

Adsorption Isothermal Analysis and Synergistic Influence of Rochelle salt on Inhibition Efficiency of *Eichhornia crassipes* (Water Hyacinth) on Mild Steel in Aqueous Medium

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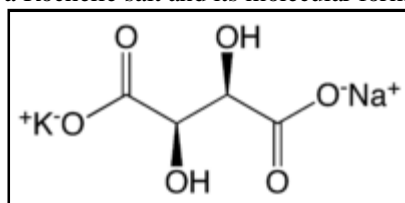
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ABSTRACT: Adsorption of ternary formulation of *Eichhornia crassipes* (Water Hyacinth) leave extract with Zn^{2+} and Rochelle salt on the corrosion of mild steel was investigated by gravimetric method at the temperature range of 308 K to 348 K in 60 ppm Cl^- containing aqueous medium. The corrosion kinetic parameter such as activation energies (E_a) and thermodynamic parameters of Standard entropy of adsorption (ΔS°_{ads}), standard heat of adsorption (ΔH°_{ads}) for the adsorption process were determined and discussed. The negative value of ΔG°_{ads} indicates that the inhibitor formulations have been spontaneously adsorbed on the surface of the mild steel. The evaluated heat of adsorption values ΔH°_{ads} are all negative, an indication that the heat of adsorption process onto mild steel surface is exothermic. The negative values of entropy of activation, ΔS°_{ads} , signify that the activated complex in the rate determining step represented an association, rather than dissociation.

KEYWORDS: Corrosion inhibition, Water Hyacinth, mild steel, Activation energy, Langmuir adsorption isotherm.

I. INTRODUCTION

Corrosion inhibitors are the chemical compounds which are used to protect the metals from aggressive corrosion environment. Chromates, phosphates, molybdates etc. and a variety of organic compounds containing heteroatom like nitrogen, sulphur and oxygen have been investigated as corrosion inhibitors⁽¹⁻⁶⁾. Sodium Potassium Tartrate Tetrahydrate (SPT), is called as a Rochelle salt and its molecular formula is $KNaC_4O_6 \cdot 4H_2O$.



Molecular structure of SPT

Sodium Potassium Tartrate (SPT) is chosen as the synergist for the present study due to presence of two carbonyl groups and two hydroxyl groups in its structure, which provide complex ability with metal ions⁷. *E. crassipes* is commonly known as Water Hyacinth, noted as one of the most important noxious fresh water weeds⁸, ranked 8th in the list of the world's ten most serious weeds⁹ according to K.R.Reddy et al., (1984). In spite of long list of harmful effect, in recent years, it has been found useful in corrosion prevention, due to the presence of certain hetero atom containing active compounds such as chlorophylls and carotenoids, phenols, alkaloids and terpenoids have been

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successfully obtained from *E.crassipes* extracts¹⁰. In our work, sodium potassium tartrate (SPT) which is an environment friendly corrosion inhibitor is used as a synergist with the formulation of 10 ppm Water hyacinth leave extract (WHLE) and 50 ppm Zn²⁺ in the aqueous environment containing 60 ppm Cl⁻.

II. MATERIALS AND METHODS

1. Preparation of Specimen

Mild steel specimens of size 1.0 cm × 4.0 cm × 0.2 cm and chemical composition 0.026 % sulphur, 0.06 % phosphorous, 0.4 % manganese, 0.1% carbon and the rest iron were polished to a mirror finish and degreased with acetone and used for the temperature studies.

2. Preparation of the Water Hyacinth Leaves (WHLE) extract

In the present work, the Water Hyacinth leaves were collected from Shanmuga River in Palani. Fresh leaves of this plant were cleaned, chopped into small pieces and shade dried. The extract was prepared by refluxing 5g of powdered leaves in 500ml dd water for 5hr and kept overnight. Then it was filtered and the volume of the filtrate was made up to 500ml using dd water and this was taken as stock solution.

3. Sodium Chloride Stock solution

Exactly 9.8g of Sodium chloride was dissolved in triple – distilled water and made up to one litre in a standard measuring flask. A hundred fold dilution yields 60ppm Cl⁻ ion concentration.

4. Zinc Sulphate Stock solution

Exactly 4.4g of Zinc sulphate was dissolved in triple – distilled water and made up to one litre in a standard measuring flask. A hundred fold dilution yields 10ppm Zn²⁺ ion concentration.

5. Weight – loss method

Mild steel specimens were immersed in 100 ml of the aqueous medium containing 60 ppm Cl⁻ ions in the absence and presence of various concentrations of the inhibitor WHLE with 50 ppm of Zn²⁺ for one day. The Inhibition efficiency (IE %) was calculated using the equation,

Inhibition efficiency,

$$IE(\%) = \frac{W_o - W_i}{W_o} \times 100 \quad \text{-----} \quad (1)$$

Surface coverage,

$$(\theta) = \frac{W_o - W_i}{W_o} \quad \text{-----} \quad (2)$$

Where W_o and W_i are the weight loss for mild steel in the absence and presence of inhibitor.

6. Determination of corrosion Rate

The corrosion rate (CR) is directly proportional to the weight loss / cm² in a specified time and was calculated by the formula,

$$CR = \frac{87.6 \times W}{DAT} \quad \text{mmpy} \quad \text{-----} \quad (3)$$

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Where, W = weight loss in mg.
D = density of mild steel (7.85 g / cm² for mild steel),
A = Area in cm²,
T = Exposure time in hours.

7. Effect of temperature

For this investigation, the effect of temperature was studied in the range 308 - 348 K. The apparent activation energies E_a for the corrosion¹⁶⁴⁻¹⁶⁶ in presence and absence of inhibitor were evaluated from Arrhenius equation.

$$CR = A \exp(-E_a / RT) \quad \text{----- (4)}$$

Where CR is the corrosion rate, E_a is the apparent activation energy of the Corrosion reaction, R is the gas constant, T is the absolute temperature and A is the Arrhenius pre-exponential factor.

The free energy of adsorption, ΔG^o_{ads}, is calculated using the equation,

$$\Delta G^{\circ}_{ads} = - RT \ln (55.5 \times K_{ads}) \quad \text{----- (5)}$$

Where 55.5 is the molar concentration of water in solution and K_{ads} = θ / C (1-θ)

III. RESULTS AND DISCUSSIONS

According to Dehri and Ozcan (2006)¹¹, the relationship between the temperature dependence of percent inhibition efficiency (IE%) of an inhibitor and the activation energy (E_a) found in its presence was given as follows:

- Inhibitors whose IE(%) decrease with temperature increase, the value of activation energy (E_a) found is greater than that in the uninhibited solution
- Inhibitors whose IE(%) does not change with temperature variation, the activation energy (E_a) does not change with the presence (or) absence of inhibitor
- Inhibitors whose IE(%) increases with temperature increases, the value of activation energy (E_a) found is less than that in the solution.

The results obtained from temperature studies of the corrosion of mild steel in 60 ppm Cl⁻ ion containing aqueous medium in the absence and presence of ternary inhibitor of various concentration of SPT with 10 ppm WHLE and 50 ppm Zn²⁺ in the temperature range 308-348K are tabulated in Table 1. The results of Table 1, revealed that increasing temperature increases corrosion rate and decreases IE at all the concentrations studied.

Table 1. CR and IE (%) of WHLE (10 ppm) – Zn²⁺ (50 ppm) in 60ppm Cl⁻ in different concentrations of SPT at various temperatures

Immersion time : One hour

Concn. of SPT (ppm)	308 K		318 K		328 K		338 K		348 K	
	IE (%)	CR mmpy	IE (%)	CR mmpy	IE (%)	CR mmpy	IE (%)	CR mmpy	IE (%)	CR mmpy
0	-	1.0043	-	1.2275	-	1.7855	-	2.0087	-	2.6782
10	71	0.2901	70	0.3683	63	0.6696	47	1.0713	42	1.5623
20	86	0.1451	73	0.3348	69	0.5580	67	0.6696	63	1.0043
40	89	0.1116	76	0.2901	75	0.4464	71	0.5914	69	0.8369
50	94	0.0558	79	0.2567	78	0.4017	72	0.5580	71	0.7811

The results of Table 1, revealed that increasing temperature increases corrosion rate and decreases IE at all the concentrations studied.

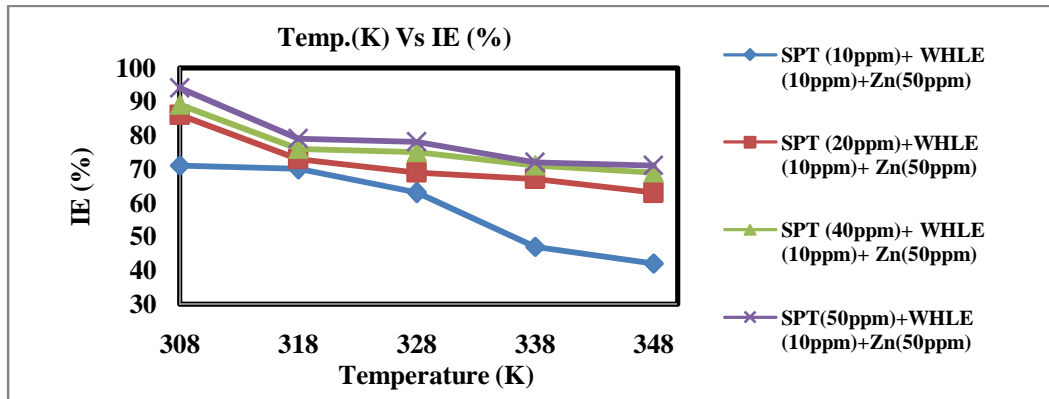


Figure 1. Variation of IE (%) for WHLE (10ppm) –Zn²⁺(50 ppm) concentration with SPT at different temperatures

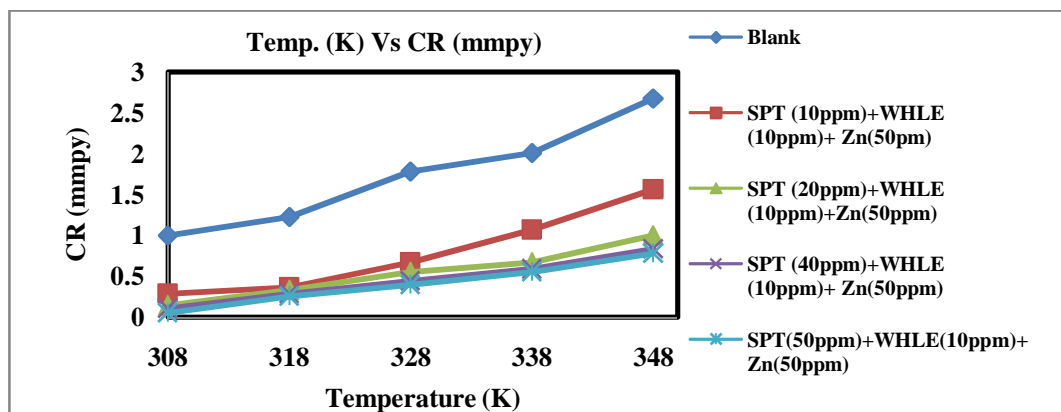


Figure 2. Corrosion rates (mmpy) for WHLE –Zn²⁺(50 ppm) concentration with SPT at different temperatures

Here, the inhibition efficiencies are found to decrease and Corrosion rate increases with increase of temperature at all concentrations of the inhibitor formulations are depicted in Figure 1 and Figure 2.

3.1. Corrosion Kinetic Parameters

3.1.1. Activation Energy (E_a)

The corrosion rate is related to temperature by the Arrhenius equation (4). Figure 3, shows the plot of log CR Vs 1/T, providing linear plots with slope gives the value of -E_a/2.303R and intercept gives the value of log A.

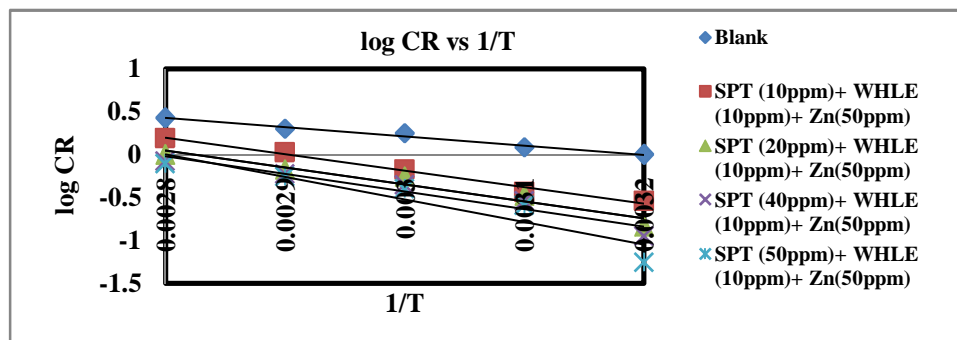


Figure 3. Arrhenius plots for the corrosion of mild steel at different concentrations of inhibitor.

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From Figure 3, the E_a values are calculated for various concentrations and are listed in Table 2. An investigating the results obtained in Table 2, it is clear that E_a values in the presence of inhibitor formulation WHLE (10 ppm) + Zn^{2+} (50 ppm) with various concentrations of SPT are higher (50.35kJ/mol) than that in the absence (-20.41kJ/mol).

Table 2. Activation energy values for different concentrations of SPT with WHLE(10ppm)- Zn^{2+} (50ppm) in 60ppm Cl⁻ at various temperatures

Concn. of SPT (ppm)	Ea (kJ/mol)
Blank	20.41
10	36.88
20	37.94
40	39.43
50	50.35

The higher the activation energies imply a slow reaction and that the reaction is very sensitive to temperature¹². The increase in the activation energy (E_a) in the presence of ternary inhibitor mixture signifies physical adsorption (from 36.88 to 50.35kJ/mol)¹³.

3.2 Interpretation of Thermodynamic Data

The thermodynamic parameter such as free energy values of adsorption (ΔG^0_{ads}) of ternary inhibitor [WHLE (10 ppm) + Zn^{2+} (50 ppm) + SPT (50 ppm)] on mild steel surface were calculated using equation (5). In the present work, the negative values of ΔG^0_{ads} (Table 3) clearly indicated the spontaneous adsorption of ternary inhibitor formulation on mild steel surface¹⁴. According to Li et.al., (2010)¹⁵, generally the values of ΔG^0_{ads} upto -20kJ/mol signify physisorption, which is consistent with electrostatic interaction between charged molecules and a charged metal. The values around -40kJ/mol (or) higher involve charge sharing (or) transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond. The obtained ΔG^0_{ads} values from Table 3 were vary (-22.06 to -25.039 kJ/mol) more or less around -25.039 kJ/mol, indicates that adsorption of ternary inhibitor on mild steel in 60 ppm Cl⁻ ion containing aqueous medium at various temperature ranges (308-348K) was physisorption¹⁶.

Table 3. Thermodynamic Parameters of adsorption of various SPT concentration with WHLE (10ppm) – Zn^{2+} (50 ppm) in 60ppm Cl⁻ medium on mild steel

Various Concn. of SPT(ppm)	ΔG^0_{ads} kJ/mol					ΔS^0_{ads} kJ/mol	ΔH^0_{ads} kJ/mol
	308 K	318 K	328 K	338 K	348 K		
10	-24.388	-25.039	-24.908	-23.857	-23.976	-0.0201	-31.0133
20	-24.863	-23.559	-23.775	-24.233	-24.421	-0.0021	-24.8590
40	-23.859	-22.233	-22.730	-22.793	-23.219	-0.0072	-25.3284
50	-25.213	-22.060	-22.499	-22.394	-22.859	-0.0437	-37.3517

Standard entropy of adsorption (ΔS^0_{ads}) and standard heat of adsorption (ΔH^0_{ads}) are obtained by the thermodynamic basic equation $\Delta G^0_{ads} = \Delta H^0_{ads} - T\Delta S^0_{ads}$. The plot of ΔG^0_{ads} Vs T is given in Figure 4. From the slope and intercept of that plots ΔS^0_{ads} and ΔH^0_{ads} were calculated are listed in Table 3. While an endothermic adsorption process ($\Delta H^0 > 0$) is attributed unequivocally to chemisorption, an exothermic adsorption process ($\Delta H^0 < 0$) may involve either physisorption (or) chemisorption (or) a mixture of both processes. From the results in Table 3, the negative value of ΔH^0_{ads} indicates that an exothermic reaction is takes place which means lower IE at high temperature. This indicated the gradual desorption of inhibitors¹⁷.

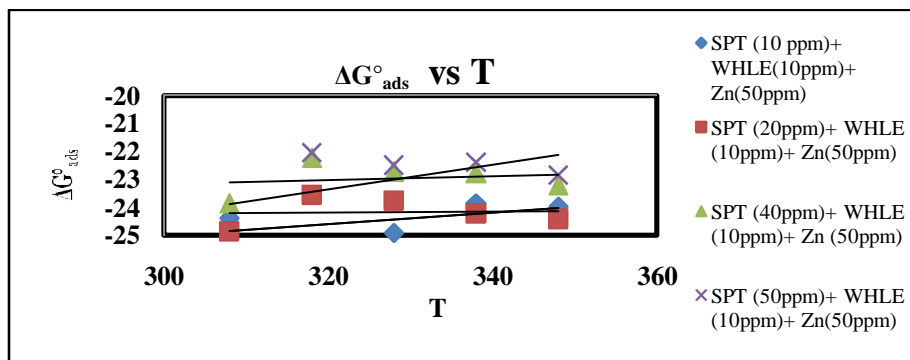


Figure 4. ΔG°_{ads} vs T

The negative values of ΔS°_{ads} might be explained that as, before the adsorption of inhibitor molecules on to surface of the mild steel, they are move freely in the bulk of the solution (inhibitor molecules were chaotic), but with the process of adsorption, inhibitor molecules were orderly adsorbed onto the mild steel surface, as a result a decrease in entropy is observed. This order may more probably be explained by the possibility of the formation of iron complex on the metal surface¹⁸.

3.3. Adsorption Isotherm

Adsorption isotherms are very important in understanding the mechanism of organo – electrochemical reactions¹⁹. The degree of surface coverage (θ) values of different concentrations of SPT with 10 ppm WHLE+50ppm Zn^{2+} at various temperature ranges (308-348K) were presented in Table 4.

Table 4. Calculated values of degree of surface coverage (θ) for mild steel in various concentrations of SPT with WHLE(10ppm) + Zn^{2+} (50 ppm) mixture at different temperatures

Concn.of inhibitor SPT (ppm)	Degree of surface coverage (θ)				
	Temperature (K)				
	308 K	318 K	328 K	338 K	348 K
10	0.7111	0.7000	0.6250	0.4667	0.4167
20	0.8556	0.7273	0.6875	0.6667	0.6250
40	0.8889	0.7636	0.7500	0.7056	0.6875
50	0.9444	0.7909	0.7750	0.7222	0.7083

By plotting the values of $\log (C/\theta)$ Vs $\log C$, a straight line was obtained with a slope of almost unity (Figure 5).

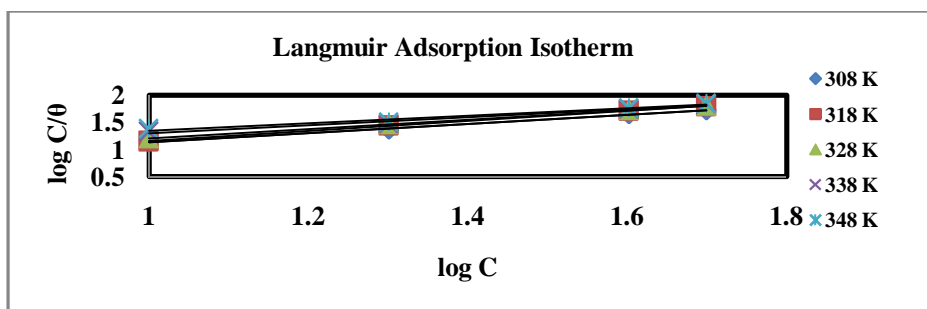


Figure 5. Langmuir Adsorption isotherm of SPT-WHLE(10ppm)– Zn^{2+} (50 ppm) in 60ppm Cl^- ion containing aqueous medium

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The results from Figure 5 are presented in Table 5. From the slope value, it indicates that the adsorption of ternary inhibitor formulation on mild steel surface obeyed the Langmuir adsorption isotherm meaning that there was no interaction between the adsorbed species²⁰.

Table 5. Correlation coefficients deduced from Langmuir isotherm for mild steel in 60ppm Cl⁻ at various temperatures

Temperature (K)	Langmuir Isotherm		
	Slope	Intercept	R ²
308 K	0.838	0.298	0.996
318 K	0.927	0.229	0.999
328 K	0.867	0.336	1.000
338 K	0.742	0.561	0.978
348 K	0.683	0.668	0.972

From the slope value, it indicates that the adsorption of ternary inhibitor formulation on mild steel surface obeyed the Langmuir adsorption isotherm meaning that there was no interaction between the adsorbed species²⁰.

IV. CONCLUSION

The following conclusions are obtained from this study,

- Inhibition efficiency increased with increase in concentration of the inhibitor, but decreased with increase in temperature.
- The increase in the activation energy (E_a) on increasing the concentration of the inhibitor indicates physical adsorption.
- The negative values of ΔG°_{ads} , indicates that the adsorption of *Eichhornia crassipes*, is physisorption and spontaneous process on the surface of the mild steel.
- The negative value of enthalpy shows that the dissolution process is exothermic.
- The adsorption of the inhibitor on the surface of the mild steel obeys Langmuir adsorption isotherm.

Thus, the phenomenon of physical adsorption is proposed from the Kinetic and thermodynamic parameters.

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