Temperature Effect on the Corrosion Behavior of Copper inhibited by3,4'-bi-1,2,4-Triazole in neutral salt-spray (NaCl 3%) Medium

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Abstract

The temperature effect on the corrosion behavior of copper that was inhibited by 3,4'-bi-1,2,4-Triazole in NaCl 3% Medium was investigated using potentiodynamic polarization techniques. Inhibition effect was found to increase with decreasing the temperature. Polarization curves showed that 3,4'-bi-1,2,4-Triazole (bTA) act as mixed type inhibitors in 3% NaCl Medium. The obtained results showed that the 3,4'-bi-1,2,4-Triazole could serve as an effective inhibitor of the copper corrosion in 3% NaCl Medium at various temperature up to 55°C.

Keywords: *copper, neutral salt-spray corrosion; electrochemical corrosion; corrosion behavior; corrosion resistance, 1,2,4-Triazole.*

1. Introduction

Corrosion problems usually have been solved by the selection of suitable materials and/or by changing the environment to make it less aggressive [1]. An inhibitor is usually added in a small amount to slow down the rate of corrosion through the mechanism of adsorption [2,3]. Over the years, several inhibitors have been synthesized, or chosen from existing compounds, others may be gotten from extracts of naturally occurring compounds and it has been found that the best inhibitors are those that have center for π electron donation (usually enhanced by the presence of hetero atoms in aromatic compound) [4-10].

Copper and its alloy are employed in many industrial applications, due to their high thermal and electrical conductivities, mechanical workability, and other desirable properties. It is widely used in electronic industries and communications as a conductor in electrical power lines, pipelines for domestic and industrial water utilities including seawater, heat conductors, heat exchangers, etc. for this reason, corrosion of copper and its inhibition in different environment, especially with presence of chloride ions, have attracted the attention of many researchers [9, 11-15].

The most widely used inhibitors in the field of copper corrosion in chloride containing media are azole derivatives. They have been and still are the subject of numerous investigations, as shown by the publication of recent reviews in this domain [16–28].

Among the azole-type compounds, benzotriazole (BTA) [29–36] is the most used inhibitor from a practical point of view, because it shows very high inhibition efficiency in neutral-chloride containing aqueous solutions. In the case of BTA, it seems well established that it acts through the formation of a Cu(I)–BTA complex involving Cu–N bonds [37–39], but the number of N-atom involved in the bond, the orientation of the complex at the metal surface, and the influence of the benzenic ring on the inhibition efficiency are not completely understood. In order to increase the strength of bonding between copper (I) and the organic molecule, different azole derivatives were investigated, changing the number or position of substituent groups and the number of nitrogen atoms on the azole ring, or adding another heteroatom like sulfur [40, 41]. For instance, 1,2,4-triazole and its amino derivatives, tetrazole, thiadiazole, pyrazole, imidazole and the corresponding derivatives have been suggested [9,27,36-52].

The inhibiting properties of a new corrosion inhibitor synthesized in our laboratory, as a derivative of 1,2, 3-triazole on the copper corrosion was investigated in an air saturated 3% NaCl solution [9]. Therefore, this work focused on the corrosion behavior and corrosion mechanism of copper plates in a salt environment and electrochemical corrosion environment at 25, 35, 45, and 55°C using electrochemical methods such as potentiodynamic polarisation techniques and weight loss measurements. The inhibition efficiency is followed as a function of immersion time at open-circuit potential, in the presence of optimal concentration inhibitor (0.001 M) at different temperature. Finally, the mechanism of inhibition will be discussed from electrochemical results.

2. Experimental methods

2.1. Reagents

The corrosive medium was an aqueous aerated 3% NaCl solution prepared from bi-distilled water. The 3,4-bi-1,2,4-triazole was prepared according to the method described by Willey and Hart [9, 53]. The temperature was

controlled by thermostat connected to three electrodes, the corrosion environment was 25, 35, 45, and 55°C ±1.

2.2. Specimen and Solutions preparation.

The electrode specimen was prepared from a square copper rod (99.99% purity) with a cross-section area of 1 cm^2, the electrode was mechanically ground with SiC abrasive papers (grade 400, 600, 1500 and 2000), washed by bi-distilled water and then dried. The solution was prepared by dissolving of 3g NaCl in 97g of bidistilled water, the concentration range of bTA employed was varied from 10^{-4} M to 5×10^{-3} M.

2.3. Polarization measurements

Electrochemical measurements were carried out in a conventional three electrode cylindrical glass cell, containing 100 ml of electrolyte at different temperature (25, 35, 45, and 55°C ±1) in which working electrode was copper, Saturated Calomel Electrode (SCE) was the reference electrode and Platinum was counter electrode. The working electrode was coated thoroughly with epoxy resin keeping surface area of 1 cm^2 for the study. The Potentiodynamic curves of the copper in 3% NaCl solution with and without inhibitor at different temperature were obtained in the potential range from -0.5 to + 0.4 V. For polarization measurements, a potentiostat Voltalab 301 PGZ monitored by a PC computer and Voltamaster 4.0 software were used for running the tests, collect and evaluate the experimental data. During each experiment, the test solution was mixed with a magnetic stirrer. The inhibition efficiency (E %) degrees of surface coverage (θ) were calculated using the following equations:

$$\theta = \frac{I^\circ - I}{I^\circ} \qquad (1)$$

$$E\% = \left(\frac{I^\circ - I}{I^\circ}\right) \times 100 \qquad (2)$$

Where I and I° are the corrosion current densities obtained in HCl solution with and without inhibitor respectively.

3. Results and discussion

3.1. Tafel polarization curves

Polarization curves of copper in 3% NaCl solution at different temperature in the absence and presence of bTA at optimal concentration (0.001M) are shown in Figure 1 and 2. As shown in the anodic polarization curve of copper without inhibitor (Figure 1) showed a monotonic increase of current with potential until the current reached the maximum value, after that, the current density declined rapidly with potential increase, forming an anodic current peak that was related to CuCl film formation. The reassign of temperature shifted the corrosion potential to fewer negative values. As shown in figure 2, in the presence of bTA, both the cathodic and anodic current densities increasing with increasing the temperature and consequently the corrosion rates were lightly increased. That explain by desorption of some molecules from the protective layer (adsorption layer), that also inhibits the oxygen reduction reaction.

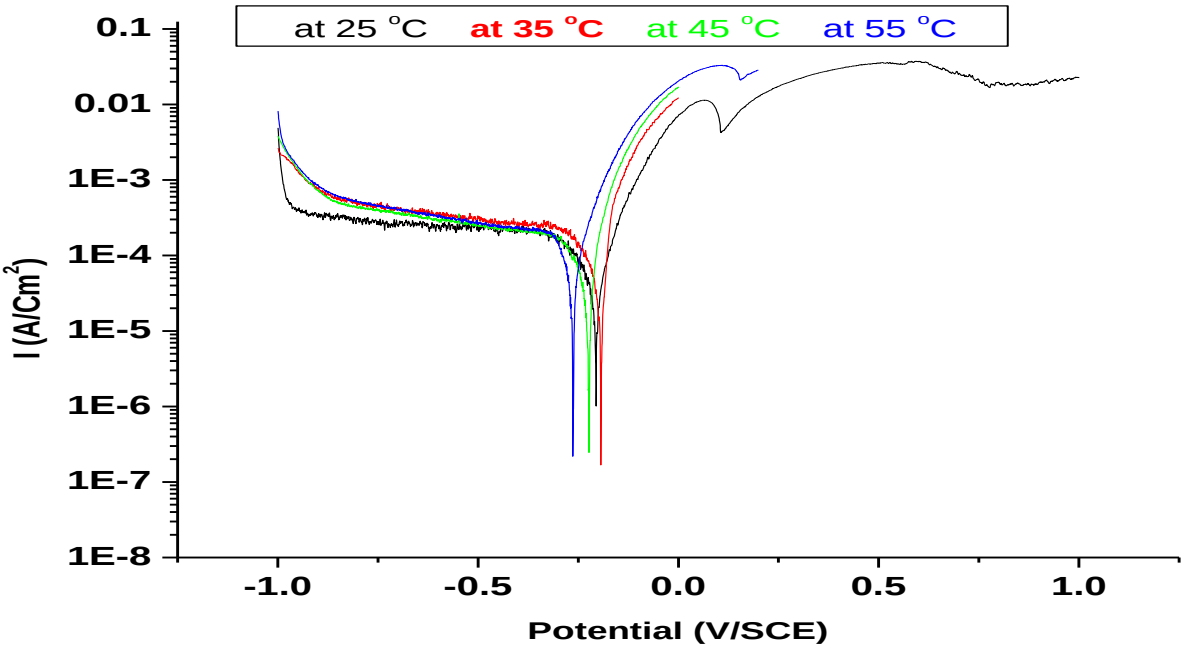

Figure 1: Tafel polarization curves of copper in 3% NaCl solution at different temperature without inhibitor (Blank)

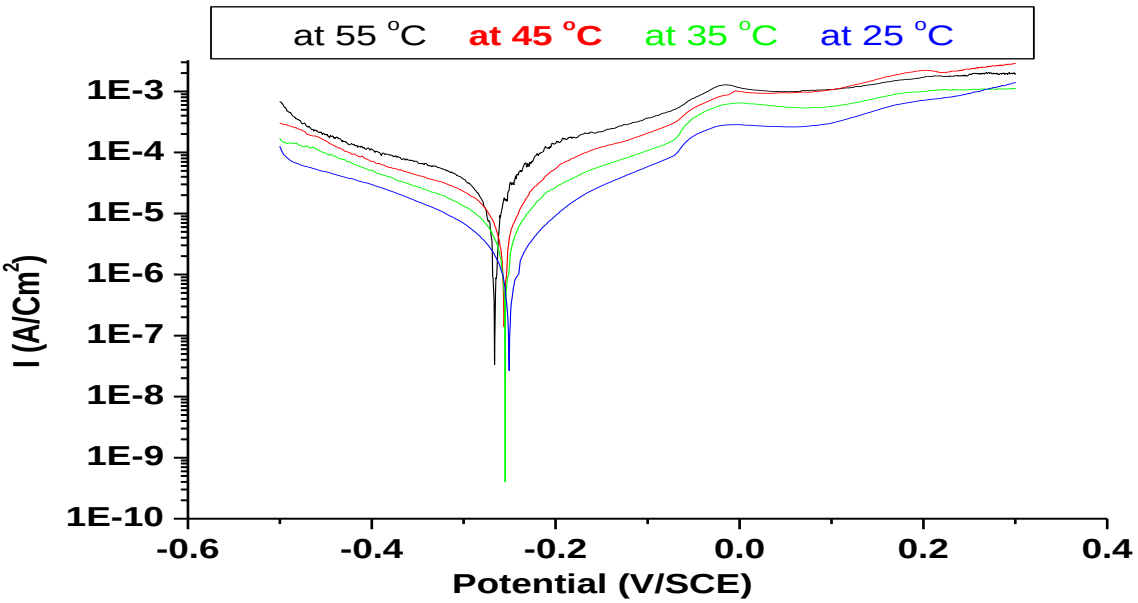

Figure 2: Tafel polarization curves of copper in 3% NaCl solution at different temperature in presence of inhibitor at optimal concentrations

The values of electrochemical kinetic parameters, like corrosion current density (Icorr) and the corrosion potential (E_{corr}), determined from these graphs by extrapolation of Tafel straight, are listed in Table 1. For all tests the inhibition efficiency (E %) was calculated using the equation (2) [54]. As can be seen from the data of Table 1, in the presence of inhibitor results in a marked shift in the cathodic branches and to a lesser extent in the anodic branches of the polarization curves. Moreover, with inhibitor the values of corrosion potential E_{corr} are nearly constant, therefore, bTA could be classified as a mixed-type inhibitor and besides, the cathodic Tafel slopes βc are approximately constant, indicating that the inhibiting action occurred by simple blocking of the available surface areas.

Table 1: Electrochemical parameters (E_{corr} and I_{corr}) and inhibitor efficiency, E(%), of the copper electrode in 3% NaCl at different temperature

Solutions	T (°C)	E_{corr}(V)	I_{corr} (A/cm^2) ×10^{-6}	βa(V)	βc(V)	E (%)
Blank (NaCl 3%)	25	-0.204	129	0.112	0.7	
	35	-0.195	138.2	0.118	0.663	
	45	-0.258	152.2	0.079	1.154	
	55	-0.262	187.7	0.103	1.588	
NaCl 3% + 1×10^{-3} M of bTA	25	-0.252	6	0.153	0.216	95
	35	-0.255	8.3	0.118	0.183	95
	45	-0.258	11.7	0.105	0.206	92
	55	-0.260	20.1	0.075	0.151	89

3.2. Adsorption isotherm behavior

The nature of corrosion inhibition has been deduced in terms of the adsorption characteristics of the inhibitor. Metal surface in aqueous solution is always covered with adsorbed water dipoles. Therefore, adsorption of inhibitor molecules from aqueous solution is a quasi-substitution process. A correlation between surface coverage (θ) defined by IE%/100 and the concentration of inhibitor (C_{inh}) in electrolyte can be represented by the Langmuir adsorption isotherm.

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh} \qquad (3)$$

Where, K is the adsorption constant. Surface coverage values (θ) for the inhibitor were obtained from polarization measurements for various concentrations, as shown in Table 2.

Table 2: Electrochemical parameters (E_{corr} and I_{corr}) and inhibitor efficiency, E(%), of the copper electrode in 3% NaCl with and without various concentration of inhibitors [9]

Solutions	C (M)	E_{corr}(V/ECS)	I_{corr}(A/cm^2)	E (%)	θ
Blank	0	-0.187	6.6×10^{-5}	-	
3,4'-bi-1,2,4-Triazole (bTA)	10^{-4}	-0.229	1.17×10^{-5}	82.27	0.8227
	5×10^{-4}M	-0.252	6.89×10^{-6}	89.56	0.8956
	10^{-3}M	-0.252	5,84×10^{-6}	91.15	0.9115
	5×10^{-3}M	-0.252	3.54×10^{-6}	94.63	0.9463

The best fitted straight line is obtained for the plot of C_{inh}/ θ versus C_{inh} with slopes around unity. The correlation coefficient (r^2) was used to choose the isotherm that best fit experimental data. The values of correlation coefficient are 1, 0.9532 and 0.942 for

Langmuir, Temkin and Frumkin isotherm, this suggests that the adsorption of 3,4-bi-1,2,4-triazole (bTA) on copper surface followed the Langmuir adsorption isotherm (Figure.3).

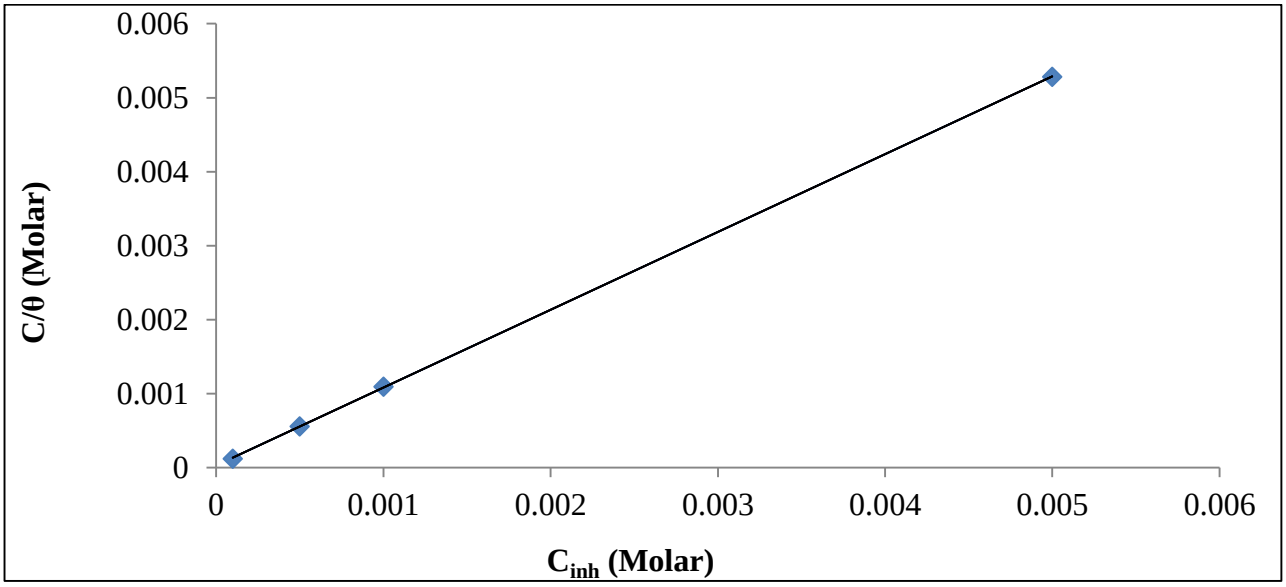

Figure 3: Langmuir adsorption plots for copper in 3% NaCl solution at room temperature

The value of adsorption equilibrium constant (K_{ads}) was calculated from the intercept of straight-line C/θ-axis, and given in table 3. The adsorption equilibrium constant related to the standard free energy of adsorption, $-\Delta G_{ads}$, with the following equation [55]:

$$K = \frac{1}{55,5} e^{(\frac{-\Delta G_{ads}}{RT})} \qquad (4)$$

Where 55.5 is the water concentration of solution in molar. The standard free energy of adsorption ($-\Delta G_{ads}$) values were calculatedand given in Table 3. The negative values of $-\Delta G_{ads}$ indicate the stability of the adsorbed layer on copper surface and spontaneity of the adsorption process [56]. Generally, the value of standard free energy around -20 KJ/mol or less (the absolute values) are involves with physisorption process and those around -40 KJ/mol or higher (becomes less negative) includes chemisoption process [57]. The (ΔG_{ads}) value was found to be -35.76 KJ/mol, this result indicated that the reaction mechanism on the surface of copper is consists of chemisorptions, or might be due to both physisorption and chemisorptions with strong interaction between the surface of copper and the molecules of inhibitor.

Table 3: Thermodynamic and equilibrium adsorption parameters for adsorption of bTA on copper surface in 3% NaCl solution.

Inhibitor	K_{ads} Mol/l	ΔG^0_{ads} KJ/mol	E_a KJ/mol	ΔH^0_{ads} KJ/mol	ΔS^0_{ads} J/mol	$E_a - \Delta H^0_{ads}$ KJ/mol
Blank	-------	--------	9.86	7.26	-295.29	2.6
bTA	33333.3	-35.76	32.17	29.57	-246.17	2.6

3.3. Activation energy calculations

The activation energies (E_a) for the corrosion of copper in 3% NaCl solution at different temperature in presence and absence of inhibitor were calculated using Arrhenius-type equation [58]:

$$\ln I_{corr} = \ln A - (\frac{E_a}{RT}) \quad (5)$$

Where E_a is the activation corrosion energy, R is the universal gas constant, A is the Arrhenius factor, T is the absolute temperature and I_{corr} corrosion courant. Arrhenius plots for the corrosion rate of copper in 3% NaCl solution are shown in Figure 4. The values of E_a for copper in 3% NaCl solution at different temperature with and without inhibitor calculated from the slope of (ln I_{corr}) versus 1/T plots and given in Table 3.

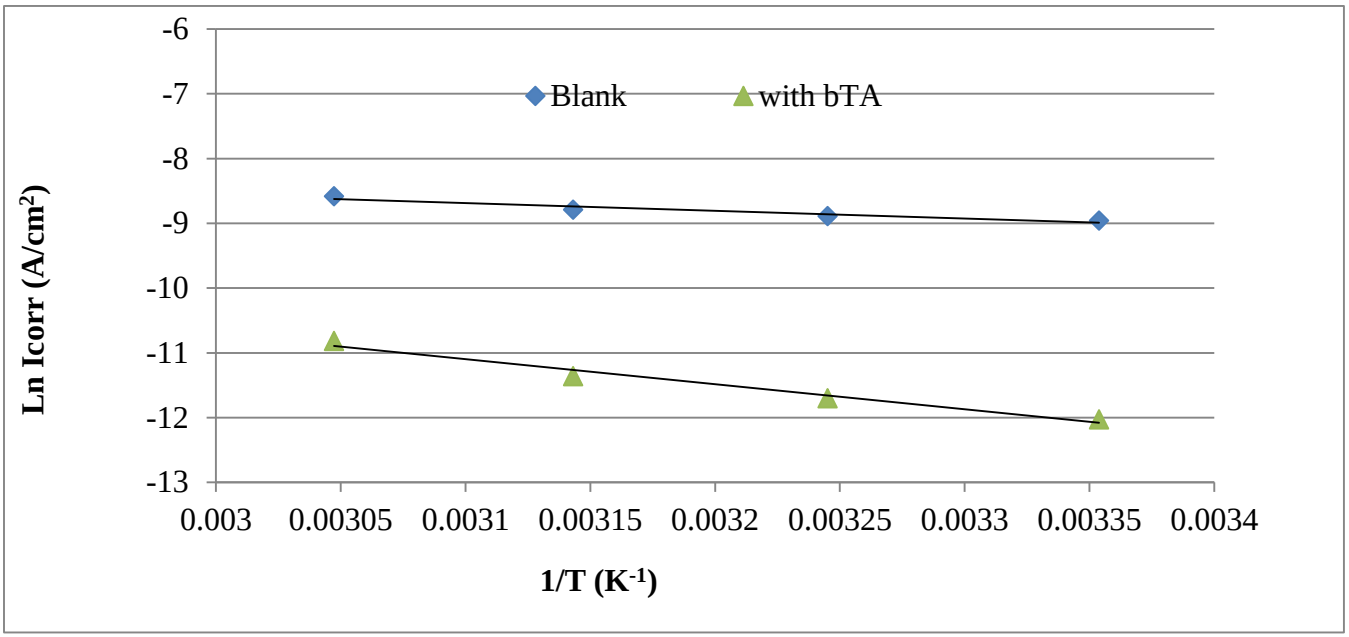

Figure 4: Arrhenius plots of Ln I_{corr} vs. 1/T for copper in 3% NaCl solution at different temperature with and without inhibitor.

The value of activation energy (Ea) increased for inhibited solution compared to the blank solution, but the change is not large to consider a mixed mode of interaction (physisorption and chemisorptions).

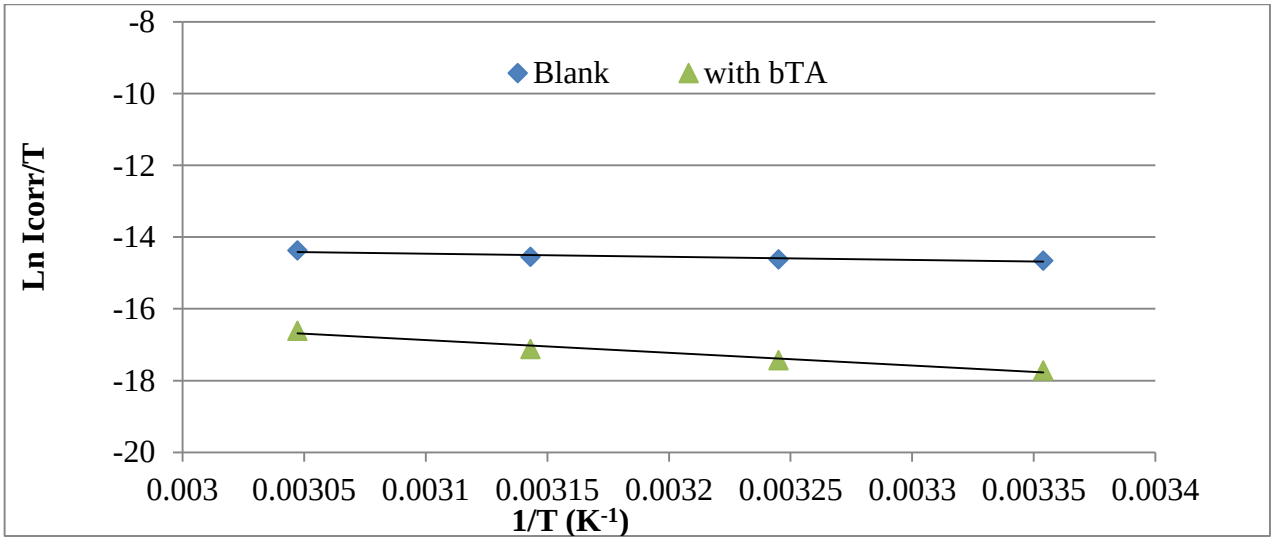

Figure 5: Arrhenius plots of Ln I_{corr}/T vs. 1/T for copper in 3% NaCl solution at different temperature with and without inhibitor.

The enthalpy (ΔH_a°) and the entropy (ΔS_a°) of activation for copper corrosion in 3%NaCl calculated using the following equation [58]:

$$\ln \frac{I_{corr}}{T} = (\ln \frac{R}{Nh} + \frac{\Delta S_a^\circ}{R}) - \frac{\Delta H_a^\circ}{RT} \qquad (6)$$

Where N is the Avogadro's number, R is the universal gas constant and h is the Planck's constant. The plot of $\ln(Icorr/T)$ against 1/T was shown in Figure 5 with a slope of $(\Delta H_a^\circ/R)$ and from the intercepts-axis of $(\ln \frac{R}{Nh} + \frac{\Delta S_a^\circ}{R})$, the values of ΔS_a° and ΔH_a° were calculated and given in Table 3. All values of Ea are larger than the values of ΔH_a°that indicated to the corrosion process must involve a gas reaction, associated with a decreasein the total reaction volume [56]. The difference value of $E_a - \Delta H_a^\circ$ are 2.60 kJ/mol which is approximately equal to the value of RT (2.63 kJ/mol). These values indicated that the corrosion process is a molecular reaction as it is defined by the following equation [59]:

$$E_a - \Delta H_a^\circ = RT \qquad (7)$$

Positive values of the enthalpies show the endothermic nature of the copper dissolution process. Negative sign of entropies reflects the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place in going from reactants to the activated complex [60, 61].

4. Conclusions

The inhibition efficiency of copper in 3% NaCl solution at different temperature with and without inhibitor decreased by increasing the temperature. Potentiodynamic polarization measurement show that 3,4'-bi-1,2,4-Triazole act as mixed type inhibitor for corrosion of copper in 3% NaCl solution with good inhibition efficiency at low temperature. The inhibition mechanism on the surface of copper is consists of both physisorption and chemisorptions with strong interaction between the surface of copper and the molecules of inhibitor.

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