

**STUDIES ON THE INHIBITION OF NICKEL CORROSION IN
DILUTE NITRIC ACID BY THIAMINE HYDROCHLORIDE****Shaily M. Bhola, Charu Chandra and Gurmeet Singh *****Department of Chemistry,****University of Delhi, Delhi-110007, India****(Email: malhotra.shaily@gmail.com, chandra_charu@yahoo.co.in,
gurmeet123@yahoo.com)****ABSTRACT**

The effect of thiamine hydrochloride on the corrosion of nickel in 1N HNO₃ solution has been studied using galvanostatic polarization measurements and various adsorption isotherms have been applied. The inhibition increases with the increase in the inhibitor concentration. Values of the activation energy suggest that the adsorption is due to physisorption. The positive heats of adsorption values show that adsorption and hence inhibition increases with the rise in temperature. El-Awady and Florry Huggins isotherms have been used to fit the experimental data and the values of $\Delta G^{\circ}_{\text{ads}}$, $\Delta H^{\circ}_{\text{ads}}$ and $\Delta S^{\circ}_{\text{ads}}$ have been reported. The values of $\Delta G^{\circ}_{\text{ads}}$ also indicate that the adsorption is physical in nature and becomes stronger at higher temperatures.

Key words- Thiamine hydrochloride, nickel, nitric acid, isotherms

INTRODUCTION

Metals are exposed to the action of acids in industry. The corrosion behaviour of nickel in acid baths in plating, electrowinning and pickling processes is of industrial concern [1] and corrosion inhibition studies on nickel in nitric acid in the presence of organic molecules are rare [2,3].

Acid inhibitors are used in several industrial processes to control the corrosion of metals. Most of the well-known acid inhibitors are organic compounds containing N, S and O as these heteroatoms are capable of donating their free electron pairs to the metal [4,5]. Compounds with π -bonds also generally exhibit good inhibitive properties due to interaction of the π -orbital with the metal surface [6].

The use of heavy metal-based and toxic corrosion inhibitors is increasingly being curtailed by recent environmental restrictions and researchers aim to substitute these with environment-friendly inhibitors [7-13]. Natural products like fruits, leaves, seeds, barks, fruit shells are being considered a good source of green inhibitors these days. These contain different organic compounds like tannins, alkaloids, pigments, organic and amino acids, vitamins, saccharides [14-25].

Recently vitamins have been investigated as corrosion inhibitors for steel and nickel and are found to be quite efficient [26-28]. The present study is about the role of thiamine hydrochloride (Vitamin B₁) as an efficient corrosion inhibitor for the corrosion of nickel in dilute nitric acid solution [3].

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MATERIAL PREPARATION-

Specimens of 99.9% pure nickel were used for the experimental studies.

A cuboidal nickel rod of 1cm length, 0.75 cm in breadth and 0.75 cm in height (measured with a vernier caliper) was soldered on one end with an insulated copper wire and carefully coated with an epoxy resin (Araldite) leaving the flat square surface exposed uncoated for the corrosion studies. The area of this base was 0.5625 cm^2 .

The corrosion current density values for the respective inhibitors were calculated by dividing the corrosion current obtained from galvanostatic measurements by the area of the electrode.

The exposed metal surface of the electrode was abraded with different grades of emery papers of variety 150, 320, 400 and 600 respectively. This was finally polished by 4/0 polishing paper to give the surface mirror like finish. It was then washed with double distilled water to remove any physical impurities bound to it, dried in acetone and finally stored in a desiccator for 24 hours. The nickel electrode prepared was then used as a working electrode for the corrosion studies [3].

IMMERSION SOLUTIONS

A stock solution of 1N HNO_3 solution was prepared and various concentrations of the inhibitor (10^{-2}M , 10^{-4}M and 10^{-6}M) were prepared in the nitric acid solution.

EXPERIMENTAL TECHNIQUE

1N HNO_3 was used for the galvanostatic polarization of nickel at four temperatures namely 298, 308, 318 and 328 K. The inhibitive action of thiamine hydrochloride was studied when 1N HNO_3 containing 10^{-2} , 10^{-4} and 10^{-6}M concentrations of the inhibitor at all the four temperatures was used for the polarization of nickel. Aerated solutions were used throughout the study.

The experimental method has already been mentioned in the earlier literature [3]. An electrochemical cell assembly of three electrodes was used for galvanostatic polarisation studies consisting of the working electrode which is the nickel electrode, saturated calomel electrode as the reference electrode and platinum as the counter electrode. The system was allowed to reach a steady state open circuit potential after keeping the electrode dipped in the respective solution for around 3-5 hrs.

For the galvanostatic studies, the current was passed through the cell at different predetermined values from a galvanostat, capable of giving current from $10 \mu\text{A}$ to 40 mA through the counter electrode and the corresponding potential was measured between the working electrode and the reference electrode. The cathodic polarization curve was determined first and then after the reestablishment of the open circuit potential, anodic curve was traced. Potential values were plotted against logarithms of the current densities and various parameters were calculated from the graphs and are reported in [3]. Values of i_{corr} and $I\%$ were used to calculate the values of surface coverage. Heat of adsorption and activation energy values were also calculated. El-Awady and Florry Huggins isotherm

were then used to fit the experimental data and to obtain the thermodynamic parameters like $\Delta G^{\circ}_{\text{ads}}$, $\Delta H^{\circ}_{\text{ads}}$ and $\Delta S^{\circ}_{\text{ads}}$.

RESULTS AND DISCUSSION-

Fig. 1 shows I% values as a function of the logarithm of the concentration of thiamine hydrochloride. It is evident that as the concentration is increased, I% also increases. It indicates that the inhibitor molecules are adsorbed on the surface of nickel.

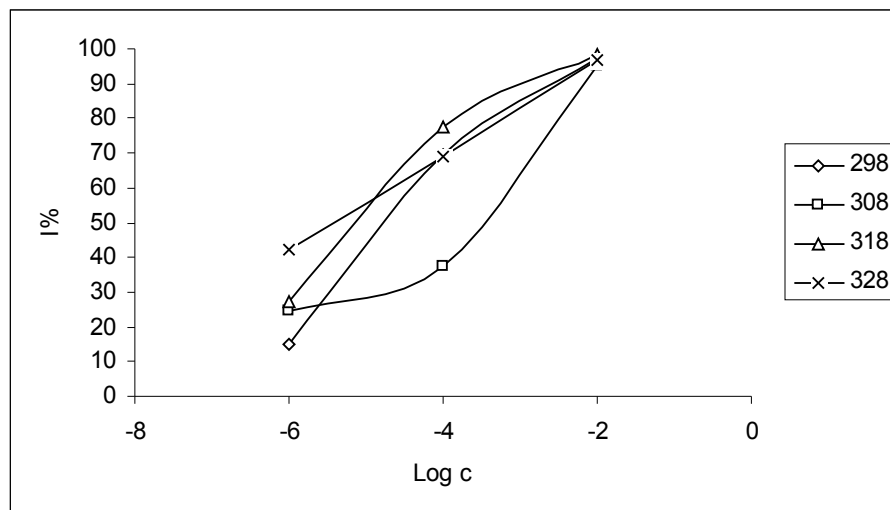


Fig. 1 - Inhibition efficiency against log c for nickel in 1N HNO₃ in the presence of Thiamine hydrochloride at different temperatures

APPLICATION OF ADSORPTION ISOTHERMS

According to **Flory-Huggins** isotherm (29-30),

$$\log (\theta / c) = \log K + x \log (1-\theta) \quad - (i)$$

where x is the number of inhibitor molecules occupying one active site (or the number of water molecules replaced by one molecule of the inhibitor).

Fig. 2 shows the Flory-Huggins isotherm for the adsorption of Thiamine hydrochloride on the surface of nickel with the corresponding parameters in table 1. Mean R² value is 0.9076.

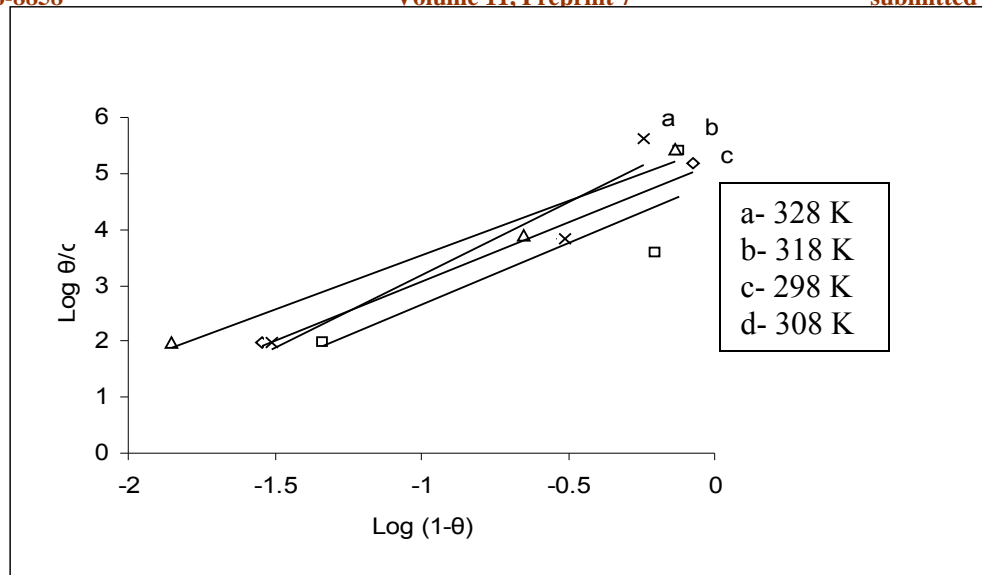


Fig. 2 - Curve fitting of the plot of $\log \theta/c$ against $\log (1-\theta)$ for nickel in 1N HNO_3 in the presence of Thiamine hydrochloride at different temperatures

Table 1 - Isotherm parameters for the curve between $\log \theta/c$ and $\log (1-\theta)$ for Thiamine hydrochloride

Temp. (K)	Slope (x)	Intercept (log K)	R ²
298	2.1047	5.1647	0.9828
308	2.2071	4.8658	0.7688
318	1.9272	5.4694	0.9718
328	2.5913	5.7699	0.9070

For the ideal **Langmuir adsorption isotherm**, the slope should be one [31].

$$\log \theta/(1-\theta) = \log K + \log c \quad \text{---(ii)}$$

The deviation in slope value from unity means that there is some interaction between the adsorbed molecules, leading to desorption.

Fig. 3 shows the plot between $\log \theta/1-\theta$ against $\log c$ for nickel in 1N HNO_3 in the presence of thiamine hydrochloride at different temperatures and table 2 gives the isotherm parameters.

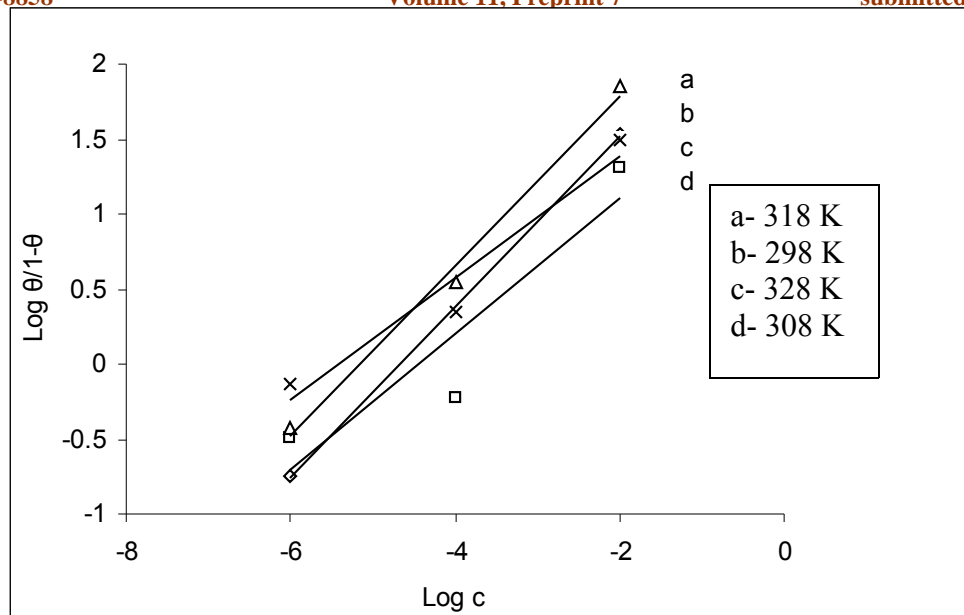


Fig. 3 - Curve fitting of the plot of $\log \theta/(1-\theta)$ against $\log c$ for nickel in 1N HNO_3 in the presence of Thiamine hydrochloride at different temperatures

Table 2 - Isotherm parameters for the curve between $\log \theta/(1-\theta)$ and $\log c$ for Thiamine hydrochloride

Temp. (K)	Slope (y)	x	Intercept ($\log K'$)	R^2	K	$\Delta G^\circ_{\text{ads}}$ (kJ/mol)
298	0.5699	1.7546	2.6597	0.9997	4.642×10^4	-36.58
308	0.4509	2.2177	2.0023	0.8574	2.7574×10^4	-36.47
318	0.5694	1.7562	2.9306	0.9928	1.4019×10^5	-41.95
328	0.4072	2.4557	2.2001	0.9474	2.528×10^5	-44.88

Since the slope values are far from unity, it can be very well concluded that the adsorption does not obey Langmuir isotherm, according to which, the adsorption is monolayer and number of inhibitor molecules occupying one active site is one.

El Awady [29, 30, 32] has modified the Langmuir isotherm to a kinetic-thermodynamic model [equation (iii)] in which the slope y represents the number of inhibitor molecules occupying one active site or the number of water molecules replaced by one molecule of the inhibitor.

According to **El Awady et al. thermodynamic-kinetic model**,

$$\log \theta/(1-\theta) = \log K' + y \log c \quad \text{---(iii)}$$

where $x (=1/y)$ is the number of inhibitor molecules occupying one active site (or the number of water molecules replaced by one molecule of the inhibitor), K is the equilibrium constant of adsorption reaction and $K = K'^{(1/y)}$.

The mean R^2 value for this isotherm is 0.9493.

The adsorption is assumed to be a quasi-substitution process between water molecules on the surface of the metal and the organic molecules [33-34].

The R^2 value for El-Awady isotherm is greater than that for the Florry Huggins isotherm, suggesting that the adsorption follows El-Awady isotherm more closely.

From the intercept of the plot, the value of adsorption equilibrium constant can be calculated which are given in table 2. The values of the change in standard Gibbs free energy for the adsorption process has been calculated from equation (iv) which is also given in table 2.

$$\Delta G_{\text{ads}}^{\circ} = -RT \ln (55.5 K) \quad - \text{(iv)}$$

where, K , the equilibrium adsorption constant has been calculated with reference to the molarity of water [35,36] under standard conditions which is 55.5 M.

The difference of the adsorption free energy calculated from equilibrium constants expressed in mole fraction and in 1M reference standard state is $-RT \ln 55.5$.

The $\Delta G_{\text{ads}}^{\circ}$ values are negative which reveal the spontaneity of the adsorption process and the stability of the adsorbed layer on the nickel surface. The rise in $\Delta G_{\text{ads}}^{\circ}$ values with the rise in temperature shows that the reaction is more favourable at higher temperatures.

The mean Gibbs free energy value is $-39.97 \text{ kJmol}^{-1}$. $\Delta G_{\text{ads}}^{\circ}$ values between -49 kJ/mol and -58 kJ/mol are indicative of chemisorption, according to G. Bereket et al [37]. The low $\Delta G_{\text{ads}}^{\circ}$ value in the present case further confirms physisorption.

$$\log K = -\Delta H_{\text{ads}}^{\circ} / 2.303 RT + (\Delta S_{\text{ads}}^{\circ} / 2.303 R) - \log 55.5 \quad - \text{(v)}$$

$\Delta H_{\text{ads}}^{\circ}$ is calculated from the slope (38) and $\Delta S_{\text{ads}}^{\circ}$ is obtained from the intercept [38] of the plot of $\log K$ versus $1/T$ in equation (v).

R^2 value of the plot of $\log K$ versus $1/T$ is 0.7154. The values of $\Delta H_{\text{ads}}^{\circ}$ and $\Delta S_{\text{ads}}^{\circ}$ were found to be 53.46 kJ/mol and 298.16 J/K respectively.

The $\Delta H_{\text{ads}}^{\circ}$ value is positive and the $\Delta S_{\text{ads}}^{\circ}$ value is also positive. Positive $\Delta H_{\text{ads}}^{\circ}$ value indicates the existence of a strong interaction between the adsorbate molecules and positive $\Delta S_{\text{ads}}^{\circ}$ indicates the existence of some structural changes at the solid-liquid interface or an increase in randomness in the system at the solid/solution interface during adsorption due to some reaction. It further implies that adsorption process is entropy favoured. Furthermore, the positive values of heat of adsorption suggests that a part of the heat is being used to orient the molecules in such a manner that the new orientation results in a proper adsorption probably by fluxional rearrangement [44].

Arrhenius equation has been used to study the relationship between the corrosion rate and temperature and hence to find out the value of the effective activation energy for the adsorption of the inhibitor on the nickel surface.

According to the Arrhenius equation [39],

$$\log (\text{rate}) = \log A - E_a/2.303RT \quad - (\text{vi})$$

This equation can also be stated as follows, where it has been related to the corrosion current.

$$\log i_{\text{corr}} = B - E_a/2.303RT \quad - (\text{vii})$$

From the fig. 4, the activation energy for the corrosion of nickel in 1N HNO₃ was found to be 44.08 kJ/mol and the average activation energy for the corrosion of nickel in 1N HNO₃ in the presence of the inhibitor for all the concentrations was found to be 35.82 kJ/mol. The lower value of the activation energy in the presence of the inhibitor than in its absence reveals that the inhibitor is effective at higher temperatures and belongs to Putilova's third category of inhibitors [35, 40].

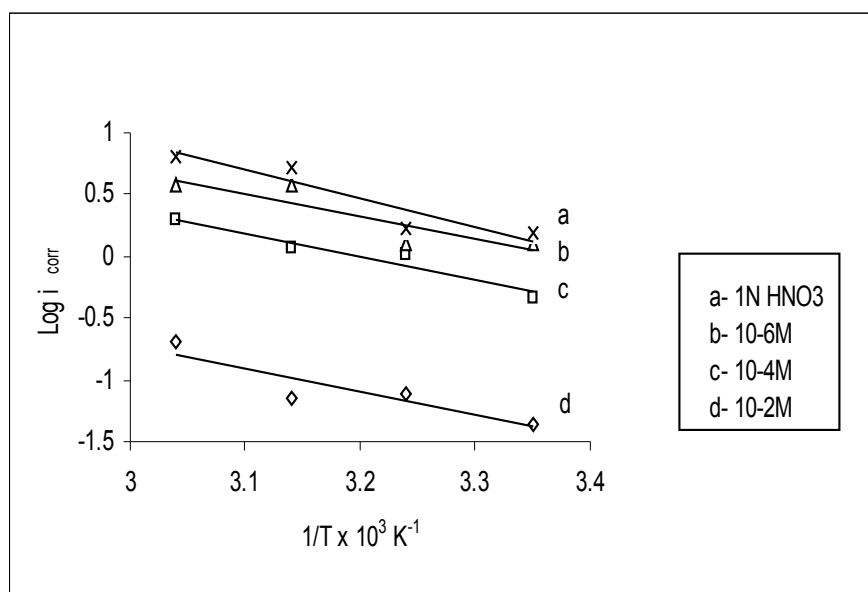


Fig. 4 - Curve fitting of the plot of $\log i_{\text{corr}}$ against $1/T$ for nickel in 1N HNO₃ in the presence of Thiamine hydrochloride at different concentrations

The fall in the value of E_{eff} is accounted for by the increase in surface area of the metal covered by inhibitor molecules as temperature rises. According to the reports by some authors [41-44], the value of the activation energy less than 80 kJ/mol indicates physisorption, hence in the present case, a considerably lower value of the E_{eff} in the presence of the inhibitor is suggestive of the fact that the adsorption occurs via physisorption.

Fig. 5 displays the relationship between $\log \theta/(1-\theta)$ and $1/T$ and the heat of adsorption has been calculated from this plot using equation (viii). It can be clearly seen from the figure that the curves are more or less parallel to the x-axis or have a low value of slope, signifying that the adsorption phenomena is unaltered by change in temperature and the inhibitor remains efficient at all the temperatures, most so at the highest concentration. Whereas as the concentration decreases, it becomes effective at higher temperatures.

$$\log \theta/(1-\theta) = \log (Kc) - Q/2.303 RT \quad \text{-(viii)}$$

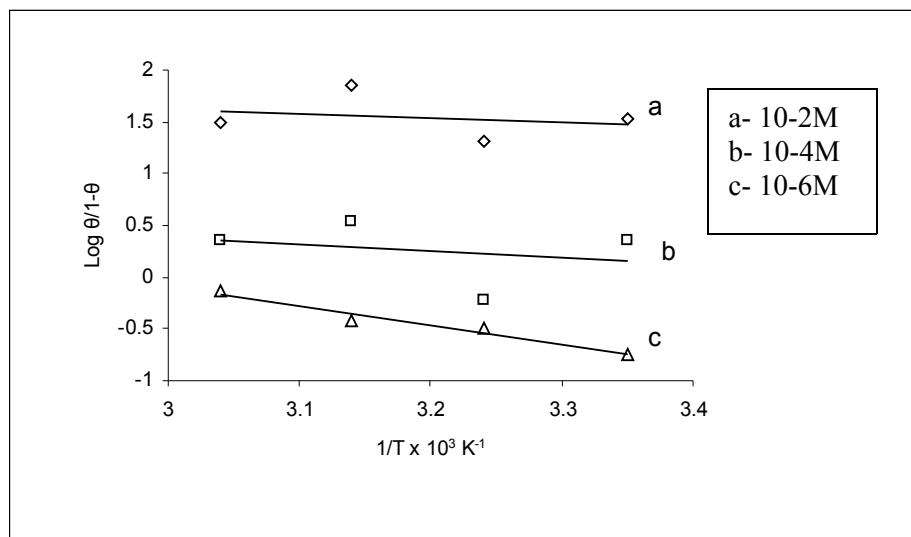


Fig. 5 - Curve fitting of the plot of $\log \theta/(1-\theta)$ against $1/T$ for nickel in 1N HNO_3 in the presence of Thiamine hydrochloride at different concentrations

Table 3 gives the values of the heats of adsorption (Q), the E_{eff} values and the square of the correlation coefficients (R^2) of the best fit lines. Correlation coefficients in case of calculations of Q ($R_{\text{av}}^2 = 0.3614$) are found to be very low. Therefore, no conclusions can be drawn from the values of Q .

Since physical adsorption is proposed, it is expected that there is the formation of a multi-layer protective coverage on the surface of nickel by the Vitamin.

Table 3 - Q and E_{eff} values for the corrosion of nickel in 1N HNO_3 in the presence of Thiamine hydrochloride

Conc. (M)	Q (kJ/mol)	R^2	E_{eff} (kJ/mol)	R^2
0	-	-	44.0801	0.8795
10^{-2}	7.8329	0.0600	36.5766	0.8330
10^{-4}	13.0081	0.0737	36.4730	0.9303
10^{-6}	35.5078	0.9506	34.4243	0.7828

CONCLUSION

- (1) Thiamine hydrochloride was found to be an effective inhibitor for nickel in dilute nitric acid solution.
- (2) Inhibition efficiency was found to increase with the increase in concentration of the inhibitor.
- (3) The values of $\Delta G^{\circ}_{\text{ads}}$ were found to be negative indicating spontaneous adsorption which is physisorption.
- (4) The adsorption follows El-Awady isotherm more closely compared to Florry Huggins isotherm.
- (5) The value of effective activation energy is less in presence compared to pure acid.

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