Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2012, 4(7):3414-3419

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Salicylideneaniline as inhibitor for the corrosion of mild steel in 1.0 N hydrochloric acid

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ABSTRACT

The inhibitive influence of salicylideneaniline on the corrosion of mild steel in 1.0 N hydrochloric acid was studied by weight loss method and polarization measurements. The values of percentage inhibition efficiency, determined by these methods, showed close agreements. The corrosion decreased with increasing addition of salicylideneaniline probably due to the progressive adsorption of the inhibitor on the metal surface. The maximum inhibition efficiency was found to be 39.71%. The inhibition process was tested for Langmuir adsorption isotherm, kinetic thermodynamic modal of El-Awady et al. Temkin and Flory-Huggins isotherms. The best fit isotherm was the isotherm of El-Awady et al, The phenomenon of physisorption was proposed for the process of inhibition. The open circuit potential of mild steel in 1.0 N HCl, in the presence of the inhibitor of varying concentrations, did not show any significant shift in its values. The polarization studies revealed that the corrosion of mild steel in 1.0 N HCl was predominantly under anodic control, in the presence as well as in the absence of the inhibitor. The nature of inhibition was found to be of mixed type.

Keywords: salicylideneaniline, anodic control , physisorption lateral interaction parameter.

INTRODUCTION

Mild steel is prone to severe corrosion in aggressive environments such as acidic medium. The influence of several aromatic organic compounds containing nitrogen, on the corrosion resistance of steel in acid media have been reported[1-8]. Among the wide range of acid solutions, HCl is used in various industries for pickling of ferrous alloys and steel. Besides, it is also used to stimulate and to increase the rate of oil flow in petroleum oil wells and to descale tubing and casing materials used in these oil production wells. So, the study of corrosion inhibition of mild steel in HCl has greater importance. The present investigation is aimed to study the inhibitive influence of salicylideneaniline on corrosion of mild steel in 1.0 N hydrochloric acid.

EXPERIMENTAL SECTION

The chemical composition of the mild steel coupons used for the study was: (wt %) Mn (0.6), P(0.30), C(0.15) and Si(0.04) besides iron, analyzed by standard method[8-10]. Mild steel coupons, measuring 3 cm x 1 cm x 0.1 cm were used in weight loss measurements. The specimens were polished with different grades of emery papers, degreased with acetone and finally rinsed with double distilled water. These were dried and stored in vacuum desiccators containing silica gel. The solutions were prepared using chemicals of Analar grade and double distilled water.

Weight loss study

The inhibitor, salicyledeneaniline ,was prepared according to the procedure reported [11]. The mild steel specimens were suspended with the help of glass hooks in beakers containing 100 ml of 1N hydrochloric acid, without and with the inhibitor for about 3 hours. The specimens were removed after the exposure period, washed with water and rubbed with bristle brush to remove any corrosion product and finally washed with acetone and distilled water. They were dried in an oven and re-weighted to determine the weight loss.

The experiments were carried out in triplicate to ensure reproducibility and the mean values of weight loss were computed. The percentage inhibition (P.I) efficiency was calculated using the following equation:

$$\text{P.I.} = \frac{w_0 - w_i}{w_0} \times 100 \qquad (1)$$

where w_0 and w_i are the weight losses in uninhibited and inhibited corroding solutions, respectively.

OCP Measurement

The mild steel specimens were immersed in the test solutions without and with the inhibitor and the potentials were measured, under open-circuit condition, as a function of time against a saturated calomel electrode using a high impedance millimeters. The measurements were made until a steady state value was attained.

Galvanostatic polarization measurement

The flag shaped metal specimens, with sufficiently long tail, were cut from the mild steel sheet, leaving a working area of $1cm^2$ on one side of the specimen and a small portion at the tip of the tail for providing electrical contact. The rest of the surface was coated with enamel lacquer. The electrochemical investigations were carried out in a three compartment cell with the mild steel electrode as the working electrode a platinum electrode as the counter electrode and a saturated calomel electrode as the reference electrode.

After measuring OCP value, the mild steel electrode was polarized cathodically by passing known values of current, in the increasing steps of 10 mA min^{-1} from a current regulator and the steady potential was measured at each current density.

After cathodic polarization was over, the working electrode was brought back to the OCP and then polarized anodically as explained above.

The corrosion current density, I_{corr}, and corrosion potential, E_{corr} were evaluated by the extrapolation of the cathodic and anodic Tafel plots. The measurements were repeated until reproducible data were obtained.

The inhibition efficiency, P.I was calculated from I_{corr} values.

$$\text{P.I.} = \frac{I_{un} - I_{in}}{I_{un}} \times 100$$

where I_{un} and I_{in} are the corrosion current densities measured in the absence and in the presence of inhibitor, respectively.

RESULTS AND DISCUSSION

The values of corrosion rate and percentage inhibition efficiency were obtained by weight loss measurement at different concentrations of salicylideneaniline. The inhibition efficiency increases with the increasing concentrations. The maximum inhibition was found to be 38.70%.

Table: 1 Effect of salicydeneaniline on the rate of corrosion of mild steel in 1.0 N HCl at 30 ± 1^0C. (weight loss studies)

[Inhibitor] x 10^3,M	Rate of corrosion x 10^4 gcm^{-2} h^{-1}	Percentage Inhibition
Blank	5.7407	-
1	5.2778	8.06
2	5.0926	11.28
3	4.7222	17.74
4	4.444	22.58
5	4.2600	25.79
6	4.0740	29.03
7	3.889	32.27
8	3.7038	35.48
9	3.6111	37.09
10	3.519	38.70

The OCP shifted towards positive direction in the presence of inhibitor and it indicates that the inhibitor acts as an anodic inhibitor. But the shift in OCP is small which suggests that complete polarization curve should be considered to confirm whether the inhibition is cathodic (or) anodic (or) of mixed type.

Table2 Anodic and cathodic polarization of mild steel in 1.0 N HCl without and with salicylideneaniline

[Inhibitor] x 10^3 ,M	**OCP , V**	**E_{corr}, V**	**I_{corr}, mA cm^{-2}**	**Percentage Inhibition**
Blank	-0.562	-0.55	34.67	-
1	-0.540	-0.52	31.63	8.76
2	-0.548	-0.49	30.21	12.86
3	-0.535	-0.50	28.82	16.81
4	-0.515	-0.55	27.53	20.55
5	-0.520	-0.52	26.29	24.13
6	-0.504	-0.53	25.10	27.55
7	-0.509	-0.46	23.97	30.82
8	-0.520	-0.53	22.89	33.93
9	-0.522	-0.50	21.87	36.88
10	-0.519	-0.43	20.89	39.71

The anodic and cathodic polarizations curves of mild steel in 1N HCl were recorded in the absence and in the presence of inhibitor under galvanostatic condition. It was observed that anodic polarization was greater than cathodic polarization in all solutions.

The cathodic and anodic polarization curves are shifted towards lower current density values in the presence of the inhibitor. Thus the nature of inhibition is of mixed type.

This observation indicates that the inhibitor suppresses both anodic as well as cathodic reactions with the increasing addition of the inhibitor. But only a small shift in E $_{corr}$ is observed.

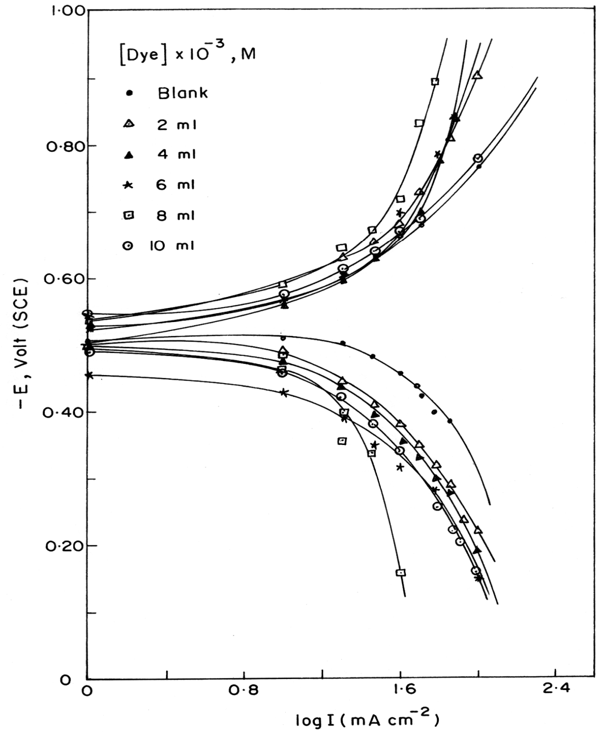

Fig:1 Anodic and cathodic polarization of mild steel in 1.0 N Hydrochloric acid with and without salicylieneaniline

According to Damaskin[11], the increase in slope, in the presence of inhibitor may be attributed to a change in the mechanism of the corrosion process when the inhibitor is adsorbed on the metal surface. However, the slope did not increase, significantly.

The inhibition efficiencies, calculated from weight loss measurements and polarisation measurements show close agreement.

Table: 3 Comparison of inhibition efficiency measured by weight loss and polarization method

[Inhibitor] $x10^3$,M	Inhibition Weight loss method	Efficiency Polarization method
1	8.06	8.76
2	11.28	12.86
3	17.74	16.81
4	22.58	20.55
5	25.79	24.13
6	29.03	27.55
7	32.27	30.82
8	35.48	33.93
9	37.09	36.88
10	38.70	39.71

No passivation is observed at any concentration of the inhibitor. The addition of these inhibitor to the acid solution did not cause any significant change in the values of $E_{corr..}$ The parallel anodic and cathodic polarization curves show that decrease in corrosion current is observed due to the simple blocking effect of inhibitor adsorbed on the metal surface, which in turn decreased the dissolution reaction rate[12,13,14]. Thus salicylideneaniline inhibit corrosion of mild steel in acid solution by blocking the active sites on steel surface.

The surface coverage 'θ' is determined from polarization data, according to the equation

$$'\theta' = \frac{I_{un} - I_{in}}{I_{un}} \quad \text{--------} \quad (2)$$

where I_{un} and I_{in} are the corrosion current densities measured in the absence and in the presence of inhibitor, respectively. It is seen that 'θ' increases with the increase of the concentration of inhibitor. The θ values were fitted to Langmuir adsorption isotherm. The Langmuir adsorption isotherm is given by,

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad \text{--------} \quad (3)$$

where K_{ads} is adsorption constant and C is the concentration of the inhibitor. A plot of θ vs. C is linear (Fig.2) with regression coefficient, R equal to 0.94 showing that the Langmuir isotherm is obeyed. The slope of the Langmuir plot is greater than one (slope =1.26). Hence the adsorption behaviour of salicylideneaniline can be more appropriately represented by a modified Langmuir isotherm suggested by Villamil et al [15] as follows

$$\frac{C}{\theta} = \frac{n}{K_{ads}} + n\,C \quad \text{--------} \quad (4)$$

The experimental values of θ were, therefore, fitted into the El-Awady's kinetic/thermodynamic model given below.

$$\log\frac{\theta}{1-\theta} = \log K + y \log C \quad \text{--------} \quad (5)$$

where the adsorption equilibrium constant, $K_{ads} = K^{1/y.}$. The values of 1/y < 1, implies multilayer adsorption, while 1/y > 1 suggests that the inhibitor occupies more than one active sites.

In the present study the value of 1/y=1.1 (Table 3), suggesting that one inhibitor occupies one active site. This is further confirmed by fitting the θ values to Flory-Huggins isotherm.

$$\log\frac{\theta}{C} = \log K_{ads} + x \log\,(1-\theta) \quad \text{--------} \quad (6)$$

where x is the number of active sites occupied by an inhibitor molecule [13].The value of x=1.39 further confirms the above result that the inhibitor occupies one active site.
The Temkin isotherm is expressed as

$$\theta = \frac{2.303 \log K_{ads}}{2a} + \frac{2.303 \log C}{2a} \quad \text{--------} \quad (7)$$

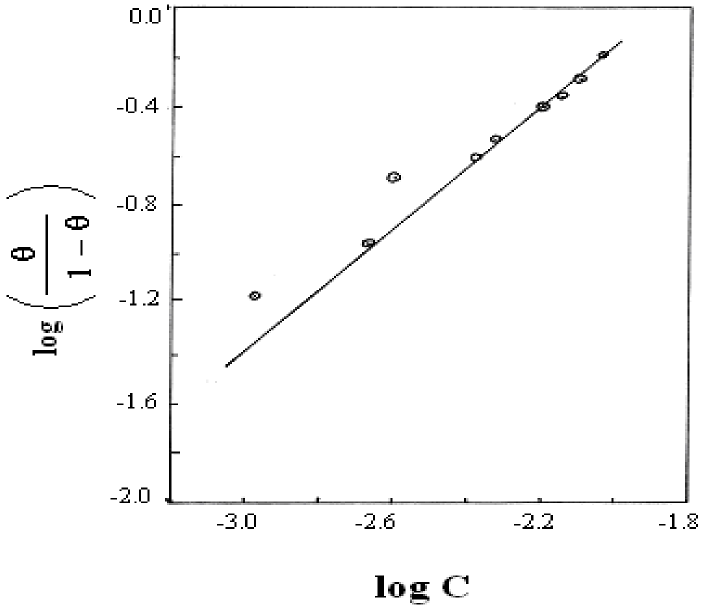

Fig. 2 El-Awady et al., plot for the inhibition corrosion of mild steel by salicylideneaniline in 1.0 N HCl.

The plots of θ against log C is linear (Fig.2) and the lateral interaction parameter a, is negative indicating that repulsion exists in the adsorption layer[14]. The K_{ads} value is low, and it shows weak interaction between the inhibitor and metal surface. The standard free energy of adsorption, $\Delta G°_{ads,}$ is given by the following equation [15].

$\Delta G°_{ads}$ = -2.303 RT (log K_{ads} x 55.55) -------- (9)

where 55.55 is the molar concentration of water. The $\Delta G°_{ads}$ was found to be -18.62 kJ mol^{-1}. The negative value of $\Delta G°_{ads}$ shows that the adsorption of the inhibitor on the metal surface is spontaneous. The value is less than -20 kJ mol^{-1}. Generally, values of $\Delta G°_{ads}$ up to -20 kJ mol^{-1} are consistent with electrostatic interactions between charged inhibitor molecules and the metal (physisorption) while those around -40 kJ mol-1 or higher are associated with chemisorption as a result of transfer of electrons from the inhibitor to the metal surface to form a co-ordinate type bond.

This observation supports the view that the inhibition is mainly by the physisorption of the salicylideneaniline on the metal surface.

Table4 Values of Langmuir, Temkin, El-Awady et al and Flory-Huggins isotherm parameters.

Adsorption Isotherm	**Correlation Coefficient,R**	**$\Delta G°_{ads}$ kJmol^{-1}**	**1/y or x**	**Lateral interaction parameter, a**
Langmuir	0.93696	-21.064	---	---
El-Awady et al	0.9890	-20.522	1.0988	---
Flory-Huggins	0.844255	-21.113	1.3931	---
Temkin	0.96211	-28.23	---	-3.4753

CONCLUSION

The corrosion of mild steel in 1N HCl was found to decrease with the increasing concentration of the inhibitor salicylideneaniline. The inhibition efficiency values obtained from mass loss studies and polarization measurements showed fairly good agreement. The type of corrosion was shown to be physisorption. The corrosion inhibition appears to be of mixed type .

Acknowledgement
The authors are thankful to the Principal, Management and the HOD of Chemistry, Bishop Heber College, Trichirappalli for providing facilities.

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