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Corrosion Protection of Rotating Copper Rod in a Solution of NaCl and Na_2S by Using 4-Amino-4H-1,2,4-Triazole as Corrosion Inhibitor

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This work investigates the possibility of improving the corrosion resistance of rotating copper parts in a solution of NaCl and Na_2S by using one of triazole derivatives namely 4-Amino-4H-1,2,4-triazole (AHT) as corrosion inhibitor. The potentiodynamic technique was used for investigation of the effect of different variables on the corrosion of rotating copper such as rotational speed, initial S^{-2} concentration, rotating copper diameter, solution temperature and initial AHT inhibitor concentration. The results showed that AHT inhibitor can improve the corrosion resistance of rotating copper parts by a factor ranging from1.30 to 1.66 depending on AHT inhibitor concentration and rotational speed. The results show that the activation energy for corrosion of copper in 3.5% sodium chloride solution and 10ppm S^{-2} without the inhibitor ranges from 0.7 to 1.07kCal/gmol while it ranges from 1.879 to 3.366kCal/gmol in the presence of 10ppm of AHT corrosion inhibitor depending on the rotational speed which indicate that the process is mainly diffusion controlled.

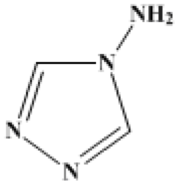
Keywords: Corrosion, rotating copper, corrosion inhibitors, triazole derivatives

1. INTRODUCTION

Copper as a material of construction is not only used for thermal conducting structures it is also widely used in printing board and integrated circuits owing to its excellent thermal conductivity, good corrosion resistance and mechanical workability[1-3]. Thus periodic descaling and cleaning in hydrochloric acid pickling solutions are necessary for preventing scale formation due to corrosion problems. Consequently, corrosion inhibition of copper in chloride solutions have attracted the attention of many investigators [4-9]. Presence of copper as part of a rotating object will enhance its corrosion especially in electrolytes where corrosion is controlled by diffusion step as the reduction of

O_2 at the cathode. It is generally believed that corrosion inhibitors effectively reduce the undesirable destructive effects of aggressive media and prevent copper dissolution. The inhibiting action of these inhibitors is usually attributed to their interactions with the copper surface via their adsorption and it was found to depend on the adsorption mode, its chemical structure, nature and surface charge of the metal, the and the type of the electrolyte solution [10,11]. Most of the excellent acid inhibitors are organic compounds containing nitrogen [12-14], oxygen [15-18], phosphorus [19] and sulphur [20-23]. The inhibition of copper corrosion using different inhibitors such as 2-amino5-ethylthio-1,3,4-thiadiazole (ATD) [24,25], N-phenyl-1,4-phenylenediamine (NPPD) [26], and 2-amino-5ethyl-1,3,4-thiadiazole (AETDA) [27] in 3% NaCl and 0.50 M HCl, was carried out and the results showed that, NPPD, ATD, and AETDA were found to be good mixed-type inhibitors for copper corrosion by strongly adsorbing on the copper surface with the inhibition efficiency increasing with increasing concentration. Different analysis techniques such as UV–visible absorption spectroscopy, FT-IR and as well as SEM and EDX investigations revealed that the molecules of these compounds adsorb on the copper and form a complex not only with the copper chloride complex on the surface but also in the solution.

The present work investigates possibility of reducing the corrosion rate of rotating copper rod in 3.5%NaCl solution in presence of Na_2S with different concentrations ranging from 2 to 10ppm by using one of triazole derivatives namely 4-Amino-4H-1,2,4-triazole(AHT) with a formula $C_2H_2N_4$ and a molecular structure that:



Potentiodynamic technique was used for measuring the corrosion rate at different conditions such as rotational speed, Na_2S concentration, AHT concentration, anode diameter and solution temperature.

2. EXPERIMENTAL PART

The main chemicals used are AHT (ACROS, 99%), hydrochloric acid (HCl, 32%), and acetone (Merck, 99.9%), NaCl as electrolyte, Na_2S as source of sulphide ions. were used as received. An electrochemical cell with a three electrode configuration was used; a rotating copper rod, silver foil surrounding the wall of the cell, and an Ag/AgCl electrode (in saturated KCl) were used as a working, counter, and reference electrodes respectively. The copper electrode was first polished successively with metallographic emery paper of increasing fineness of up to 1000 grits. The electrode was then washed with distilled water, degreased with acetone, washed using doubly distilled water again and finally dried with tissues. Electrochemical experiments were performed by using an Autolab 263 electrochemical interface Potentiostat- galvanostat. Potentiodynamic examination was used for determining the corrosion rate of rotating copper , by using Tafel plots and the slopes of anodic and cathodic slopes the corrosion current can be calculated and then the corrosion rate can be evaluated by using the Nova soft ware. under different rotational speed ranged from 100 to 400 rpm, initial S^{-2} concentration ranging from 2 to 10ppm, different AHT concentrations ranging from 2 to 10ppm, in addition, different rotating electrode diameter were used to be within the range from 0.2 to 1.0 cm and finally the effect of solution temperature was investigated for a temperature range up to 80°C. in all experiments NaCl concentration was kept constant at 3.5%.

3. RESULTS AND DISCUSSIONS

3.1. Effect of rotational speed and sulphide ion concentration

Figures 1.a and 1.b show the potentiodynamic results of the corrosion of rotating copper in 3.5% NaCl solution for different rotational speed (1.b) and different S^{-2} c oncentration(1.a)

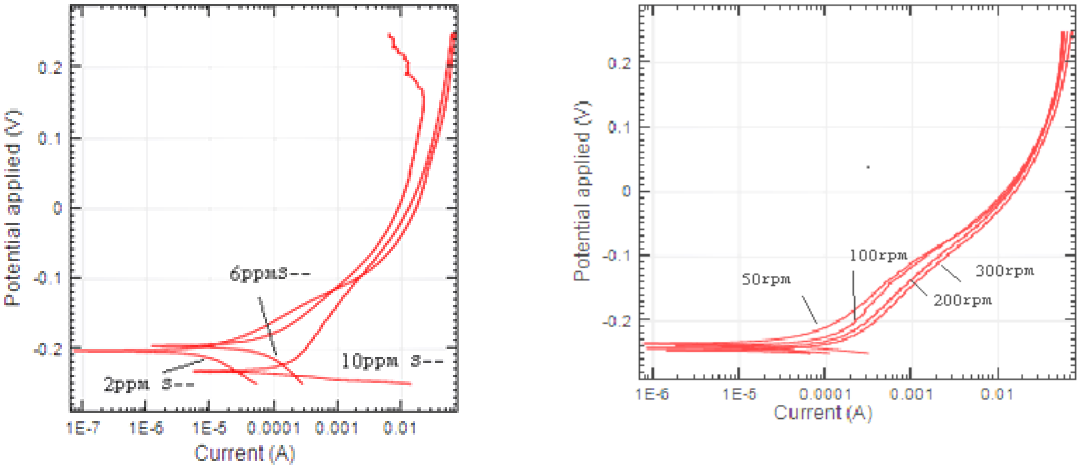


Figure 1. A: Potentiodynamic curves for corrosion of rotating copper in 3.5% NaCl at different S^{-2} concentrations. B: Potentiodynamic curves for corrosion of rotating copper in 3.5% NaCl at rotational speed.

Figure 2 shows that the corrosion rate has been increased by increasing the sulphide ion concentration, which can be clarified by the fact that direct contact between Cu and S^{-2}can go through the ionization of the copper anode and formation of cuprous ions followed by the reaction of the cuprous ions with sulphide ions to form cuprous sulphide in the form of a porous black-scale of cuprous sulfide on the surface according to the reactions that:

$$2Cu = 2Cu^{+} + 2e \qquad (1)$$

$$2Cu^{+} + S^{-2} = Cu_2S \qquad (2)$$

with an overall reaction:

$2Cu + S^{-2} = Cu_2S + 2e$ (3)

The Cu_2S film formation on the basis of specific adsorption of OH^- and S^{-2} (or HS^-) on the metal surface was explained by the mechanisms that, the S^{-2} ions which are adsorbed on the metal oxide will ultimately produce islands of Cu_2S. The non-stoichiometric Cu_2S will induce the outward diffusion of Cu ions to the film solution interface and allows cuprous sulfide scale growth on the top of the oxide film. The OH ions at the boundary between oxide film and sulfide film may react with the anodically formed Cu^+ ion and allow some growth of the oxide film or even if not previously formed. The oxide film may or may not doped with sulfur content never approach that of CuS scale that grows on top of it then an oxide-type may begin to grow beneath the sulfide film as suggested by More and Baccaria[28].

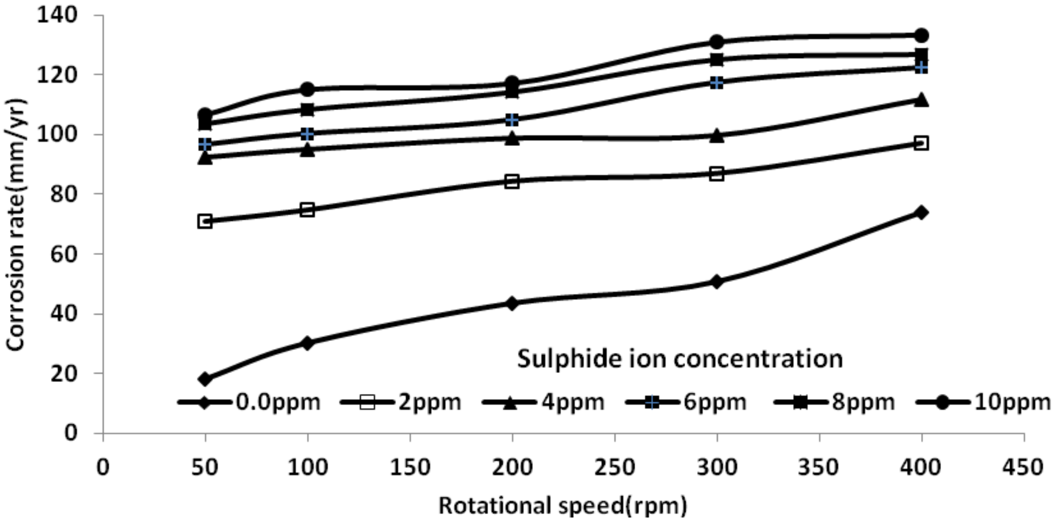


Figure 2. Corrosion rate vs rotational speed for different sulphide ion concentrations, at 3.5%NaCl, 25°C, 6mm anode diameter and no inhibitor.

As shown in figure 2 the corrosion rate has been increased by increasing the rotational speed which can be ascribed to the fact that the anodic and cathodic reactions are totally or partially diffusion controlled as follows:

At the anode:

$Cu = Cu^+_{(ads)} + e$ (fast step) (4)

$Cu^+_{(ads)} = Cu^{++} + e$ (slow step) (5)

where Cu^+ is an adsorbed species at the copper surface and does not diffuse into the bulk solution [29,30]. The dissolution of copper is controlled by the diffusion of soluble Cu^{++} species from the outer surface to the solution bulk.

At the cathode:

$1/2O_2 + 2OH + 2e = 2OH^-$ (6)

This reaction is also controlled by the diffusion of O_2 from the solution bulk to the Cu surface, thus the main controlling steps are diffusion controlled that were increased by increasing the rotational speed.

3.2. Effect of AHT inhibitor concentration

Figure 3 shows that the corrosion rate has been decreased by increasing AHT inhibitor concentration which can be interpreted by the fact that inhibitors are believed to be adsorbed on the metal surface and preventing diffusion of metal ions generated at the anode surface according to reaction 5 from the metal surface to the solution bulk and/or preventing cathodic reduction of oxygen. The inhibitor may affect either of them or both anodic and cathodic processes [31].

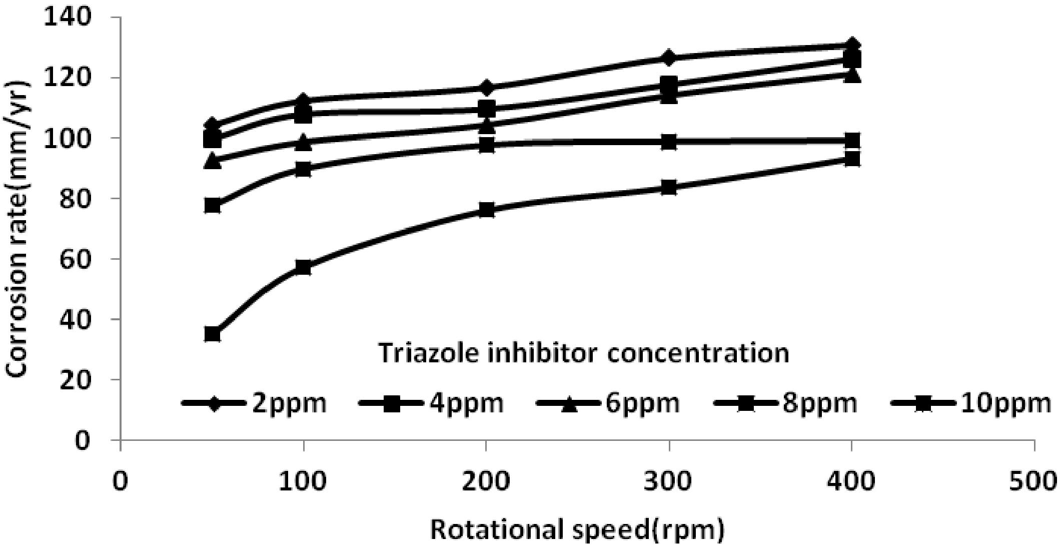


Figure 3. Corrosion rate vs rotational speed for different triazole inhibitor concentration; D=6cm, rotational speed 50rpm and T=25^{o}C.

As shown in figures 4.a and 4.b, upon addition of AHT inhibitor it is obvious that the slopes of the anodic and cathodic Tafel lines remain almost unchanged, giving rise to a nearly parallel set of anodic lines, and an almost parallel cathodic plots results too. Thus the adsorbed inhibitor acts by simple blocking of the active sites for both anodic and cathodic processes. In other words, the adsorbed inhibitor decreases the surface area for corrosion without affecting the corrosion mechanism of copper in these solutions, and only causes inactivation of a part of the surface with respect to the corrosive medium [32,33].

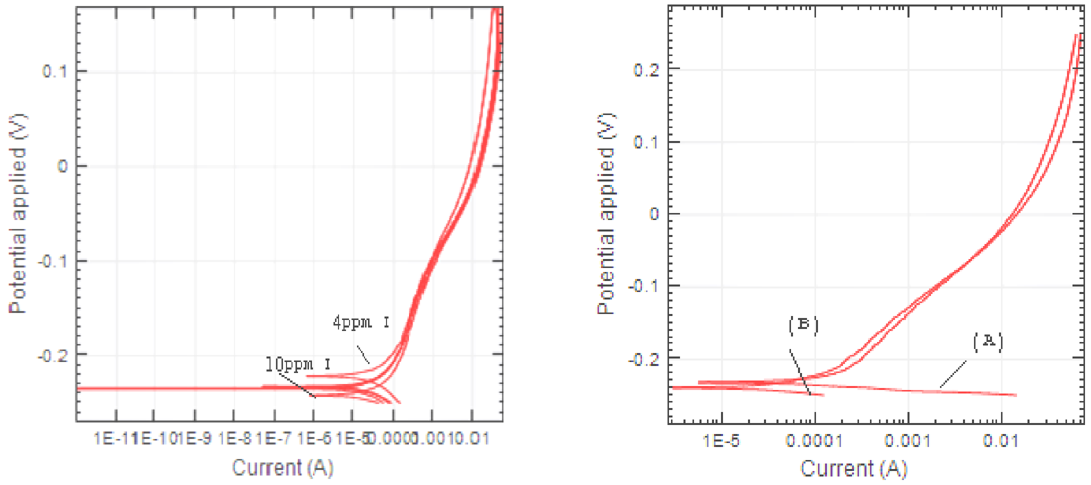


Figure 4. A: Potentiodynamic curves for corrosion of copper in 3.5% NaCl in presence of 10ppm S^{-2} for different AHT inhibitor concentrations at D=6cm, rotational speed 50rpm and T=25°C. B: Potentiodynamic curves for corrosion of copper in 3.5%NaCl +10ppm S^{-2} (A) 0.0ppm inhibitor and (B) 10ppm AHT inhibitor

It is clear that increasing the AHT inhibitor concentration will reduce the corrosion rate by a factor ranging from 1.30 to 1.66 depending on AHT inhibitor concentration and rotational speed.

3.3. Effect of anode diameter

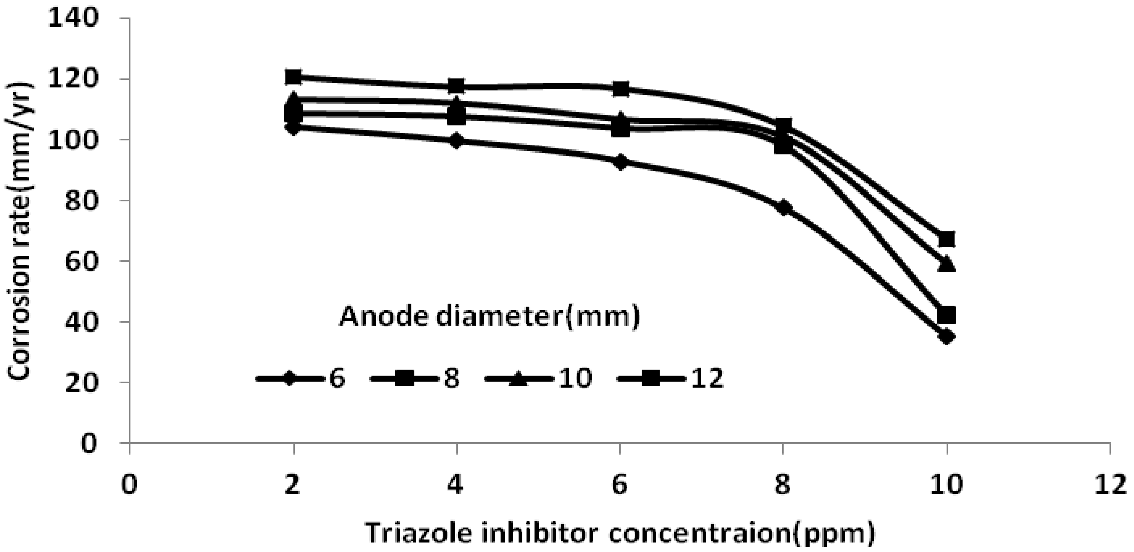


Figure 5. Corrosion rate vs AHT inhibitor concentration for different anode diameter, at 3.5% NaCl and 10 ppm S^{-2} and 25°C.

Figure 5 shows that the corrosion rate has been increased by increasing the anode diameter which can be ascribed to the fact that increasing the anode diameter will reduce the annular space between the rotating anode and the cathode and that will increase the turbulences generated between rotating anode and cathode and that reduce the thickness of diffusion layer which enhance the rate of mass transfer and hence corrosion rate. It is also clear that the corrosion rate has been decreased by increasing the AHT inhibitor concentration for different rotational anode diameter.

3.4. Thermodynamic aspects of the process:

Figures 6 and 7 show that the corrosion rate has been increased by increasing the solution temperature with and without the presence of the corrosion inhibitor which can be ascribed to the fact that at pH range from 4 to 10 where O_2 reduction is the cathodic reaction, the corrosion rate will increase by increasing the solution temperature up to 80^{o}C due to the increase in diffusion coefficient of O_2 at that range of temperature. The activation energy of the corrosion reaction was calculated for both cases using Arrhenius equation that:

$$K = Ae^{-E/RT}$$

Where K is the corrosion rate, A, E, R and T are Arrhenius constant, activation energy, gas constant and absolute temperature respectively. The value of activation energy for both cases can be calculated by plotting lnK versus 1/T at different rotational speed.

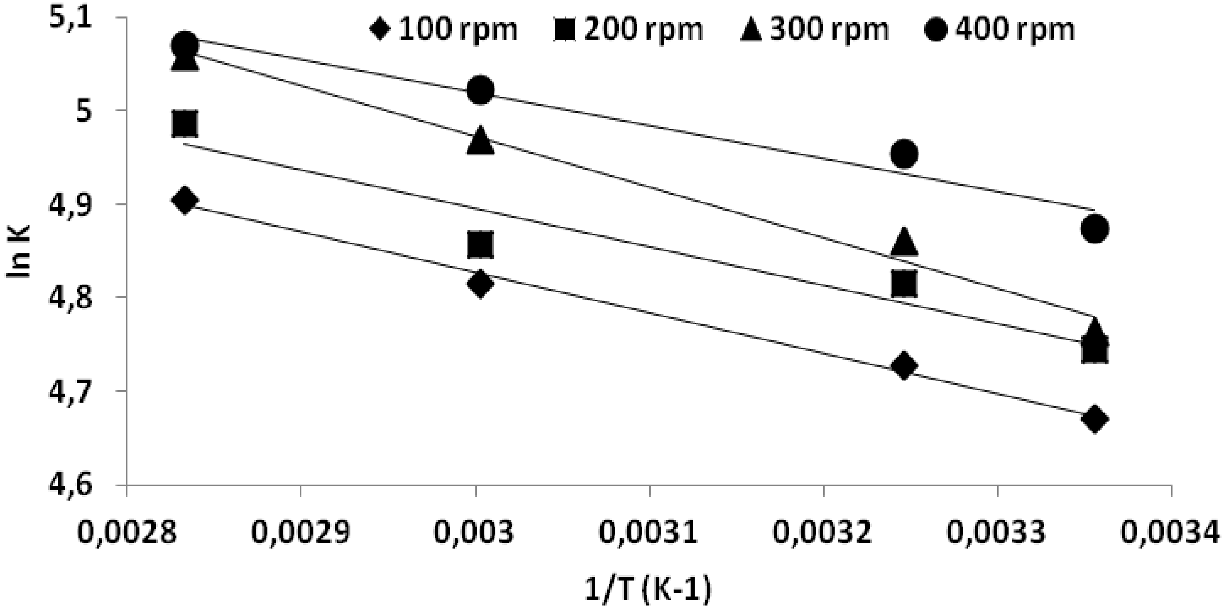


Figure 6. lnK vs 1/T for corrosion of rotating copper in 3.5% NaCl and 10ppm S^{-2} at different rotational speed without inhibitor.

The results of figures 6 and 7 show that the activation energy for corrosion of copper in 3.5% sodium chloride solution and 10ppm S^{-2} without the inhibitor ranges from 0.7 to 1.07kCal/gmol while it ranges from 1.879 to 3.366kCal/gmol in the presence of 10ppm of AHT corrosion inhibitor depending on the rotational speed. The above results indicate that corrosion of rotating copper in a solution of NaCl and Na_2S is diffusion controlled with and without the presence of the AHT corrosion inhibitor second and important fact is that the activation energy for the corrosion of copper in that solution has been increased by adding the AHT corrosion inhibitor, which indicates that required energy for copper corrosion has been increased by adding the inhibitor i.e. corrosion resistance has been increased by addition of triazole corrosion inhibitor. The increase in the apparent activation energy may be interpreted as physical adsorption that occurs in the first stage [34].

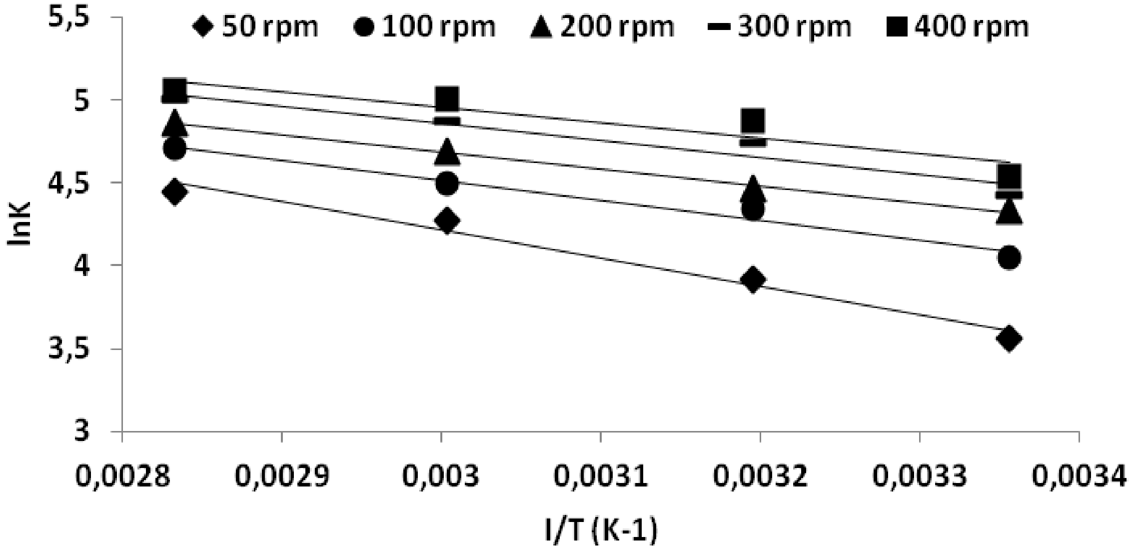


Figure 7. lnK vs 1/T for corrosion of rotating copper in 3.5% NaCl and 10ppm S^{-2} at different rotational speed with 10ppm AHT inhibitor.

One important point has to be clarified that the adsorption process is usually exothermic and proceed well at lower temperature which will affect the performance of the AHT inhibitor at higher temperatures, previous investigations of Guan etal[35] showed that the dissolution of copper in chloride solution is an endothermic reaction which can improve the performance of AHT inhibitor to a certain temperature range.

4. CONCLUSIONS

The corrosion inhibition of rotating copper rod in a solution of NaCl and Na_2S by using 4-Amino-4H-1,2,4-triazole inhibitor (AHT) was investigated under different conditions of rotational speed, initial S^{-2} concentration, rotating copper rod diameter, solution temperature and initial AHT inhibitor concentration. The results showed that AHT inhibitor can improve the corrosion resistance of rotating copper parts by a factor ranging from1.30 to 1.66 depending on AHT inhibitor concentration and rotational speed. The results show that the activation energy for corrosion of copper in 3.5% sodium chloride solution and 10ppm S^{-2} without the inhibitor ranges from 0.7 to 1.07kCal/gmol while it ranges from 1.879 to 3.366kCal/gmol in the presence of 10ppm of AHT corrosion inhibitor depending on the rotational speed which indicate that the process is mainly diffusion controlled.

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