\% = \frac{I^{o}_{corr} - I_{corr}}{I^{o}_{corr}} \times 100$$

where I^{o}_{corr} and I_{corr} are the corrosion current densities in presence and absence of inhibitor and were obtained from Tafel plots.

Electrochemical impedance measurements were performed using an instrument Autolab PGSTAT 30 (Meltrohm SWISS MADE). A Cell containing three-electrodes(same polarization setup) was used. Impedance measurements were performed in the frequency range 10 MHz to100 mHz with AC amplitude of ± 5mV.

In order to study the surface nature of the steel sample, the SEM images of steel specimen was taken after anodic polarization in presence and absence of the inhibitor.

Table 1. Corrosion rate and inhibition efficency values obtained by weight loss measurements

Concentration of metol (M)	η (%)	corrosion rate(mmY^{-1})
For 1 M HCl		
Blank		18
0.02	52.4	8.5
0.04	61.9	6.5
0.06	76.04	3.96
0.08	81.9	3.01
0.5 M H_2SO_4		
Blank		21
0.02	46.4	10.8
0.04	55.4	8.82
0.06	64.7	6.23
0.08	77.4	4.87

3. RESULTS AND DISCUSSION

3.1. Weight-loss measurements

The corrosion rate and inhibition efficiency of metol in 1M HCl and 0.5 M H_2SO_4 was given in Table 1. The inhibition efficiency values were increases with increasing in concentration of metol. Inhibition efficiency values were almost same after increasing the concentration of 0.08M metol. Inhibition efficiency values are maximum in case of HCl than H_2SO_4. This is probably due to the lesser surface coverage in H_2SO_4 solution. Again chloride ions have a greater adsorption tendency than sulphate ions on steel[19].

3.2. Polarization study

The polarization studies of steel specimens were carried out in 1M HCl and 0.5M H_2SO_4, solutions separately in absence and presence of different concentrations of metol and they are given in figure 2 and 3. These studies indicated that metol act as mixed type of inhibitor because in presence of inhibitor, the cathodic and anodic curves are shifted towards more negative and positive directions respectively. After increasing the concentration of inhibitor there is marginal change in the %IE values. The polarization parameters such as corrosion potential (E_{corr}) and corrosion current density (I_{corr}) obtained by extrapolation of the Tafel lines are listed in Table 2. The inhibitor present on the surface of metal hinders the attack of corrosive medium and thereby reduces the I_{corr}. The values of cathodic Tafel slope b_c in the presence of inhibitor was changing, which clearly indicates that the prepared compound influence the kinetics of hydrogen evolution reaction. This indicates an increase in the energy barrier for proton discharge leading to less gas evolution. The value of %IE increased with increase in concentration of inhibitor, which indicates higher surface coverage of the metal. The action to corrosion resistance is related to the formation of a passive film on the steel surface, which was further supported by SEM images of the electrode surface.

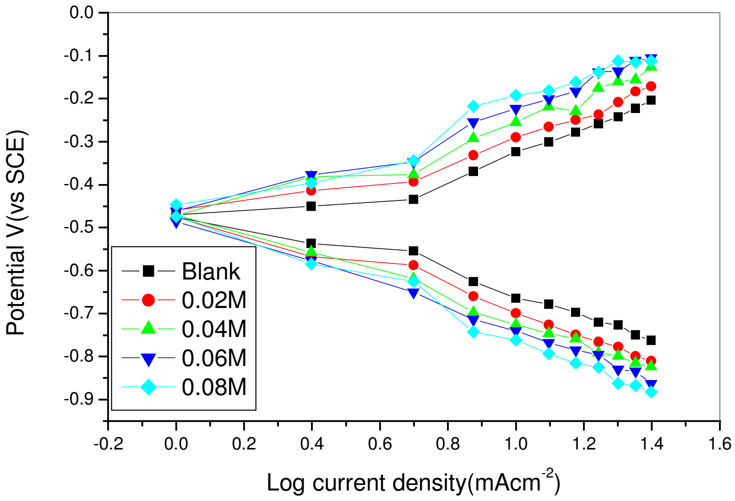

Figure 2. Polarization curves of mild steel in 1 M HCl

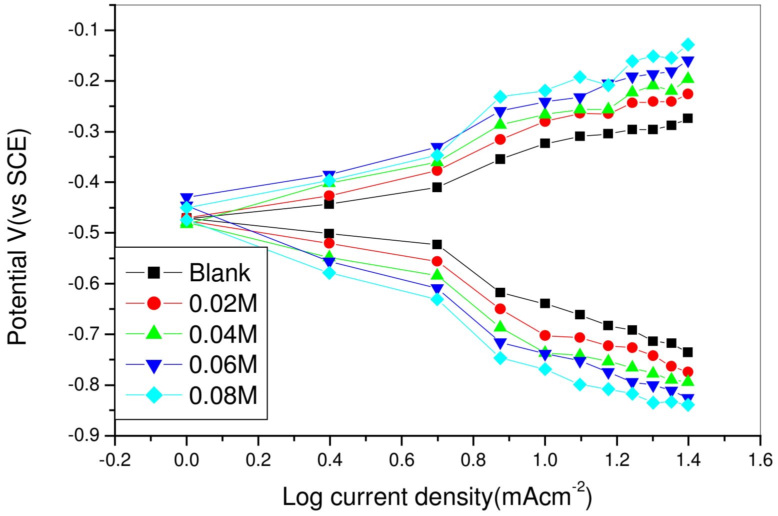

Figure 3. Polarization curves of mild steel in 0.5 M H_2SO_4

Table 2. Electrochemical parameters and inhibition efficiency for corrosion of steel in different corrosive medium at 298 K obtained by Polarization method

Concentration of metol(M)	$-E_{corr}$ (mVolts)	$-b_c$ (mvcm^{-1})	$-b_a$ (mvcm^{-1})	I_{corr} (x10^{-2}mAcm^{-2})	η (%)
For 1 M HCl					
Blank	-0.475	0.240	0.340	4.1	
0.02	-0.485	0.200	0.246	1.9	53.65
0.04	-0.495	0.181	0.284	1.4	65.85
0.06	-0.505	0.190	0.208	1.1	73.17
0.08	-0.525	0.170	0.205	0.9	78.04
For 0.5 M H_2SO_4					
Blank	-0.45	0.245	0.150	2.89	
0.02	-0.475	0.270	0.197	1.57	44.98
0.04	-0.5	0.168	0.197	1.31	54.67
0.06	-0.525	0.192	0.192	1.1	61.93
0.08	-0.535	0.190	0.190	0.8	72.31

It was found from the values in Table 2, the corrosion current density decreases with increase in treatment time and consistent increase of protection efficiency. The protection efficiency was increased with increase in concentration of inhibitor. The corrosion protection efficiency at higher concentration may be attributed to the formation of more stable film on the electrode surface.

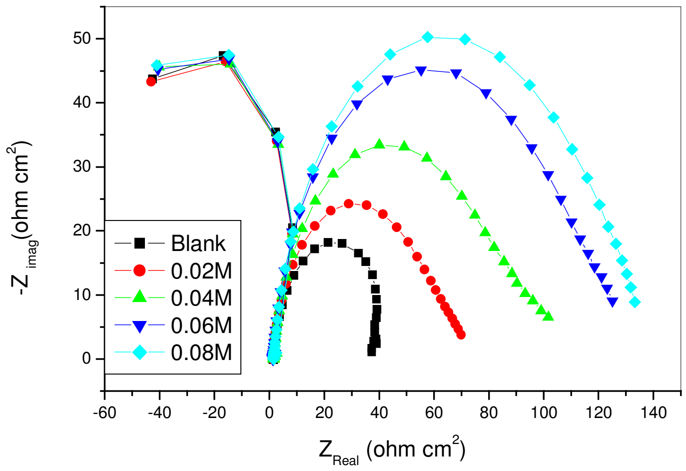

Figure 4. Nyquist plots of mild steel in 1M HCl

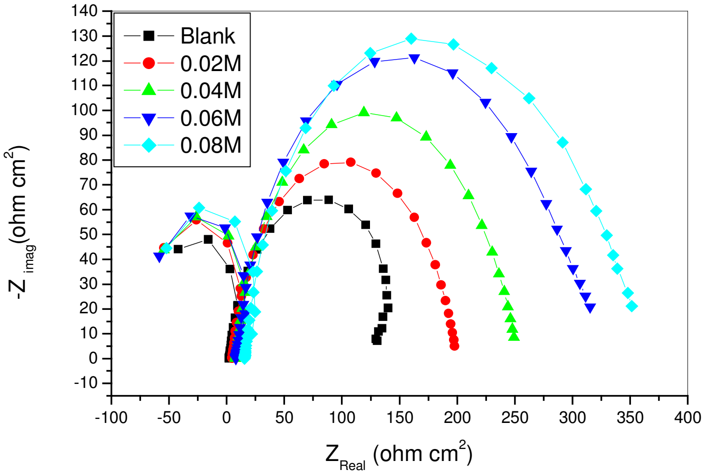

Figure 5. Nyquist plots of mild steel in 0.5 M H_2SO_4

3.3. Impedance measurements (EIS)

Corrosion behavior of mild steel in different corrosive media in the presence of metol was investigated by EIS at room temperature and is given in figure 4 and 5. Various impedance parameters such as polarization resistance (R_p), double layer capacitance (C_{dl}) and $\eta(\%)$ are given in Table 3. The impedance diagrams obtained are not perfect semicircles. This feature had been attributed to frequency dispersion[20]. The results can be interpreted in terms of equivalent circuit of the double layer shown in figure 6. which has been used previously to model the iron/acid interface. The semicircle in all cases corresponds to a capacitive loop. The semicircle radai depend on the concentration of metol. The diameter of the capacitive loop increases with increasing the concentration of metol. The results show R_P values to increase with concentration of inhibitor. Since R_P is inversely proportional to the corrosion current and it can be used to calculate the inhibition efficiency ($\eta_{EIS}\%$) from the relation.

$$(\eta(\%) = \frac{R_p - R_p^I}{R_p^I} \times 100$$

where R_p and R_p^I are the polarization resistances in the presence and absence of inhibitors. It should be noted from Table 3 that polarization resistance values increase with increase in concentration of inhibitor, and the decrease in capacitance values indicated the formation of a surface film.

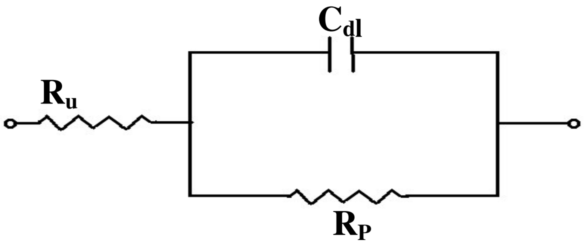

Figure 6. Equivalent circuit

Table 3. Electrochemical parameters and inhibition efficiency for corrosion of steel in different corrosive medium at 298 K obtained by Impedance method.

Concentration	R_p(Ωcm^2)	capacitance(μFcm^{-2})	η_{EIS} (%)
For 1 M HCl			
Blank	30	108	
0.02	70	75	57
0.04	110	76	72
0.06	130	62	76
0.08	140	56	79
For 1 M H_2SO_4			
Blank	110	78	
0.02	200	71	45
0.04	250	69	56
0.06	300	64	63
0.08	375	45	71

3.4. Mechanism of corrosion inhibition

The organic compounds containing S, N and O are known to be effective inhibitors. Its effectiveness depends on the electron density at the functional groups. The electron density can be varied with the help of suitable constituents and thus the inhibition action of an inhibitor [21].

The corrosion inhibition property of the metol can be attributed to the presence of heteroatom and π electrons on benzene ring. These factors play the vital role in the adsorption of the inhibitor and the formation of co-ordinate bond with metal. The adsorption of inhibitor on the steel surface can occur either directly by the interactions between the π electrons of the inhibitor and the vacant dorbitals of metal surface atoms. Also there may be an interaction of inhibitor with adsorbed sulphate ions leads to the adsorption of inhibitor [22-23]. The adsorption of inhibitor on steel may also be due to the interaction of sulphur and oxygen with the surface atoms of metal. The interaction causes the adsorption of metol on corroding sites of metals and prevents the anodic reaction. As inhibitor concentration increases, it covers more and more surface area and results in the reduction of corrosion rate.

3.5. SEM analysis

The surface morphology of steel surface was studied by scanning electron microscopy (SEM). figure 7 Shows the SEM photograph of the steel surface with and without inhibitor after anodic polarization (15 min) in the current density range of 5 mA cm^{-2} in hydrochloric acid media. The SEM photographs showed that the surfaces of metal has pits and corrosion product, but in presence of inhibitor they are minimized on the metal surface. It indicates the formation of passive layer on the metal surface. So the corrosion rate is decreased in the presence of inhibitor and reduces the electrochemical reaction.

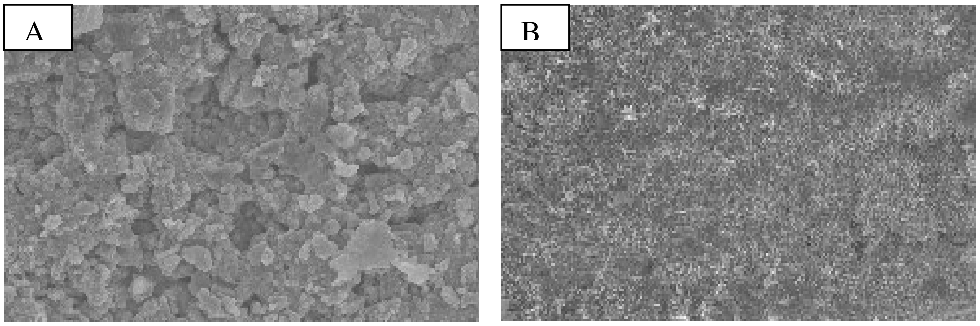

Figure 7. SEM images of mild steel in absence (A) and presence of inhibitor(B)

4. CONCLUSIONS

1. metol act as good corrosion inhibitors for mild steel in HCl and H_2SO_4 medium
2. metol acts as mixed type of inhibitor
3. The inhibition action of the metol against corrosion is due to the process of adsorption which is revealed by scanning electron micrographs
4. Corrosion inhibition efficiency of metol increased with increasing concentration
5. Inhibition efficiencies of the metol obtained from weight loss, polarization, EIS methods match one another
6. Small amount of inhibitor is gives more efficiency.

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