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Contribution to the electrochemical behavior of Part I: copper in different solutions of adrenaline and catechol

O.S.Shehata*, I.Z.Selim, K.M.El Sobki, A.M.Abd El karym

Physical Chemistry Dept. National Research Center, Dokki, (EGYPT)

Tel : 202 (0161801664)

E-mail: Omniashehata@yahoo.com

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ABSTRACT

Galvanic anodic polarization of copper electrode in electrolytes of different pH values containing different proportions of adrenaline hydrogen tartarate (AHT) and catechol (Cat.) at different current densities has been studied. The effect of complex formation on the underlying anodic reactions and inhibition effect of these compounds on these electrodes is also studied. The cathodic deposition of copper in the prepared complexes on the surface of the cathode is involved to check their stability at different pH values and the effect of this stability on cathodic behavior of copper electrode. © 2008 Trade Science Inc. - INDIA

INTRODUCTION

Galvanostatic anodic polarization studies of copper metal in presence of some organic compounds revealed appreciable influence of complex formation on the metal dissolution potential in different pH values. The complex stability can be examined by cathodic reduction of their dilute aqueous solutions.

Studies on the mode of oxidation of metallic copper in acid, neutral and alkaline media had been conducted mainly by galvanostatic polarization. The mechanism of cathodic and anodic behavior of copper has been deduced^[1].

The polarization behavior of acid copper solution was studied^[2] using both direct and pulsed reverse current. The use of pulse reverses current in solutions containing both polyether and sulphopropyl sulphide was found to inhibit the adsorption/ diffusion at the cathode surface. The effect of pulsed current on additive containing solutions can improve dramatically the metal dis-

tribution in low current density areas on plated items.

Organic films electrodeposited on a copper electrode from imidazole basic solutions were investigated^[3] by different methods. The coating on the electrode was found to consist mainly of copper (I) imidazolate with either a random or perpendicular orientation to the crystalline surface. The IR data indicate that the film was formed at the solution metal oxide/hydroxide interface and a more compact film was formed closer to the metal surface.

The electrochemical behavior of copper and its alloys in different media is a current interest, because they are widely used in industry. Hydric phenols were considered as strong colored complexing and chelating agents.

Catechol and its important derivative adrenaline have the chemical properties of phenols and property of powerful reducing agents. Their complexing reactions with metals can be used either to determine the essential metal ions in solution or to determine these phenolic compounds in natural extracts.

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The present investigation comprised galvanostatic anodic polarization of copper electrode in electrolytes of different pH values containing different amounts of adrenaline hydrogen tartarate (AHT) and catechol (Cat.) with the aim of elucidating the effect of complex formation on the underlying anodic reactions. Another approach to the relative stabilities of the different complex species involved the cathodic reduction of these complexes in dilute aqueous solutions using spectroscopically pure copper as cathodes.

EXPERIMENTAL

Materials

Highest purity of adrenaline hydrogen tartarate (AHT) $C_9H_{13}NO_3 \cdot C_4H_6O_6$, and catechol (Cat) $C_6H_6O_2$, in addition to spectroscopically pure copper were used in this study.

Solutions

Stock solutions of (AHT) and Cat., were prepared by dissolving the calculated weights in the proper volume of distilled water and standardized using recommended procedure⁽⁴⁾. Fresh accurate dilute solutions were prepared at each study, keeping them in black bottle.

The buffered solutions free from AHT and Cat., such as acetate buffer (pH = 4.5), phthalate buffer (pH = 6.5) and borate buffer (pH = 9.5) were prepared. Buffered solutions of the above pH values were also prepared so as to contain varying amounts of AHT and Cat.

Electrodes and cell

Spectroscopically pure copper formed the working electrode, fitted to a glass tube by means of epoxy resin leaving a special surface area of 0.25 cm^2 to contact the solution. Before every run the electrode surface was mechanically polished using successive grades of emery papers up to 1000 grit. The electrode was rubbed with a smooth polishing cloth, degreased with acetone, revised with distilled water and transferred quickly to the electrolytic cell containing a fresh test solution. Saturated calomel electrode (SCE) was used as a reference electrode. Its stability was checked after each experiment to ensure the reliability of the experiments. A lugging capillary introduced and kept very close to the surface of the working electrode to minimizing the ohmic drop. Platinum sheet was used as a counter

electrode.

All measurements were carried out at a constant room temperature of 25°C .

The cell used was made of Pyrex glass without rubber connection and consists of two components with a sintered glass disk in between to ensure the separation of the anolyte and catholyte as shown in the schematic diagram.

Polarization measurements

Electrode potential measurements and polarization (anodic and cathodic measurements) at different current densities were utilized for copper electrode in absence and presence of ligand (AHT and Cat.), using Prazisions Potentiometer E 353 Metrom AG Herisau, Schweiz and constant current devise (local instrument).

Anodic polarization

The open circuit potential (OCP) measurements of the working copper electrode were followed with time till steady state potential values were reached^[5], and recorded in different buffer solutions without and with various amounts of ligand (AHT or CAT). Plotting the steady state potential values with logarithm of ligand concentration gives a straight line, from the slopes the ratio between metal and ligand was calculated^[6].

The anodic behavior of copper electrode was studied in the same solutions at different current densities, by passing the current through the cell for five minutes, the charging and decay curves were recorded at each current density. The process was repeated along a wide range of current density on the same electrode surface, the variation of anodic potential with time was recorded.

Cathodic polarization experiments were extended for appropriate time at each current density till steady state. Then shut off the applied current and repeated this step for various current densities, the decay potentials were followed with time.

RESULTS AND DISCUSSION

The present investigation involves the study of anodic polarization of copper electrode in electrolytes of different pH values 4.5, 6.5 and 9.5 containing various proportions of adrenaline hydrogen tartrate (AHT) and catechol (Cat.) at different current densities (c.d.). The effect of complex formation on the underlying anodic reactions and inhibition effect of these compounds on

TABLE 1: The open-circuit potential values (mV) of copper electrode in absence and in presence of different concentrations of ligand in various pH values

% of ligand	pH = 4.5		pH = 6.5		pH = 9.5	
	AHT	Cat.	AHT	Cat.	AHT	Cat.
0	211.4	211.4	168.0	168.0	185.9	185.9
0.1	219.5	225.7	163.0	190.8	159.2	136.5
0.2	216.3	222.9	159.0	198.6	156.0	134.0
0.3	213.3	220.0	157.0	203.5	153.0	128.2

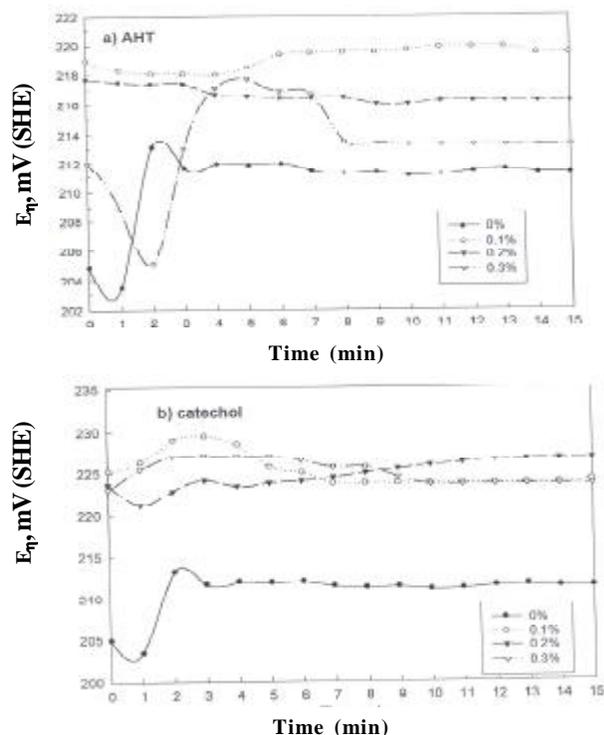


Figure 1: The open circuit potential-time relation for copper electrode at pH- 4.5 in absence and in presence of different concentrations of (a) AHT (b) Catechol

these electrodes is studied. This study involves also the cathodic deposition of copper in the prepared complexes on the surface of the cathode to check their stability at different pH values and the effect of this stability on cathodic behavior of copper electrode.

Anodic polarization

The variation of open circuit potential (OCP) with time of copper electrode in acidic buffer solutions of pH= 4.5 in absence and in presence of various concentrations of AHT and Cat. are shown in figure (1) as representative curve.

The results show that the steady state open circuit potential in absence of AHT lies at a value of 211.4 mV (SHE). It corresponds to very small concentration of copper ions in the vicinity of the electrode surface; this

may be attributed to the slight dissolution of spectroscopically pure copper in such acid medium.

The open circuit potential values obtained for copper electrode in absence and presence of various concentrations of AHT and Cat. in different pH values are represented in TABLE 1.

It can be observed that, the open circuit potential shifts to more positive value in presence of 0.1% AHT, then it decreases by increasing AHT concentration but it is still more positive than the value in absence of AHT. These values show that the equilibrium concentration of copper ions near the electrode surface decreases by increasing AHT concentration due to its tendency to form Cu-complexes.

This behavior may be explained on the basis that, in presence of 0.1% AHT ligand, the first adsorbed molecules are attached to the most active anodic sites, usually considered to be the corners or edges of incomplete layer of atoms on the metal surface. This would interfere with the anodic reaction by hindering the escape of Cu (II) ions from the metal surface into the solution. Upon increasing AHT concentration, more molecules of the ligand would be adsorbed due to Van der Waals forces between the AHT molecules. The increasingly close packed film thus built up would further inhibit the anodic reaction, by steric hindrance to escape of Cu (II) ions.

This behavior is confirmed by the fast increase of potential to more positive values with time. At 0.1 % the OCP reached 219.5 mV due to the thickening of complex layers, it decreases again to a constant value of stable complex tightened layer to the surface.

These results indicate that the rate of dissolution increased, but the copper ions decreased with increasing the concentration of AHT due to the capturing Cu (II) ions in Cu-AHT complex formation.

This phenomenon is clearer at 0.3 % AHT. at time from 0 to 1.0 minutes, the ligand molecules penetrate fast into the surface of the electrode to react with Cu (II), Therefore Potential fastely dropped to 205 mV.

The potential values starts again to raise up to 217 mV at time 2 to 4.5 minutes, may be attributed to the fast thickening of Cu-AHT complex layer, causing the electrode polarizable to the more positive value. Some molecules of this complex layer leaves the electrode surface to give finally the tightened layer at which the electrode equilibrium potential arrived a steady state value of 216 mV.

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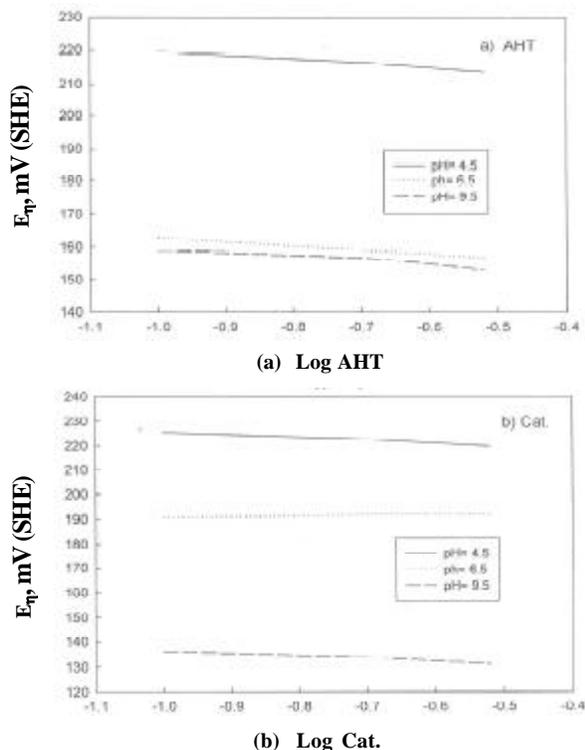


Figure 2: Variation of open circuit potential of copper electrode at various pH values with log conc. of (a) AHT (b) Cat.

The rate of penetration of AHT into the electrode surface decreases with increasing of AHT concentration, which may be attributed to the thicker Cu-AHT layer at the electrode surface.

Also, it can be seen that, the open circuit potentials obtained in presence of 0.1, 0.2 and 0.3% catechol shifts to more positive value than the buffer alone (211.4 mV). This behavior as in case of AHT indicating that, the equilibrium concentration of copper ion decreases with increasing ligand concentration, due to the formation of Cu-Cat. complex.

The thickening of complex layer of Cu-Cat., takes also 5 minutes as in case of Cu-AHT; at the same pH=4.5

In near neutral phthalate buffer solution of pH=6.5 in absence of AHT ligand, the open circuit potential is about 168 mV (SHE) which corresponds to small copper ion concentrations that react with oxygen in aerated medium to give oxide in the vicinity of the electrode surface, according to the reaction.



This indicates that the pre-immersion oxide film is retained in neutral solutions^[7] where it dissolves in acid medium. CuO and Cu_2O are possible oxides but Cu_2O

is the reaction product usually formed on copper immersed in aerated aqueous media and the anodic dissolution was controlled by diffusion of copper ions in the oxide films (Cu_2O)^[8].

The open circuit potential values obtained in the same buffer solution of pH = 6.5 containing 0.1%, 0.2% and 0.3% AHT indicate that the potential values shift to less positive direction with increasing AHT concentration than buffer alone due to the increasing rate of copper dissolution as a result of complex formation.

In presence of different concentrations of Cat., such as 0.1%, 0.2% and 0.3% in buffer solution of pH = 6.5; the potential values shifted to more positive values, indicating the formation of film of Cu-Cat. complex on the electrode surface, while its thickness increases with increasing catechol concentration.

The careful inspection of these results refers to the fast built up of the Cu-Cat. complex layer on the surface of the electrode within the time interval from 0 to 8.0 minutes in case of 0.1% to 0.2% catechol. The built up of the Cu-Cat. layer is faster at 0.3% catechol and takes only time interval from 0 to 4 minutes to get more positive steady state equilibrium potential of 202 mV. The built up of the Cu-Cat. complex layer is more regular than the fluctuated one in case of Cu-AHT as indicated by the regular variation of polarization potential in case of catechol, and its non-regular variable in case of AHT.

In alkaline borate buffer solution of pH=9.5 in absence of AHT, the potential has a value of 185.9 mV (SHE) which corresponds to passive layer consists of an inner Cu_2O and outer CuO hydrated layer⁽⁹⁾, but in presence of 0.1%, 0.2% and 0.3% AHT, the potential shifts to less positive values. These values indicate that the dissolution of copper increases with increasing ligand concentration due to migration of copper ions to bulk solution forming the Cu-AHT complex. The potential values of the open circuit potential of copper at pH = 9.5 in different concentrations of catechol shifted to less positive value than in case of AHT.

It can be noticed that there is a wide difference in OCP values of electrode in buffer alone and with AHT or Cat. in alkaline buffer solutions. This may be due to the high dissolution of copper in such solution leading to the formation of Cu-AHT or Cu-Cat. complexes, which mask the copper ions leading to less potential values than that with buffer alone.

The relation between the steady state potential

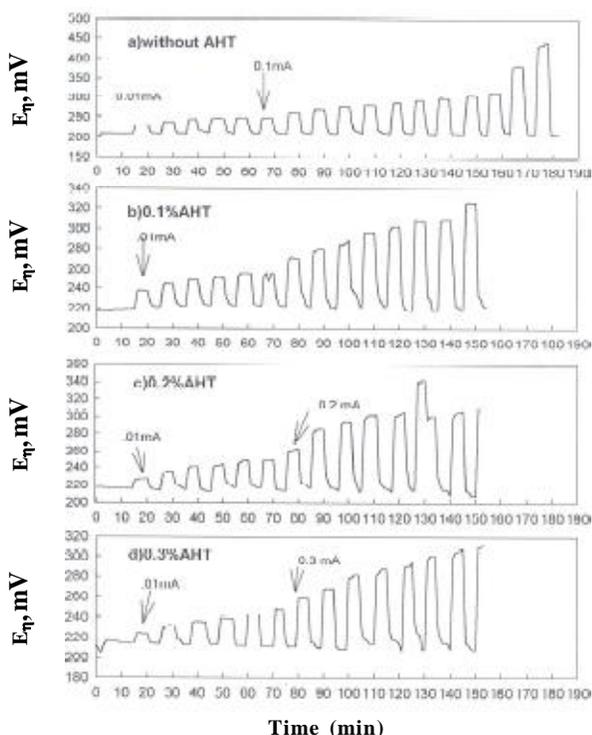


Figure 3 : Charging and decay curves of copper electrode in acetate buffer pH=4.5 in absence and in presence of different AHT concentrations

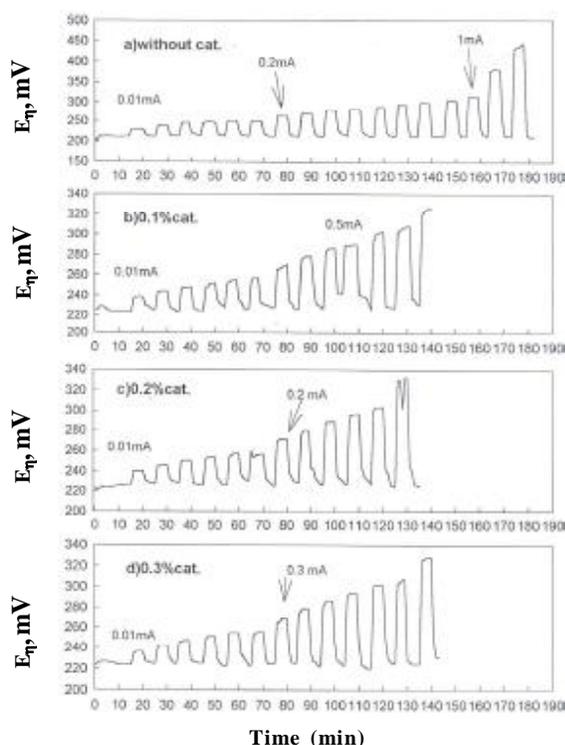


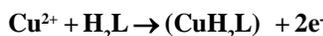
Figure 4 : Charging and decay curves of copper electrode in acetate buffer pH=4.5 in absence and in presence of different catechol concentrations

TABLE 2: The slope of logarithmic relation of copper electrode with different concentrations of AHT and Cat. with open circuit potential values at various pH values

pH	Slope mV	
	AHT	Cat.
4.5	30	28
6.5	30	31
9.5	31	32

(OCP) and log concentration of AHT or Cat. at various pH values is shown in figure (2). the relation is straight lines with slopes represented in TABLE 2, which is independent of pH of the solution.

This behavior may be explained on the basis that the anodic dissolution of copper in presence of ligand (AHT or Cat.) may be represented by:



Applying Nernst equation it was found that the $\text{slop} = 29.5 \text{ mV}$ at 25°C , which is in agreement with the experimentally measured value of $30 \pm 1 \text{ mV}$.

The charging and decay curves of copper electrode in absence and presence of AHT and Cat. in different buffer solutions using pulse current are represented to study the effect of current on the behavior of the electrode in such buffer solutions.

Figures (3, 4) show the charging and decay curves obtained of copper electrode in acetate buffer solution of pH= 4.5 in absence and presence of different concentrations of AHT and Cat. as representative curves. It can be observed that, in absence of AHT the curve refers to the slow gradual increase in polarization potential with increasing of current density this is due to the presence and thickening of the resistive oxide film^[10]. On shut off the current, the electrode potential returns rapidly to the initial steady state potential value, indicating that the film formed is rapidly dissolved or the oxide may be in equilibrium with copper ions.

In presence of 0.1% AHT, a slight increase of polarization at all current densities occurred due to the formation of a thin film of copper complex on the electrode surface. The increase in the polarization behavior may be due to the ohmic potential drop across the film as well as the charge transfer polarization. The resulting potential gradient is necessary to drive the dissolving copper ions through the surface film. When shut off the current, the electrode potential returns to have a value slightly positive than that of OCP due to persistence of the film of Cu-complex and /or copper oxide on the

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surface of the electrode.

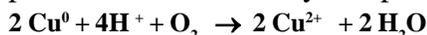
In presence of 0.2% AHT, the potential shifted to the less positive direction than 0.1% up to 0.2 mA Cm⁻², due to the depletion of Cu ions near the surface of the electrode via migration of Cu ions to the bulk solution to form Cu-AHT complex. With increasing of the applied current; the potential increases again to a value more anodic than that in the buffer alone. This is due to adsorption of complex at the surface of the electrode. When shut off the current the potential returns to a value less positive than that of the OCP due to decomposition of the complex or rearranging itself towards copper ions that diffused in solution.

In presence of 0.3% AHT the potential as in 0.2% has a value less than that in buffer alone up to 0.3 mA Cm⁻², then it takes the same value as in buffer with increasing current. This is due to the fact, that the force of ligand attraction towards copper ions at lower current density is more preferable than that of the electrode surface. So copper ions migrate to the bulk solution but with increasing current, AHT migrates to the surface, forming the complex on the electrode surface. On shut off the current the potential shifts to the less positive direction than OCP indicating the presence of a thin film at the electrode surface.

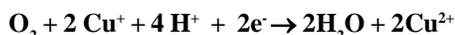
It can be noticed from figure (3) that there are two arrests (plateau), one is the formation arrest when applying the current and the second is the decomposition arrest when shut off the current. The two arrests are linear in absence or presence of different concentrations of AHT except in presence of 0.3% AHT, the decomposition arrest is nonlinear at current density (c.d) more than 0.3 mA Cm⁻², due to the dissociation or diffusion of Cu (II) ions via the film formed into the bulk solution. The formation and decomposition arrests are nonlinear at all current densities.

In case of Cat. (figure 4) the formed film needs higher current density to be adsorbed on the electrode surface more than in case of AHT.

The overall reaction during the dissolution of copper in acidic solution may be represented by:



Which is the sum of galvanic reaction

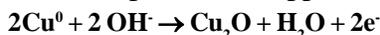


The behavior of copper electrode in near-neutral buffered solution (PH= 6.5) shows initial oxidation⁽¹¹⁾ followed at slight higher potential by oxidation of Cu to

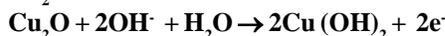
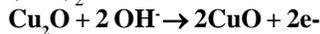
Cu₂O and oxidation of Cu₂O to CuO



In alkaline solution (pH= 9.5), Cu₂O is firstly the oxidation product of copper:



Followed by oxidation of Cu₂O to CuO or Cu(OH)₂



Dissolution of copper in neutral and alkaline solution leads to the formation of an oxide film consisting of Cu₂O or duplex⁽¹²⁾ Cu₂O/CuO depending on the electrolyte composition. The passivation of copper in alkaline solution is due to oxide layer whose electrochemical character and structure depends considerably on the solution composition and applied current.

It is noticed that a green precipitate was formed at the copper electrode in presence of AHT in different buffer solutions but it more compact in borate buffer and black precipitate was formed in presence of Cat. So the precipitate found on the electrode surface depends on the ligand not on the buffer.

The effect of ligand concentration on the mechanism and kinetics of anodic dissolution of copper may be visualized from the current polarization relations at various pH values. The anodic Tafel lines for various pH values at a various ligand concentrations from 0 to 0.3% are determined in the TABLE (3). The measured overpotential would thus be the sum of both activation and ohmic polarization of the surface film of copper complex and possible copper oxide formed on the electrode surface. The lugging capillary was positioned very close to the electrode surface; hence the ohmic potential drop on the solution side was negligible. Furthermore; the polarization was taken at the moment of switching on the current and before any signification film thickening occurred, hence the polarization is essentially activation one. The over potential values depend on the metal nature, the kind of the electrolyte solution, pH and the c.d. values.

Figure (5) representes the relation between η and logarithm of current density as representative curve where η is the change in electrode potential that occurs by applying current to the electrode surface in absence and presence of different concentrations of AHT and Cat. At pH = 4.5 It can be seen that, there are two distinctive Tafel regions, the first at low polarization and

TABLE 3: Tafel slope values of copper electrode with different ligand concentrations in various pH values

Ligand %	pH=4.5		pH=6.5		pH=9.5	
	AHT	Cat.	AHT	Cat.	AHT	Cat.
0.0	162	162	478	478	-	-
	63	63	65	65	-	-
0.1	171	162	394	261	695	1005
	65	67	54	134	554	912
0.2	225	162	334	300	512	980
	67	71	59	107	482	950
0.3	246	179	225	290	916	1100
	65	76	71	102	606	980

the second at higher polarization. It can also be noticed that, the presence of ligand increases the Tafel slope in the low polarization region as well as in high polarization region as shown in TABLE (3).

The first Tafel region corresponds to diffusion controlled mechanism, whereas the electron transfer in the second Tafel region is under activation control.

The overpotential values shifted to less positive value with the increasing of the ligand concentration in first Tafel region but in the second Tafel region the potential has nearly equal values. The anodic transfer coefficient, symmetry factor, takes the value between 0 to 1,

Its effect on the potential difference across the double layer promotes the forward reaction, and it can be calculated from the following equations:

$$\eta = E_i - E^0$$

Where E_i is the electrode potential value in the moment of switching on the applied current before any significant film appeared at the electrode surface and E^0 is the potential at the equilibrium. This relationship is expressed by Tafel equation:

$$\eta = a + b \log I$$

$$b = 2.303RT / (1-\alpha) ZF$$

Where b is Tafel slope, α is transfer coefficient, z is the number of transfer electrons, T is the temperature ($= 298K$) and R is the gas constant $8.314 JK^{-1}ml^{-1}$ and F is Faraday constant ($9.6519 \times 10^4 C$). Tafel slope in acidic solution in presence of different concentrations = $63-71 mVdec^{-1}$, indicating that the initial anodic step is essentially the same in all solutions.

The high values of Tafel slopes may be due to diffusion of dissolved oxygen in solution or in the surface films^[13]. The Tafel slopes in alkaline solutions were found to be much larger than in acidic due to the presence of the surface oxide and/ or complex films on the electrode surface at such a high anodic potentials.

The relation of over potential and log c.d. for cop-

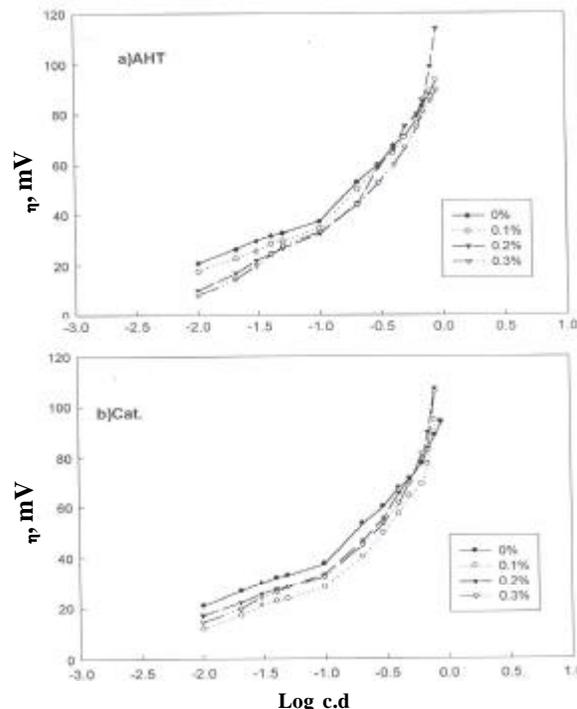


Figure 5 : Current polarization curves for copper electrode at pH= 4.5 in absence and in presence of (a) AHT (b) Cat.

per electrode in different pH values of 4.5, 6.5 and 9.5 in absence and presence of different concentrations of AHT and Cat. is studied.

Figure (6) shows the current polarization curves for copper electrode in presence of 0.2% ligand at different pH values as representative curve. It shows that the potential in acidic solution is less positive than that in neutral and alkaline solutions at all current densities and constant ligand percent indicating that the film is much thicker in alkaline solution.

The passivation is described through the formation of Cu_2O monolayer followed by the growth of a passive CuO layer, and the build of the $CuO-Cu(OH)_2$ layer, so in buffer solution without ligand the formation of these oxide is appeared. In presence of ligands the overall process being accompanied by the formation of $Cu(II)$ soluble species^[10] which form the complex film at the electrode surface.

It was also found that the relative contribution of these processes and the structure of the passive layer depend on the number of variables such as, the solution composition, chemical structure of the organic compounds, the nature and surface charge of the metal ion, distribution of charge in the molecule and the type of

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interaction between organic molecules and the metallic surface^[14]. The physical (electrostatic) adsorption and chemisorptions are the principal types of interaction between and organic compound and the metal surface, the chemisorptions occurs more slowly than physical adsorption.

AHT and Cat. can be oxidized giving ketone namely adrenochrome in alkaline medium. The ketonic compounds become chemisorbed on the active centers of the metal surface through the lone pair of the ketonic oxygen electron, and also lone pair on the nitrogen of the amino group of AHT. The presence of compact film of Cu-AHT and thin film of Cu-Cat. complex at electrode surface indicate that the adsorption ability of AHT is large than that of catechol especially in low concentration but in high concentration the other factor effect is steric hindrance.

In general the mechanism for growth of the films beyond the chemisorbed mono-layer stage usually involved transport of Cu ions through the porous complex surface films.

These ions then react with physically adsorbed AHT or catechol molecules to precipitate insoluble Cu-ligand complexes at the surface. With a reservoir of ligand maintained in the treatment solution, the availability of Cu ions at the solid-liquid interface controlled the growth of the Cu-ligand film.

The effect of adsorbed molecules on the metal is to retard the anodic dissolution reaction of this metal by means of different mechanisms as changes in the electrical double layer, formation of a physical barrier, reduction of metal reactivity, participation of the inhibitor in partial electrochemical reactions.

Cathodic polarization

This part aims chiefly to check the cathodic deposition of Cu (II) from its phenolic complexes and how this process depend partly on the stability of these compounds in relation to process conditions (pH, concentrations of complexes, current density, polarization potential..... etc.) therefore the cathodic charging and decay curves of copper electrode in presence of 0.05% w/v Cu-AHT or Cu-Cat., complexes in different pH values and applied different current are studied

Representative charging and decay curves obtained on cathodic polarization at a spectroscopically pure copper cathode for solutions of 0.05% w/v Cu-AHT and Cu-CaT. complexes in acetate buffer of pH = 4.5

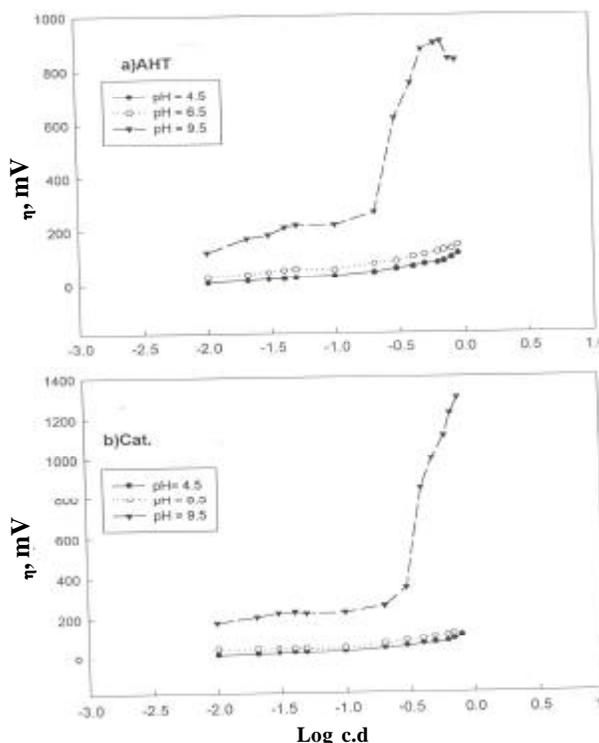


Figure 6 : Current polarization curves for copper electrode presence of 0.2 % AHT or catechol at different pH values (a)AHT (b) Cat.

at different current densities (0.03, 0.05 and 1.0 mA cm⁻²) are shown in figure (7). At 0.03 mA cm⁻² the potential decreases very slowly within 5 minutes from 150 mV to 130 mV and keeps its value constant up to 40 minutes. On shut off the current the potential returns to a more positive potential 190 mV than the starting value.

On increasing the current to 0.05 and 1.0 mA cm⁻² the initial potential values is 30 mV and -75 mV representively and taking constant value up to 45 minutes. On shut off the current the potential shifts to more positive values 150 mV and 40 mV in case of 0.05 and 1.0 mA cm⁻² respectively. The slow deposition of copper is explained by the high stability values of this complex in acid medium. It is noticed that the potential shifts to more negative value with increasing the applied current.

In case of Cu-Cat. Complex, on applying 0.03 mA and 0.05 mA, it is noticed that abrupt decrease of potential, this may be due to hydrogen evolution. On shut off the current the potential taking 5 minutes to reach steady value and it shifted to less positive values.

When applying 1.0 mA the potential decreases slowly within 15 minutes then decreases sharply, then the potential takes constant value up to 55 minutes. This

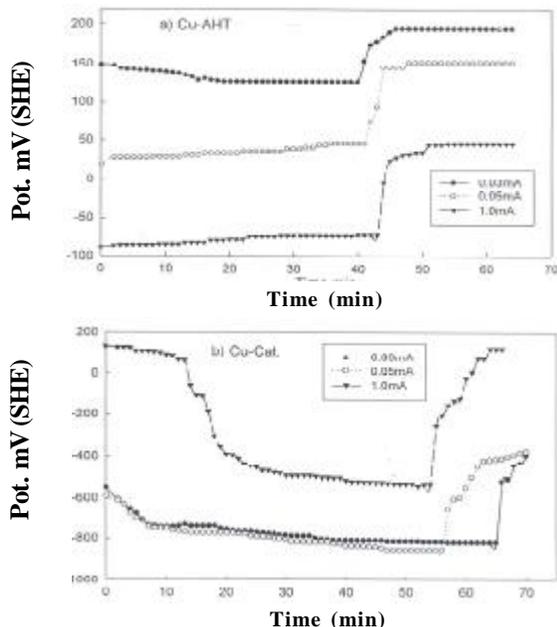


Figure 7 : Cathodic charging and decay curves of copper electrode at pH = 4.5 and different c.d. (a) 0.05% (w/v) Cu-AHT complex (1:2). (b) 0.05% (w/v) Cu-Cat. complex (1:2)

may be explained by the dissolution of Cu-Cat., complex. When shut off the current the potential return to its original value within 8 minutes, is presumably needed to establish a steady state concentration profile of Cu-Cat. complex near the electrode surface; the potential return to initial value, indicating the absence of any strong adsorption at the electrode surface.

Figure (8) shows the cathodic charging and decay curves of copper electrode at c.d. = 0.03 mAcm⁻² and different pH values (4.5, 6.5 and 9.5) in 0.05% (w/v) of both Cu-AHT and Cu-Cat. complexes.

In case of Cu-AHT it shows that, the potential has mostly constant value of 150 mV at pH = 4.5 up to 40 minutes and on shut off the current the potential returns to a value nearly equal its original value. With increasing of pH the charging potential decreases to more negative values. This is essentially due to the pH effect, i.e. increase of pH shifts the equilibrium potential towards more cathodic values.

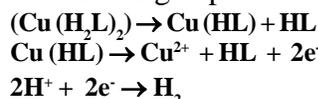
Furthermore, increase of pH decreases the hydrogen ion concentration, hence at a certain current density the electrode has to be polarized more cathodically at pH = 9.5 more than 6.5 and 4.5 this may be related to minimum decomposition of the Cu-AHT complex and consequently less copper deposition with the de-

crease of pH, which confirmed by the fact that on shut off the current the potential returns to more positive values. This behavior may be explained by the competition between OH⁻ and ligand to deposit copper as different possible compounds such as Cu(OH), Cu(OH)₂ or Cu₂O, CuO on the electrode surface.

In case of Cu-Cat. complex at different pH values, it shows an easier release of Cu(II) from this complex (due to its stability less than Cu-AHT) to the electrode surface in acidic, neutral or alkaline pH. Therefore there is a slow decrease of potential to more negative values at different pH values, and on shut off the current potential abruptly goes to highly positive values in acidic pH than in alkaline pH which may be related to the H⁺ reduction and charging of double layer in acidic medium. The increase of potential due to the liberation of the ligand molecules overcomes the decrease in potential due to the pH increase.

It is known that in pH 4.5, 6.5 and 9.5, the equilibrium potential of hydrogen electrode is about 0.26, 0.38 and 0.56V (SHE) respectively.

In the course of the cathodic deposition of copper, the following stepwise reactions may take place:



The equilibrium electrode potential of these cathodic reactions may be represented by:

$$E_h = E^0 - [2.303RT/F] \text{pH} + (2.303RT/F) \text{Log} [(Cu(HL)_2)/(Cu(HL))] \quad (1)$$

Where E⁰ is the standard electrode potential of copper, given by:

$$K(\text{HL}) = \text{Cu}(\text{HL})_2 / \text{Cu}(\text{HL}) \quad (2)$$

$$E^0 = [2.303RT/F] \text{Log} K \quad (3)$$

$$E_h = [2.303RT/F] \text{pH} + [2.303RT/F] \text{log} (\text{HL}) \quad (4)$$

Where K is the formation constant of the respective complex. Substituting in equation (1) we have:

$$E_h = -0.059 \text{pH} + 0.059 \text{Log} [\text{HL}] \quad (5)$$

The successive transformation leads to the liberation of two moles of AHT from each mole of copper complex. The E_h values obtained, becomes less negative in the direction of the increased dissociation. It should be duly recognize that the occurrence of the arrests on the charging curves might be correlated with the decreased hydrogen overpotential due to the enhanced catalytic action according to the above mechanism.

The cathodic deposition of copper follow a stepwise mechanism where the electron transfer step cupric to

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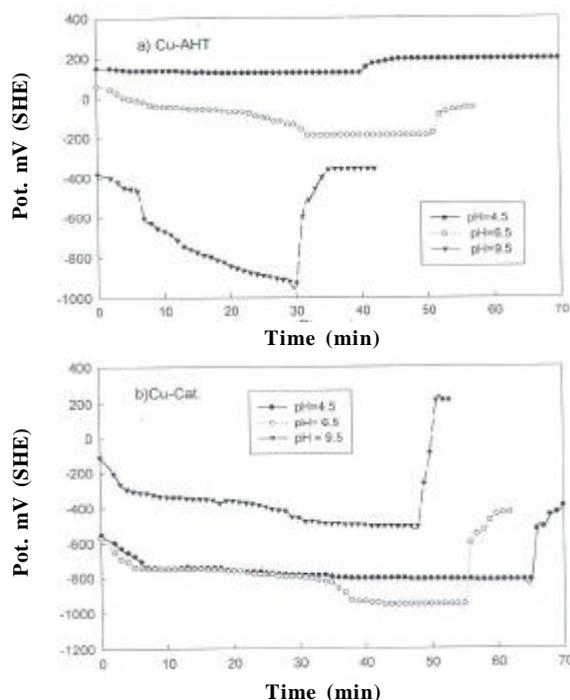


Figure 8 : Cathodic charging and decay curves of copper electrode at c.d.=0.03 mAcm⁻² and different pH values (a) 0.05% (w/v) Cu-AHT complex (1:2) (b) 0.05 % (w/v) Cu-Cat. complex (1:2)

cuprous ion is rate limiting step at high current density, both activation and mass transfer processes control the rate of deposition^[15]

CONCLUSION

- In acidic buffer solutions, the open circuit potential values obtained for copper electrode in presence of AHT and Cat shifts to more positive value than the buffer alone. This behavior indicating that, the equilibrium concentration of copper ion decreases with increasing ligand concentration, due to the formation of cu- ligand complex.
- In near neutral buffer solution, the built up of the Cu-cat. complex layer is more regular than the fluctuated one in case of Cu-AHT.
- In alkaline buffer solutions, it can be notice a wide difference in OPC values, due to the high dissolution of copper in such solution leading to formation of complexes.
- The relation between the steady state potential and concentration of ligand at various pH values is straight line with slopes which is independent of pH of the

solution.

- The charging and decay curves of copper electrode in absence and presence of AHT and Cat. in different buffer solutions using pulse current are represented to study the effect of current on the behavior of the electrode in such buffer solutions. There are two arrests one is formation when applying the current and the second is decomposition when shut off the current, the two arrests are nonlinear at all current densities.
- The study of the effect of ligand concentrations on the mechanism and kinetics of anodic dissolution of copper, give high values of Tafel slopes in alkaline solutions than in acidic due to the presence of the surface oxide and /or complex film on the electrode surface at such a high anodic potentials.

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