3-[(4-amino-2- methyl-5-pyrimidinyl) methyl]-5-(2-hydroxyethyl)-4-methyl thiazolium chloride hydrochloride as green corrosion inhibitor of copper in HNO$_3$ solution and its adsorption characteristics

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RESEARCH LETTER

3-[(4-amino-2- methyl-5-pyrimidinyl) methyl]-5- (2-hydroxyethyl)-4-methyl thiazolium chloride hydrochloride as green corrosion inhibitor of copper in HNO₃ solution and its adsorption characteristics

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The inhibitory effect of 3-[(4-amino-2-methyl-5-pyrimidinyl) methyl]-5-(2-hydroxyethyl)-4-methyl thiazolium chloride hydrochloride (thiamine hydrochloride) or vitamin B_1 hydrochloride on acid corrosion of copper in 2.5 M nitric acid (HNO₃) solution was investigated using a weight loss method. Thiamine hydrochloride inhibited the corrosion of copper in 2.5 M HNO₃ solutions. The inhibition efficiency increased with increasing concentration of thiamine hydrochloride but decreased with increasing exposure. Adsorption of thiamine hydrochloride molecules on copper surface was found to obey Langmuir adsorption isotherm with standard free energy of adsorption (ΔG^o_{ad}) –30.55 kJ mol^{-1}. The inhibition mechanism was characterized from trends of inhibition efficiency, thermodynamic, and kinetic parameters.

Keywords: corrosion inhibitors; copper; adsorption; thiamine hydrochloride; HNO₃; kinetic parameters

Introduction

Studies on acid corrosion and inhibition of copper in nitric acid solution are generating a lot of interest because nitric acid solution is the corrosive solution of choice for both the chemical dissolution and electroplating processes used in the fabrication of electronic devices and copper is susceptible to corrosion in nitric acid solution (1,2).

Numerous inorganic and organic compounds have been reported as corrosion inhibitors for metals in different media, but the toxic nature of some of them limits their application. Attention has been focused on the need to design and develop green or non-toxic corrosion inhibitor to replace toxic ones for a sustainable development. Amino acids (3–5), phthalazine derivatives (6), caffeine (7), imidazole derivatives (8), and guanidine (9) have been reported as nontoxic corrosion inhibitors for copper in acid media and their inhibitive action was found to depend on molecular structures, the nature of the metal surface, types of ions in the electrolytes, ability to form complexes, and the extent of adsorption on the metal surface. We have also reported the inhibitive and adsorption properties of 3-[(4-amino-2-methyl-5-pyrimidinyl) methyl]-5-(2-hydroxyethyl)-4-methyl thiazolium chloride hydrochloride or thiamine

hydrochloride, a naturally occurring substance and its derivative on mild steel (10–12) and aluminum (13) in HCl solutions using weight loss and hydrogen evolution techniques. The literature on nontoxic corrosion inhibitors for copper in nitric acid solution is not in a large number in comparison with that for copper in both HCl and H_2SO_4 solutions. However, to the best of our knowledge there is no reported work in the open literature on the inhibitive and adsorption properties of AMMPTC on copper in nitric acid solutions.

This paper is a follow-up effort on our previous work (10–12) on the development of nontoxic (green) corrosion inhibitors of metals that do not contain heavy metals and organic phosphates. Thiamine hydrochloride, nontoxic organic compound consists of pyrimidine ring and thiazollium ring bridged by methylene group is already known for its complex formation owing to its coordination sites (14). It is of interest to note that thiamine hydrochloride contains sulfur atom and many organic compounds containing sulfur atom have been developed as copper corrosion inhibitors for different industrial application (15) owing to the ability of S atom to be strongly adsorbed on copper surface. Therefore, thiamine hydrochloride may be a potential nontoxic corrosion inhibitor for

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copper in nitric acid solution. The aim of this work is to investigate the inhibitive effect of thiamine hydrochloride on the acid corrosion of copper in 2.5 M HNO_3 solution and its adsorption characteristics using weight loss technique.

Results and discussion

The results obtained are presented in Figures 1–7 and Tables 1–3 for different concentrations of thiamine hydrochloride in 2.5 M HNO_3 solutions from gravimetric measurements.

The weight losses of copper versus concentration of thiamine hydrochloride for 30 min immersion time at 30°C are presented in Figure 1.

In Figure 1 the addition of thiamine hydrochloride resulted in low material loss (mg/cm^2) as compared with that of control at 30°C. The weight losses (mg/cm^2) of copper coupon in the presence of 0.01, 0.05, 0.1, 0.2, 1, and 2 mM concentrations of thiamine hydrochloride decreased by a factor of 0.96, 0.89, 0.68, 0.58, 0.31, and 0.30, this in reference to the blank (control, Figure 1), respectively. These results implied that thiamine hydrochloride inhibited the corrosion of copper in 2.5 M HNO_3 solution at these concentrations at 30°C for 30 min immersion period. The percentage inhibition efficiency values are listed in Table 1 for triplicate specimens and were precise to ±4% and this indicates good reproducibility.

These results are indicative of the inhibition of the dissolution of copper in HNO_3 solution, with the maximum inhibition efficiency values of 69.9% at 2 mM thiamine hydrochloride at 30°C. The inhibitory activity of thiamine hydrochloride with respect to acid dissolution of copper in HNO_3 solution may be
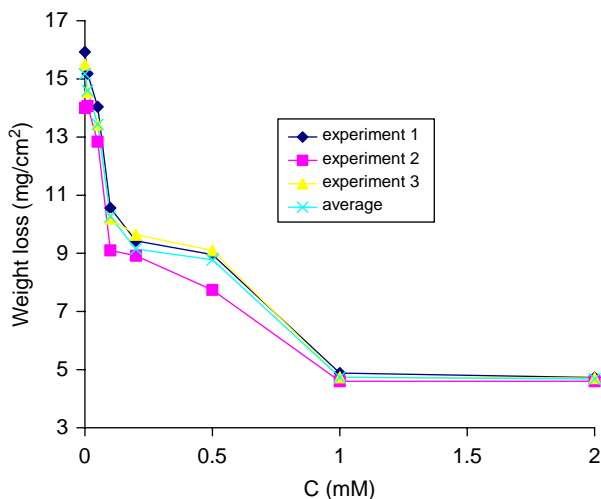
Table 1. Percentage inhibition efficiency, corrosion rate, and surface coverage of thiamine of thiamine hydrochloride on copper at 30°C 30 min immersion period.

Concentration (mM)	Corrosion rate ($mg\ cm^{-2}\ min^{-1}$)	% inhibition efficiency	Surface coverage
0	0.506 ± 0.03	—	—
0.01	0.487 ± 0.02	7.7 ± 2	0.08
0.05	0.448 ± 0.02	11.4 ± 3	0.11
0.1	0.342 ± 0.01	32.4 ± 2	0.32
0.2	0.305 ± 0.01	39.7 ± 3	0.40
0.5	0.293 ± 0.03	42.1 ± 4	0.42
1.0	0.158 ± 0.005	68.8 ± 1	0.69
2.0	0.156 ± 0.002	69.9 ± 2	0.70

associated with their adsorbability due to the presence of adsorption centers of S, N, and O in thiamine hydrochloride. A similar view has been reported previously [13] on the behavior of thiamine hydrochloride on aluminum surface in HCl solution. It is evident in Table 1 that the corrosion rate decreased with increasing concentration of the inhibitor in the acid solutions and the percentage inhibition efficiency values increase with increasing inhibitor concentration. This indicates that the inhibition is due to the adsorption of inhibitor's molecule onto copper surface and the inhibitor acts as an adsorption inhibitor. Previously, similar views have been put forward on the inhibition of acidic corrosion of metals [16–20].

The effect of immersion time on inhibition efficiency is shown in Figure 2. As seen in Figure 2, the inhibition efficiency decreases with increase in immersion time. The decrease in the value of percentage inhibition efficiency with immersion time may be

Figure 1. Variation of weight loss with thiamine hydrochloride concentration for copper in 2.5 M HNO_3 at 30°C.
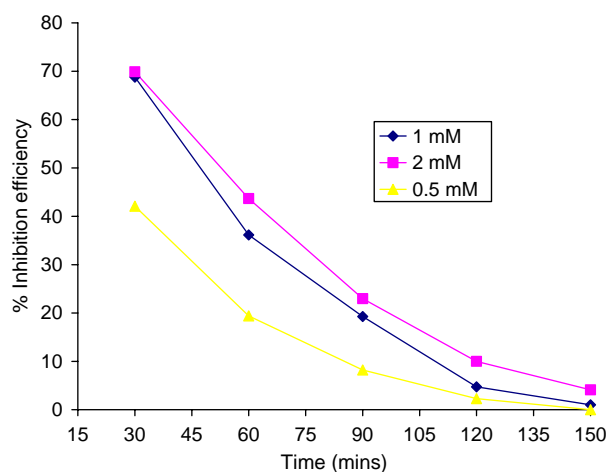

Figure 2. Variation of percentage inhibition efficiency of thiamine hydrochloride with immersion period.

ascribed to increase in desorption of the inhibitor molecules from metal surface with increasing immersion time.

Adsorption isotherms and characteristics of adsorption process

A detailed mechanism for inhibition is not possible without an understanding of the adsorption process at the metal/electrolyte interface. To clarify the nature of adsorption, the fits of various adsorption isotherms to the empirical data were tested. For organic corrosion inhibitors inhibiting through adsorption mode, as in this case, the degree of surface coverage, θ can be determined from the value of inhibition efficiency with $\theta = I\%/100$.

The experimental data were applied to different adsorption isotherm equations and found to fit the Langmuir adsorption isotherm (19,21–23) with correlation coefficient of 0.980 (Figure 3), which may be formulated as equation (1):

$$\frac{C}{\theta} = C + \frac{1}{K},\qquad(1)$$

where C is the concentration of the inhibitor and K is the equilibrium constant of the adsorption/desorption process.

The K is related to the standard free energy of adsorption by the equation:

$$K = 1/55.5 \exp\left(-\Delta G^{\circ}_{ad}/RT\right).\qquad(2)$$

Though, the data deduced from the Langmuir isotherm ($R^2 = 0.980$) confirms the applicability of the isotherm to describing the adsorption process of thiamine hydrochloride onto copper surface, the slope (Figure 3) was found to deviate from 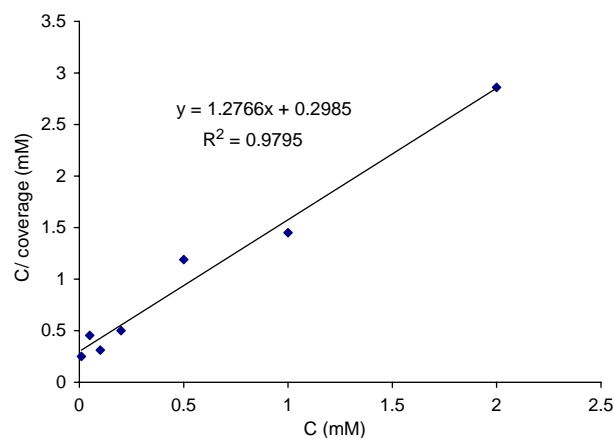unity (1.28). This deviation from unity may be explained on the basis of the interaction among adsorbed molecules on the copper surface, the interaction that was not taken into account during the derivation of the Langmuir isotherm equation. The interaction between the adsorbed organic molecules with polar groups on the anodic and cathodic sites of the metal surface plays a crucial role that cannot be overlooked. This interaction may be either mutual attraction or repulsion (17).

The value of standard free energy of adsorption, ΔG°_{ad} was obtained from the values of K. The value for ΔG°_{ad} for the inhibition of acid corrosion of copper by thiamine hydrochloride was found to be –30.55 kJ mol^{-1}. The negative value of adsorption free energy suggests the spontaneity of the adsorption of thiamine hydrochloride molecules and the stability of the adsorbed layer on copper surface.

The adsorption process is adjudged physical adsorption due to the value of ΔG°_{ad} that was below –40 kJ mol^{-1}. There is a general concession that adsorption with ΔG°_{ad} values below –40 kJ mol^{-1} are physical in nature (11,12,18,19,25–29).

Kinetic model

The kinetic model was employed to give further insight into the inhibition properties of AMMPTC. The effect of temperature on the corrosion rate of copper in nitric acid solution in the absence and presence of 0.5–2 mM thiamine hydrochloride was studied at 30, 35, 40, and $45 \pm 0.2^{\circ}$C by gravimetric measurements.

Figure 4 shows the dependence of thiamine hydrochloride efficiency on temperature when different concentrations of thiamine hydrochloride were added. Inhibitor efficiency decreased as the temperature increased and this indicates physisorption

Figure 3. Langmuir adsorption plot for copper in 2.5 M HNO$_3$ solution containing thiamine hydrochloride at 30°C.
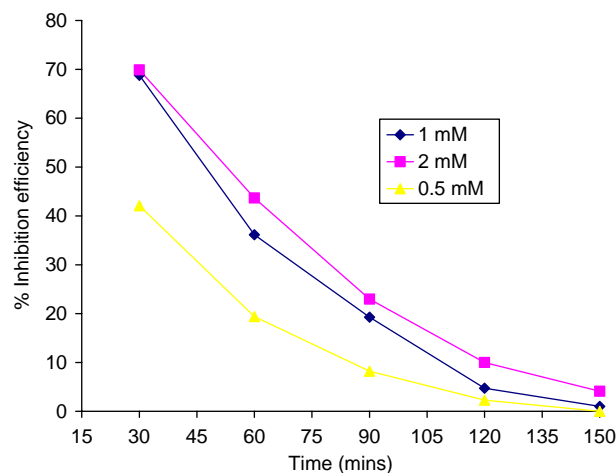

Figure 4. Variation of percentage inhibition efficiency of thiamine hydrochloride with temperature.

of thiamine hydrochloride at the copper surface. Desorption of inhibitor molecules with increased temperature is usually observed in cases of physisorption. According to Noor (30) and the reference there in, the kinetic – thermodynamic model represent the modified form of Langmuir adsorption isotherm; log $(\theta/1\text{-}\theta) = \log K^{/} + y \log C$, reformulated by including the heat of adsorption parameter as follows:

$$\log \left(\frac{\theta}{1-\theta}\right) \log K' + Y.\log C - \frac{Q_{\text{ads}}}{2.303\ RT}. \quad (3)$$

Figure 5 depicts linear variation between log $(\theta/1 - \theta)$ and I/T at 30, 35, 40, and 45°C with R^2 in the range of 0.991 to 0.994 (Table 2). The negative sign of heat of adsorption indicates that the adsorption process is exothermic in nature. This observation further confirms physical adsorption theory for thiamine hydrochloride on copper surface in 2.5 M HNO_3 solution. Other thermodynamic parameters such as apparent activation energy E_a, Arrhenius pre-exponential factor, A, the enthalpy change of activation ΔH^* and the entropy change of activation, ΔS^* were obtained from the Arrhenius – type plot (Equation 4) and Eyring transition – state plot (Equation 5):

$$\ln(rate) = \ln A - \frac{E_a}{RT}, \quad (4)$$

$$\frac{\ln(rate)}{T} = \ln R/Nh + \Delta S^*/R - \Delta H^*/RT, \quad (5)$$

where E_a represents the apparent activation energy, R the universal gas constant, A the pre-exponential factor, T the absolute temperature, N the Avogadro's number, h the Plank constant, ΔH^* the enthalpy of activation and ΔS^* is the entropy change of the activation.

Table 2. Heat of adsorption, Q_{ad} and the correlation coefficients for thiamine hydrochloride on copper surface in 2.5 M HNO_3.

Thiamine hydrochloride (mM)	Q_{ad} (kJ mol^{-1})	R^2
0.5	−185.47	0.994
1.0	−224.58	0.990
2.0	−175.24	0.991

Figures 6 and 7 depict the fitting of the corrosion data to Arrhenius and Errying equations for inhibited and uninhibited copper in 2.5 M HNO_3 solution. The activation parameters obtained from Figures 6 and 7 are listed in Table 3.

The plot of ln(*rate*) versus $1/T$ and ln(*rate*/T) versus $1/T$ gave straight lines with slopes of $-E_a$ and $(-H^*/R)$, respectively. The intercepts are A and $(\ln R/Nh) + \Delta S^*/R)$ for the Arrhenius and Eyring transition state equations, respectively.

The linear regression coefficients in Table 3 show that the relationship between ln(*rate*) and $1/T$, and ln (*rate*/T) and $1/T$ can be described by the Arrhenius equation and Eyring transition state equations, respectively. The activation parameters; Ea, ΔH^* and ΔS^* for the corrosion process were determined and presented in Table 3. The free energy change, ΔG^* for the corrosion process was calculated using the relationship $\Delta G^* = \Delta H^* - T\Delta S^*$ and the results obtained given in Table 3. The values of pre-exponential factor and apparent activation energy are higher in the presence of the inhibitor. The values of pre-exponential factor and apparent activation for the unhibited solution are 5.76×10^{15} gm^{-2}h^{-1} and 93.10 kJ mol^{-1}, respectively, while 2.39×10^{20} to 1.3×10^{25} gm^{-2} h^{-1} and 121.16–155.88 kJ mol^{-1} are obtained for pre-exponential factor and apparent
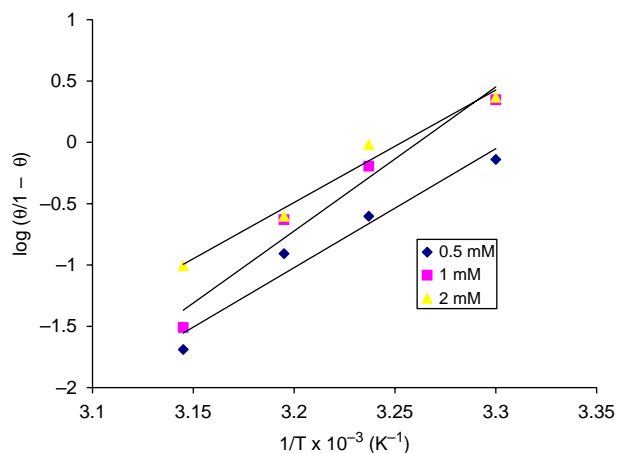

Figure 5. Plot of log $(\theta/1 - \theta)$ versus 1/T at concentrations of 0.5, 1, and 2 mM thiamine hydrochloride.

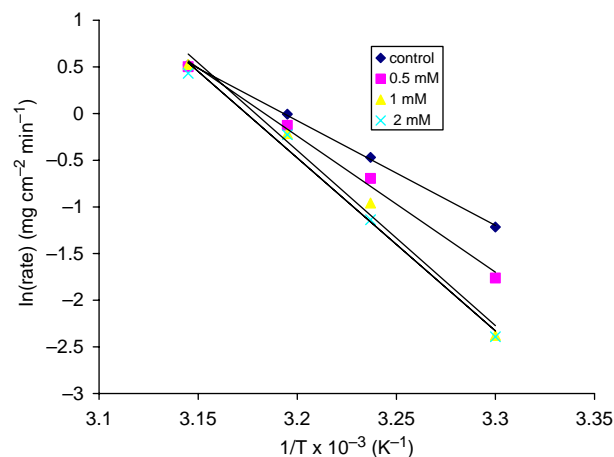

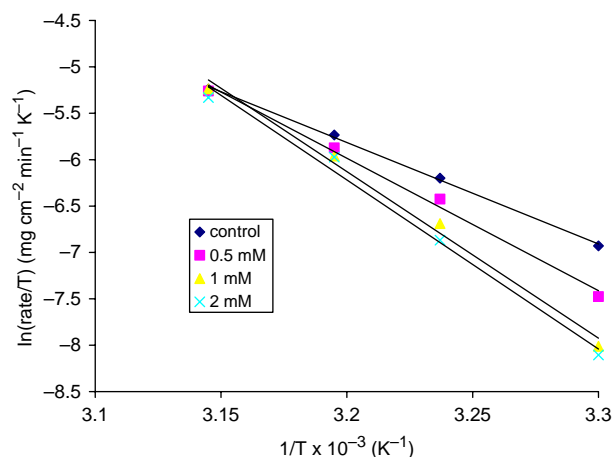Figure 6. Arrhenius plots for copper in 2.5 M solution with and without thiamine hydrochloride.

Figure 7. Errying plots for copper in 2.5 M solution with and without thiamine hydrochloride.

activation energy, respectively, for the inhibited solutions. This result suggests that both the increase in apparent activation energy and pre-exponential factor leads to an increase in energy barrier for the corrosion of copper in HNO_3 solution. Foudal et al. (31) has reported similar trend in the value of apparent activation energy for copper corrosion in HNO_3 acid solution in the presence of phthalimide derivatives.

In uninhibited and inhibited solutions the values of E_a are larger than for the corresponding values of ΔH^* with 2.66 kJ mol^{-1}; this is in agreement with the well-known equation for a unimolecular reaction, $E_a - \Delta H^* = RT$ (32,33). The positive values of ΔG^* in the absence and presence of AMMPTC show that the activated complex was not stable both in the absence and presence of the inhibitor. As presented in Table 3, ΔG^* becomes more positive with increasing concentration of the inhibitor. The implies that in the presence of the inhibitor the activated complex becomes less stable as compared to its absence.

The mechanism of inhibition

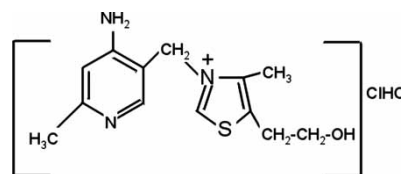Corrosion inhibition of copper in nitric acid solution by thiamine hydrochloride can be explained on the basis of adsorption of its molecule on the metal surface. In acid solutions, thiamine hydrochloride exists as cationic species by being protonated at the sulfur atom, since such compounds are known to be protonated at the sulfur atom (11,12). The charge molecules adsorb on the charge metal surface, thereby reducing the surface area that is available for the attack of the aggressive ions from the acid solutions.

The value of ΔG_{ad}^o obtained (-30.55 kJ mol^{-1}) is in support of electrostatic interaction between the charge inhibitor and the charge metal surface (that is physisorption mechanism).

Experimental

Material preparation

The chemical structure of the compound of interest, 3-[(4-amino-2-methyl-5-pyrimidinyl)methyl]-5-(2-hydroxyethyl)-4-methyl thiazolium chloride hydrochloride or thiamine hydrochloride is presented below:

The thiamine hydrochloride (CAS 67 – 03 – 8) and HNO_3 were analytical grade reagents and used as received.

Rectangular specimens in sizes of $5 \times 2 \times 0.04$ cm were cut from copper sheet (98.61% Cu) for weight loss measurements. The coupons were used for the study as received without further polishing, but were degreased in absolute ethanol, dried in acetone, and stored in a moisture free desiccators before their use in corrosion studies. Doubly distilled water was used for the preparation of all the solutions. Additive concentrations of 0.01, 0.05, 0.1, 0.2, 0.5, 1, and 2 mM were prepared in the electrolyte solution (2.5 M HNO_3).

Table 3. Corrosion activation parameters and the correlation coefficients for copper in 2.5 M HNO_3 with and without thiamine hydrochloride.

AMMPTC (mM)	A(mg cm^{-2} min^{-1})	Ea (kJ mol^{-1})	$\triangle$H* (kJ mol^{-1})	$\triangle$G* (kJ mol^{-1})	$\triangle$S* (JK mol^{-1})	R^2
0	5.76×10^{15}	93.10	90.49	75.93	48.05	0.999
0.5	2.39×10^{20}	121.16	118.55	77.20	136.47	0.994
1	1.30×10^{26}	155.88	153.27	78.65	246.28	0.992
2	5.57×10^{25}	153.88	151.26	78.78	239.18	0.990

Weight loss determination

The procedure for weight loss determination was similar to that reported previously (*11,13*). The pre-weighed copper coupons were immersed in 50 ml of 2.5 M HNO_3 solutions (in open beakers) without and with different concentrations (0.01–2 mM) of the additive at 30°C. The variation of weight loss was monitored at 30 min interval progressively for 120 min per coupon at 30°C. Each reading reported is an average of three experimental readings recorded to the nearest 0.0001 g on a Mettler digital analytical balance.

The effect of temperature on the corrosion rate of copper coupon in 2.5 M HNO_3 for 30 min immersion period at 35, 40, and 45 ± 0.2°C was also studied with 0.5, 1, and 2 mM thiamine hydrochloride. The temperature was thermostatically controlled using water thermostat with precision of ± 0.2°C. Corrosion rate (r_s), and percentage inhibition (% I) were calculated using Equations (*6*) and (*7*):

$$r_s = \frac{W}{At},\qquad (6)$$

where W is weight loss of materials in mg, A is area of test coupon in cm^2, t is time of exposure in minutes, and r_s is the corrosion rate in mg cm^{-2} min^{-1};

$$\%I = \frac{r_{sa} - r_{sp}}{r_{sa}} \times 100,\qquad (7)$$

where r_{sa} and r_{sp} are the corrosion rates in the absence and presence of inhibitor, respectively, for the same immersion period.

Conclusions

Based on the results obtained, the following conclusions can be drawn:

The studied compound thiamine hydrochloride can be used as nontoxic corrosion inhibitor for copper corrosion in HNO_3 solution.

The inhibition efficiency of thiamine hydrochloride increases with increasing inhibitor concentration over the concentration range 0.01–2 mM and decreases with increasing temperature.

The inhibitive action of the inhibitor was attributed to adsorption of its molecule on to copper surface in the acidic solution and the data fit well into Langmuir adsorption isotherm.

The value of ΔG^{o}_{ad} was negative and this confirmed the spontaneity of the adsorption process on the surface of copper in nitric acid solution. The

corrosion activation parameters (E_a, ΔH^*, ΔS^*, and ΔG^* were higher in the presence of thiamine hydrochloride than in the absence of thiamine hydrochloride.

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