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Effect of Some Organic Compounds on Electrodeposition of Copper Metal in Copper Cathode

MERVETTE EL-BATOUTI*, SOAD H. SALAAM, ABDEL-MONEIM M. AHMED and HAMDY-EL-SHAMY

Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt

*Corresponding author: Tel: +212 85150304; E-mail: mervette_b@yahoo.com

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In this article, copper electrodeposition in the presence of various types of organic compounds was studied. The effects of operating variables, including organic additives concentrations and temperature on the limiting current were investigated by the potentio-dynamic polarization technique. The adsorption of all inhibitors on copper cathode was found to obey Temkin, Flory-Huggin and kinetic adsorption isotherm. The calculated free energy of adsorption ($\Delta G_{ads.}$) of inhibitor on copper surface indicated that the adsorption reactions were spontaneous ($\Delta G_{ads.} < 0$). The thermodynamic activation parameters (E_a , ΔH^* , ΔS^* and ΔG^*) were also estimated. It was found that activation energy values for copper electrodeposition in inhibited solutions were higher than that for uninhibited solution. The high inhibitor efficiency was discussed in terms of strong adsorption of inhibitor molecules on the copper surface.

Keywords: Electrodeposition, Corrosion inhibition, Thermodynamic parameters, Organic additives.

INTRODUCTION

The properties of copper and its alloys that makes it a major metal of commerce may be summarized as follows: high electrical conductivity, high thermal conductivity, ease of casting, extrusion, rolling and drawing to produce wire, tubing and strip, low corrosion rate of copper when used for food preparation, excellent alloying characteristics high esthetic appeal and low toxicity to humans [1]. The occurrence of copper in nature in the metallic form used since early times either as metallic copper or alloyed with tin as bronze.

Fire refined copper is adequate for non-critical applications such as water tubing, bar stock, or ingots for alloying. Copper intended for electrical uses, however, is produced by electrorefining or sometimes electrowinning techniques [2]. The methods of purifying copper include ionic exchange, vacuum distillation region smelting, low halide and electro-refining [3].

Electro-refining is an important step in pyrochemical reprocessing, which is a non-aqueous method for reprocessing spent metal fuel. The apseliminary demonstration facility has been erected to demonstrate the various mechanisms and associate interlocks here the electrolysis of copper in the acidified copper sulphate electrolyte will be carried out to demonstrate the electrifying process. Acid copper solutions containing organic brightening and leveling agents are used extensively to deposit smooth copper rough steel and etched plastias [4].

It is well known that the introduction of small amounts of certain substance in electrorefining bath leads to marked changes in the nature of metallic deposits obtained at the cathode [5]. It is well known that small quantities of these substances may stop dendrites growing and improve significantly the smoothness of the cathode surface [6]. In the present work, an attempt was made to examine the effect of different organic compounds such as acetic acid, formamide, ethylamine, 2-methoxy ethanol, glycine and acetonitrile on copper electrorefining from sulfate electrolyte. And also investigated the influence of structure of the organic additives related inhibitors on the mechanism and kinetics of inhibition of electrodeposition process.

EXPERIMENTAL

Natural convection: The bath solution (CuSO₄, H_2SO_4) was placed into a single compartment of two electrode cell. The electrofining experiments were performed using copper plate (10 cm \times 5 cm \times 0.2 cm) as cathode and anode.

The current was supplied by DC power supply Model 34BDCPSC Testronx). All experiments were carried out at 25, 30, 35 and 40 $^{\circ}$ C \pm 0.1 $^{\circ}$ C. The temperature of the bath renamed almost constant during the experiments.

The morphological analysis was performed by scanning electron microscope (JEOL, JSM-5300, scanning microscope, the OXFORD instrument. For this purpose, the copper sheet cathode was $(1 \text{ cm} \times 1 \text{ cm})$.

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Forced connection (rotating cylinder electrode) (RCE):

The apparatus used in the present work consists of the cell and the electric circuit. The cell consisted of 15 cm diameter cylindrical plexiglass container of 30 cm hertz. The cathode was a rotating copper red connected to the shaft of variable speed motor and copper cylindrical cathode lining the inner wall of the container. The cathode diameter is 1 cm and length 5 cm. Rotation speed of cathode ranges from 125 to 625.

Preparation of solutions: All chemicals were of AnalaR grade and supplied by BDH Chemicals Ltd. The concentration of organic compounds was varied from 1.74×10^{-3} to 10.04×10^{-3} mol/L. The sulphate and sulphuric acid (98 %) w/w concentration were 0.15 M and 1.5 M, respectively. For all experiments, copper sulphate concentration was checked iodometry. The total volume of the electrolytic bath solution was made up to 300 mL. Double distilled water with measured resistivity > 18 M Ω cm used in preparation of solutions. The organic additives are acetic acid, formamide, ethylamine, 2-methoxy ethanol, glycine and acetonitrile.

RESULTS AND DISCUSSION

Effect of additives concentration: Table-1 showed that increasing the CuSO₄ content in bath decreases the cathodic polarization and decreases the limiting current plateau. These results were expected due to an increase in relative abundance of uncomplexed Cu²⁺ ions in solution [7].

TABLE-1 EFFECT OF DIFFERENT CONCENTRATION OF CuSO ₄ ON LIMITING CURRENT AT 298 K, USING 5 cm HEIGHT						
CuSO ₄ concentration (mol L ⁻¹)	log C	I ₁ (mA) {Cu-Cu}	log I			
0.01	-2.00	90	1.95			
0.05	-1.30	180	2.25			
0.10	-1.00	260	2.41			
0.15	-0.82	320	2.50			
0.20	0.64	400	2.60			

Potentiodynamic cathodic polarization curves: The observed changes in cathodic polarization in the presence of organic compound suggest that it must be acting as an inhibitor, which confirmed by the fact that at any given over-potential, the current density for copper deposition from solutions containing organic compound is lower than that found in the corresponding organic free solution. This inhibition of the organic compound in copper electroplating reaction may be due to the adsorption of organic compound on cathode surface.

Therefore, the limiting current decreases with increasing organic concentration (Fig. 1), which may be attributed due to a lowering of Cu²⁺ complexes ions. Limiting current values for all solutions at different temperatures using copper anode are given in Table-2.

Table-2 showed that the limiting current decreases with increasing organic additives concentration and increases with temperature. The values of limiting current density (I₁) for all solutions at different temperatures were used to calculate the mass transfer coefficient (K) from the following equation [8]:

$$K = i_L/zFAC_o$$
 (1)

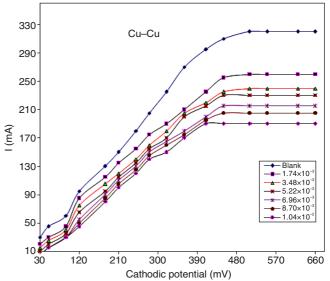


Fig. 1. Polarization curves in case of (copper anode) at 298 K for different concentration of compound I

TABLE-2 VALUES OF LIMITING CURRENT FOR ALL SOLUTION AT DIFFERENT TEMPERATURES USING COPPER ANODE

· ·		Limiting current (mA)				
Organic additives						
additives	(IIIOI/L) -	25 °C	30 °C	35 °C	40 °C	
	Blank	320	350	375	400	
	1.70×10^{-3}	260	280	295	310	
jq	3.48×10^{-3}	240	255	270	280	
Acetic acid	5.22×10^{-3}	230	245	260	270	
etic	6.96×10^{-3}	215	230	240	255	
Ac	8.70×10^{-3}	205	220	230	240	
	1.04×10^{-2}	190	205	215	225	
	2.95×10^{-3}	310	330	350	370	
de	5.90×10^{-3}	290	310	330	350	
Formamide	8.85×10^{-3}	270	290	305	320	
Ë	1.18×10^{-2}	255	270	285	300	
Fo	1.48×10^{-2}	235	250	265	280	
	1.77×10^{-2}	220	235	250	260	
	1.53×10^{-3}	230	240	255	270	
ne	3.04×10^{-3}	215	230	250	265	
E	4.56×10^{-3}	200	220	235	250	
Ethylamine	6.11×10^{-3}	190	205	220	235	
E	7.64×10^{-3}	170	180	200	220	
	9.16×10^{-3}	150	170	185	200	
	1.26×10^{-3}	290	310	325	345	
x xy	2.52×10^{-3}	280	300	320	340	
tho	3.78×10^{-3}	260	280	295	310	
2-Methoxy ethnaol	5.04×10^{-3}	245	260	275	300	
2-7	6.30×10^{-3}	225	240	260	280	
	7.56×10^{-3}	210	225	245	260	
	2.14×10^{-3}	270	285	200	215	
43	4.28×10^{-3}	255	270	290	305	
Glycine	6.44×10^{-3}	235	250	270	285	
Gly	8.56×10^{-3}	215	225	240	260	
	1.07×10^{-2}	195	210	230	250	
	1.28×10^{-2}	180	200	220	235	
Acetonitrile	1.90×10^{-3}	315	335	350	370	
	3.80×10^{-3}	300	320	330	350	
	5.70×10^{-3}	290	305	320	335	
	7.60×10^{-3}	270	290	310	320	
	9.50×10^{-3}	255	275	295	310	
	1.14×10^{-2}	235	250	270	290	

where, z = number of electrons involved in the reaction, F = Faraday constant (As mol⁻¹), $C_o =$ bulk concentration of copper sulphate (mol/cm³) and A = electrode area.

The percentage of inhibition (% IE) can be calculated as:

Inhibition (%) =
$$(I-I_1/I) \times 100$$
 (2)

where I and I_l are the electrodeposition limiting current values without and with inhibitor, respectively. Fig. 2 and Table-3 showed that the addition of organic compounds reduces the limiting current by amounts ranging from 3.1 to 53 % (Cu-Cu cell).

Under natural convection, mass is transferred outside the diffusion layer by natural convection which arises from the density difference between the interface solution and the bulk solution while mass is transferred inside the diffusion layer by diffusion only by virtue of the existence of concentration gradient across the diffusion layer. In view of above mechanism, the adverse effect of organic compounds on the limiting current can explain as follows:

TABLE-3 VALUES OF % INHIBITION FOR ALL ORGANIC COMPOUNDS AT DIFFERENT TEMPERATURES

	Conc. – (mol/L) –	% Inhibition				
Organic additives		Copper anode				
additives	(IIIOI/L) -	25 °C	30 °C	35 °C	40 °C	
	1.74×10^{-3}	18.7	20.0	21.3	22.5	
<u>.</u>	3.48×10^{-3}	25.0	27.1	28.0	30.0	
; ac	5.22×10^{-3}	28.1	30.0	30.6	32.5	
Acetic acid	6.96×10^{-3}	32.8	34.3	36.0	36.2	
Ac	8.70×10^{-3}	35.6	37.1	38.6	40.0	
	1.04×10^{-2}	40.6	41.4	42.6	43.7	
	2.95×10^{-3}	3.1	5.7	6.7	7.5	
de	5.90×10^{-3}	9.4	11.4	12.0	12.5	
. <u>E</u>	8.85×10^{-3}	15.6	17.1	18.7	20.0	
Formamide	1.18×10^{-2}	20.3	22.8	24.0	25.0	
Fo	1.48×10^{-2}	26.5	28.6	29.3	30.0	
	1.77×10^{-2}	31.2	32.8	33.3	35.0	
	1.53×10^{-3}	28.1	31.4	32.0	32.5	
ne	3.04×10^{-3}	32.8	34.3	33.3	33.7	
Ethylamine	4.56×10^{-3}	37.5	37.1	37.1	37.5	
1yl	6.11×10^{-3}	40.6	41.4	41.3	42.5	
臣	7.64×10^{-3}	46.8	48.5	46.6	46.2	
	9.16×10^{-3}	53.1	51.4	50.6	50.0	
	1.26×10^{-3}	9.4	12.9	13.3	13.7	
x xy	2.52×10^{-3}	12.5	14.3	14.6	15.0	
2-Methoxy ethanol	3.78×10^{-3}	18.7	20.0	21.3	22.5	
Me	5.04×10^{-3}	23.4	25.7	26.6	26.6	
2-7	6.30×10^{-3}	29.7	31.4	30.7	30.0	
	7.56×10^{-3}	34.4	35.7	34.7	35.0	
	2.14×10^{-3}	15.6	18.6	20.0	21.2	
o	4.28×10^{-3}	20.3	22.8	22.6	23.7	
cin	6.44×10^{-3}	26.5	28.6	28	28.7	
Glycine	8.56×10^{-3}	32.8	35.7	36.0	35.0	
· ·	1.07×10^{-2}	39.1	40.0	38.6	37.5	
	1.28×10^{-2}	43.7	42.8	41.3	41.2	
rile	1.90×10^{-3}	1.5	4.3	6.6	7.5	
	3.80×10^{-3}	6.2	8.5	12.0	12.5	
nit	5.70×10^{-3}	9.4	12.8	14.6	16.2	
Acetonitrile	7.60×10^{-3}	15.6	17.1	17.3	20.0	
Ac	9.50×10^{-3}	20.3	21.4	21.3	22.5	
	1.14×10^{-2}	26.5	28.6	28.0	27.5	

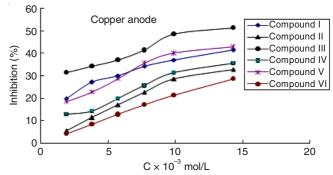


Fig. 2. Relation between percentage of inhibition and concentration of organic compounds at 298 K incase of Cu-Cu cell

Organic compounds adsorbed on the cathode surface increases the interfacial viscosity (η) of solution with a consequent decrease in diffusivity (D) of Cu²⁺ according to the Stokes-Einstein equation (3) [10].

$$D \eta/T = Constant$$
 (3)

where D = diffusion coefficient, $\eta = viscosity$ and T = temperature.

Table-3 summarizes the percentage of inhibition for all of the organic compounds slightly decreases with increasing temperature from 298 to 313 K. This may be explained by desorption of adsorbed inhibitor on the copper surface [11].

The deposition rate (I_l values) and inhibition efficiency percentage (IE %) values for all studied organic compounds at different concentration and different temperature are given in Table-3. It revealed that for each organic compounds studied I_l decreases and IE % increase with the increase of concentration. The following order was observed:

Ethyl amine > Acetic acid > Glycine > 2-Methoxy ethanol > Formamide > Acetonitrile

In acidic medium, NH₂ functional group is readily protonated. The cation (protonated form) is then adsorbed by columbic interaction on the metal surface. It could be electrostatically attracted to cathodic sites on the copper surface.

It can be deduced that the nature of functional group significantly affects the inhibition efficiency. The presence of COOH, NH₂, CO-NH, OH, C=-N cause significant inhibition for procus, electron pair on oxygen or nitrogen atoms can be shared to copper orbital forming insoluble complex and consequently decrease deposition rate [12-14]. This study reveals that the ethylamine give more inhibition than other organic compounds, It is known that alkyl (-R), alcohol (-OH) and amino group (-NH₂) is electron releasing group but CO, CN, COOH, NH₃⁺, NR₃⁺, CO-R, are electron withdrawing groups. And as result of acidic copper sulphate both, ethylamine, formamide and acetonitrile will exist on protonated form. In case of ethylamine, presence of ethyl group which recorded electron donating group, a property which recorded as electron donating group and is reflected into greater tendency towards coordi-nation of NH2 group with Cu2+ more than -CH3 group exist in acetic acid, the reduced electron density make the electron transfer between -COOH group and Cu2+ ions more difficult, which in turn weaken the binding of molecules to Cu²⁺ ions. Accordingly, the percentage inhibition of ethyl amine is more than acetic acid but for glycine, the simplest

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form of amino acid NH₃⁺ exists as side chain decrease the electron density on oxygen atom and reduce the chance for adsorption of glycine on the Cu cathode surface so glycine exhibits moderate inhibition efficiency.

It is observed that formamide and acetonitrite exhibit lower inhibition efficiency. This behaviour can explain as follows:

Formamide or acetonitrile exist as protonated form which make repulsion between Cu²⁺ and NH₂+, group between Cu²⁺ and N=-NH⁺ group and mark on the binding between N and Cu is comparably difficult [15].

Alternatively, the inhibition of copper deposition by organic compounds can be explained in terms of their adsorption on copper cathode surface, molecular species as CH₃COOH, HOCH₂CH₂OH, H₂N-CH₂-CO-OH, H-CO-NH₂, CH₃CH₂NH₂, CH₃-CN and protonated form H₃N⁺-CH₂-COOH, H-CO-NH₃⁺, CH₃-CN-H⁺ can adsorb metal surface, considering the adsorption of organic compound *via* molecular form, it may be deduced that the molecules self aggregates at copper arranging into an array of well ordered strips of uniform width and separation depending on the concentration. The molecules have a long range of interaction among them and thus able to cover the surface effectively and results into lowering in deposition rate.

Since, the self-assembly of molecules does not lead to chemical bonding between them. The optimization of the adsorption geometry is only governed by non-bonding forces, *e.g.* van der Waals repulsive forces at close range, electrostatic coulombic interaction forces and hydrogen bonding force.

The organic compounds molecules lie flat on the copper surface. The energetically most favourable situation is attained when the functional groups are close to the copper surface. One of the internal axes of molecules is nearly parallel with the surface. The increased inhibition efficiency (IE) with concentration, with increasing organic compound concentration indicates that more organic compounds molecules are adsorbed on copper surface at higher concentration. Leading to greater surface coverage and hence formation of protective film. A relatively low inhibition efficiency at lower concentration of organic compounds could be attributed to the modest surface coverage owing to their smaller molecular area and solubility of adsorbed intermediates formed on the surface [16,17].

Adsorption isotherm: The adsorption of inhibitor molecules from aqueous solutions can be regarded as quasisubstitution process [18] between organic compound in the aqueous phase ($org_{(aq)}$) and water molecules at electrode surface ($H_2O_{(S)}$).

$$Org_{(aq)} + xH_2O = Org_{(S)} + x(H_2O)_{(aq)}$$
 (4)

where x (size ratio) is the number of water molecules displaced by one molecule of organic inhibitor.

Adsorption isotherms are very important for determining the mechanism of organo-electrochemical reactions. The most frequently used isotherms are those of Frumkin, Temkin, Florry-Huggins, Langmiur and kinetic isotherms [19,20].

All these isotherms are of the general form:

$$f(\theta, \mathbf{x}) \exp(-a \theta) = \mathbf{K} \mathbf{C}$$
 (5)

where $f(\theta, x)$ is the configuration factor depends essentially on the physical model and assumptions underlying the derivation of isotherm [7]. The mechanism of inhibition of electrodeposition is generally believed to be due to the formation and maintenance of a protective film on metal surface [21-23]. Table-4 shows all data for Cu-Cu used for plotting the characteristic adsorption isotherms.

The values of fractional surface coverage (θ) at different concentrations of organic additives and at constant temperature have been used to explain the best isotherm to determine the adsorption process from [7,24].

$$\theta = I - I_I / I \tag{6}$$

Inhibitor adsorption characteristics can be estimated by using Langmiur isotherm, which is based on the assumption that all adsorption sites are equivalent and that molecule binding occurs independently from nearby sites being occupied or not [7,24] given as follows:

$$C/\theta = 1/K + C \tag{7}$$

where C is the concentration of organic additives (inhibitor), θ is fractional surface coverage and K is the adsorption equilibrium constant. Organic molecules having polar atoms or groups, which are adsorbed on the metal surface may interact by mutual repulsion or attraction and this may be advocated as the reason for the departure of slope values from unity [25].

The characteristic of Temkin adsorption isotherm [20] given by:

$$Exp(-2a\theta) = KC \tag{8}$$

where "a" is the lateral interaction parameter describing the molecular interaction in adsorption layer and the heterogeneity of metal surface. Linear plots obtained indicated that for all the studied additives obeyed Temkin adsorption isotherm.

The adsorption parameter deduced from Temkin adsorption isotherm is presented in Table-4. It is seen in Table-4 that the values of "a" in all cases are negative indicating that repulsion exists in the adsorption layer. It is generally known that K denotes the strength between adsorbate and adsorbent. Thus, large values of K implies more efficient adsorption [20].

TABLE-4 LINEAR FITTING PARAMETERS OF ORGANIC COMPOUNDS FOR (Cu-Cu) AT 298 K									
	Models parameters								
Organic compounds	Langi	miur	Te	mkin	Florry-	Huggins	Kinetio	adsorption i	sotherm
compounds	K	Slope	a	K	X	K	у	1/y	K
Acetic acid	1.376	0.1896	-0.1213	3473.8230	3.099	55.082	0.5370	1.861	13.451
Formamide	-	_	-0.1781	354.56	_	_	1.4590	0.685	117.27
Ethylamine	2.3635	0.1564	-0.1516	4495.9200	2.4330	121.3220	0.4820	2.0750	17.45500
2-Methoxy ethanol	_	-	-1.6220	1191.6270	_	_	0.9325	1.0724	48.0900
Glycine	7.28×10^{-1}	0.1325	-0.1817	1022.4240	1.49	49.299	0.8103	1.234	29.7520
A aatamitrila			0.1422	522 6210			1 5600	0.627	252 2000

The equation of Florry-Huggins isotherm is as follows:

$$\log \theta / C = \log xK + x \log (1-\theta)$$
 (9)

where x is the number of active sites occupied by one inhibitor molecule or number of water molecules replaced by one molecule of adsorbate. The value of x > 1, implied that one inhibitor molecule replace more than one water molecule [24,25].

The kinetic-thermodynamic model is given by:

$$\log \left[\theta/(1-\theta)\right] = \log K' + y \log C \tag{10}$$

where y is the number of inhibitory molecules occupying one active site. The binding constant (K) is given by Ashassi-Sorkhabi *et al.* [26] as

$$\mathbf{K} = \mathbf{K}^{\prime (1/\mathbf{y})} \tag{12}$$

If the slope y of the relation between $\log \theta/1-\theta \ vs. \log (C)$ for all organic compounds, is greater than unity implies the formation of multi-layers of the additive on metal surface, while if less than unity, it means that the given additive molecule occupied more than one active site.

Values of y and number of active sites 1/y of the metal surface that occupied by one molecule of the organic additives under the present conditions have given in Table-4. It was concluded from the values in Table-4 that the number of additive molecules, which occupy one active site, in some cases less than unity and in other cases greater than unity [26,27]. Also the efficiency of electrodeposition is an essential function of the magnitude of its binding constant (K).

The free energy of adsorption (ΔG_{ads}) at different concentrations of organic additives calculated from the following equation [25].

$$\Delta G_{ads} = -RT \ln (55.5 \text{ K}) \tag{13}$$

where, the value 55.5 is the molar concentration of solvent (water) (mol/L). The negative values of ΔG_{ads} in all cases (Table-5) means that spontaneous adsorption of inhibitor on the copper surface and strong interaction between inhibitor molecules and metal surface. The most efficient inhibitor shows the most negative (ΔG_{ads}) value. This suggests that they strongly adsorbed on the metal surface. The ΔG_{ads} values are negative in the case of Cu-Cu and, so more positive than - 40 kJ mol $^{-1}$ indicating the physical adsorption, whichmeans the adsorption of organic additives take place through electrostatic interaction between the inhibitor molecule and the metal surface. While (ΔG_{ads}) values about - 40 kJ mol $^{-1}$ or higher involve charge sharing or a transfer from the inhibitor molecules to metal surface to form, a coordinate type of bond indicates chemical adsorption [28-31].

TABLE-5 CALCULATED VALUES OF FREE ENERGY OF ADSORPTION $\Delta G_{ads.}$ (kJ mol $^{-1}$) FOR DIFFERENT ORGANIC COMPOUNDS USING DIFFERENT ADSORPTION FOR Cu-Cu

	Temkin	Flory-	Kinetic	
Organic compound	Tellikili	Huggins	adsorption	
	ΔG_{ads}	ΔG_{ads}	ΔG_{ad}	
Acetic acid	-30.14	-19.88	-16.38	
Formamide	-24.49		-21.80	
Ethylamine	-30.78	-21.83	-17.00	
2-Methoxy ethanol	-27.49		-19.50	
Glycine	-27.10	-19.60	-18.30	
Acetonitrile	-25.50		-23.70	

Temperature effect and thermodynamic parameters:

The study of temperature effect on the deposition rate and inhibition efficiency facilitates the calculation of kinetic and thermodynamic parameters of inhibition and adsorption process. These parameters are useful in interpreting the type of adsorption of the organic compounds added to deposition bath. The deposition rate I_1 increase with increasing temperature in the absence and presence of organic compounds added to deposition bath also inhibition efficiency increases with temperature rise (Table-6). This increase in the deposition rate with temperature could be explained on the basis that increasing temperature enhances the transfer rate of Cu^{2+} ions and conductivity also increase. Also, increase in temperature reduces viscosity of solution with a consequent increase in Cu^{2+} diffusivity which lead to an increase in the deposition rate [5,27].

TABLE-6
ACTIVATION ENERGY AND THERMODYNAMIC
PARAMETERS FOR ELECTRODEPOSITION OF COPPER
IN PRESENCE OF DIFFERENT ORGANIC ADDITIVES

Blank	Organic	Conc.	E _a (kJ	$\Delta H^* (kJ)$	$\Delta S^* (J)$	$\Delta G^* (kJ)$
Acetic acid $\begin{array}{cccccccccccccccccccccccccccccccccccc$	compound	(mol/L)	mol ⁻¹)	mol ⁻¹)	mol ⁻¹ k ⁻¹)	mol ⁻¹)
Acetic acid 3.48×10^{-3} 8.30 5.83 -179.77 59.40 6.96×10^{-3} 8.67 6.19 -178.88 59.50 6.96×10^{-3} 8.95 6.48 -178.52 59.68 8.70×10^{-3} 8.95 6.48 -178.52 59.68 8.70×10^{-3} 8.31 5.83 -181.05 59.78 1.04×10^{-2} 8.92 6.44 -179.62 59.97 Blank 11.76 9.28 -165.77 58.68 2.95×10^{-3} 9.49 7.01 -173.67 58.77 5.90×10^{-3} 10.10 7.62 -172.18 58.93 Formamide 8.85×10^{-3} 9.03 6.55 -176.33 59.09 1.18×10^{-2} 8.70 6.22 -177.94 59.25 1.48×10^{-2} 9.40 6.92 -176.30 59.46 1.77×10^{-2} 9.05 6.57 -177.96 59.61 Blank 11.76 9.28 -165.77 58.68 1.53×10^{-3} 8.73 6.26 -178.76 59.53 3.04×10^{-3} 11.44 8.96 -170.21 59.69 Ethylamine 4.56×10^{-3} 11.48 9.93 -169.41 59.84 6.11×10^{-3} 11.38 8.90 -171.41 59.98 7.64×10^{-3} 14.21 11.74 -162.97 60.30 9.16×10^{-3} 15.28 12.80 -160.24 60.55 Blank 11.76 9.28 -165.77 58.68 1.26×10^{-3} 10.43 7.95 -171.39 59.03 3.78×10^{-3} 9.18 6.70 -175.28 59.93 2.52×10^{-3} 10.43 7.95 -171.39 59.03 3.78×10^{-3} 9.34 6.86 -175.61 59.19 9.03 3.78×10^{-3} 10.70 8.23 -171.63 59.37 6.30×10^{-3} 11.84 9.37 -168.51 59.58 7.56×10^{-3} 11.66 9.19 -169.65 59.74 Blank 11.76 9.28 -165.77 58.68 2.14×10^{-3} 8.27 5.99 -174.30 59.26 Glycine 6.44×10^{-3} 10.57 8.09 -172.39 59.46 6.44×10^{-3} 10.57 8.09 -172.39 59.46 6.44×10^{-3} 10.25 7.77 -174.27 59.71 1.07×10^{-2} 13.52 11.04 -164.09 59.94 1.28×10^{-2} 14.42 11.94 -161.65 60.11 Blank 11.76 9.28 -165.77 58.68 1.90×10^{-3} 10.57 8.09 -172.39 59.46 6.50 10.70 10.57 10.90 10.57 10.90 10.57 10.90 10.57 10.90 10.57 10.90 10.57 10.90 10.57 10.90 10.57 10.90 10.57 10.90 10.57 10.90 10.57 10.90 10.59 10.59 10.59						
Acetic acid 5.22×10^{-3} 8.67 6.19 -178.88 59.50 6.96 $\times 10^{-3}$ 8.95 6.48 -178.52 59.68 8.70 $\times 10^{-3}$ 8.31 5.83 -181.05 59.78 1.04 $\times 10^{-2}$ 8.92 6.44 -179.62 59.97 Blank 11.76 9.28 -165.77 58.68 2.95 $\times 10^{-3}$ 9.49 7.01 -173.67 58.77 5.90 $\times 10^{-3}$ 10.10 7.62 -172.18 58.93 Formamide 8.85 $\times 10^{-3}$ 9.03 6.55 -176.33 59.09 1.18 $\times 10^{-2}$ 8.70 6.22 -177.94 59.25 1.48 $\times 10^{-2}$ 9.40 6.92 -176.30 59.46 1.77 $\times 10^{-2}$ 9.05 6.57 -177.96 59.61 Blank 11.76 9.28 -165.77 58.68 1.53 $\times 10^{-3}$ 8.73 6.26 -178.76 59.53 3.04 $\times 10^{-3}$ 11.44 8.96 -170.21 59.69 Ethylamine 4.56 $\times 10^{-3}$ 11.38 8.90 -171.41 59.98 7.64 $\times 10^{-3}$ 14.21 11.74 -162.97 60.30 9.16 $\times 10^{-3}$ 15.28 12.80 -160.24 60.55 Blank 11.76 9.28 -165.77 58.68 1.26 $\times 10^{-3}$ 10.43 7.95 -171.39 59.03 3.78 $\times 10^{-3}$ 9.18 6.70 -175.28 59.93 2-160.24 60.55 75.04 $\times 10^{-3}$ 11.84 9.37 -168.51 59.58 7.56 $\times 10^{-3}$ 11.84 9.37 -168.51 59.58 7.56 $\times 10^{-3}$ 11.84 9.37 -168.51 59.58 7.56 $\times 10^{-3}$ 11.66 9.19 -169.65 59.74 4.28 $\times 10^{-3}$ 8.27 5.79 -178.93 58.11 4.28 $\times 10^{-3}$ 8.27 5.79 -178.93 58.11 4.28 $\times 10^{-3}$ 8.27 5.79 -178.93 59.16 Blank 11.76 9.28 -165.77 58.68 8.56 $\times 10^{-3}$ 10.57 8.09 -172.39 59.46 8.56 $\times 10^{-3}$ 10.57 8.09 -175.52 59.71 1.07 $\times 10^{-2}$ 13.52 11.04 -164.09 59.94 1.28 $\times 10^{-2}$ 13.52 11.04 -164.09 59.94 1.28 $\times 10^{-2}$ 13.52 11.04 -165.55 60.11 Blank 11.76 9.28 -165.77 58.68 1.90 $\times 10^{-3}$ 8.48 6.01 -176.92 58.73 3.80 $\times 10^{-3}$ 7.79 5.48 -179.08 58.84 Acet						
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$						
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Acetic acid					
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$						
$\begin{array}{c} \text{Blank} & 11.76 & 9.28 & -165.77 & 58.68 \\ 2.95 \times 10^{-3} & 9.49 & 7.01 & -173.67 & 58.77 \\ 5.90 \times 10^{-3} & 10.10 & 7.62 & -172.18 & 58.93 \\ \hline \text{Formamide} & 8.85 \times 10^{-3} & 9.03 & 6.55 & -176.33 & 59.09 \\ 1.18 \times 10^{-2} & 8.70 & 6.22 & -177.94 & 59.25 \\ 1.48 \times 10^{-2} & 9.40 & 6.92 & -176.30 & 59.46 \\ 1.77 \times 10^{-2} & 9.05 & 6.57 & -177.96 & 59.61 \\ \hline & & & & & & & & & & & & & & & & & &$						
Formamide $\begin{array}{cccccccccccccccccccccccccccccccccccc$						
Formamide 8.85×10^{-3} 9.03 6.55 -176.33 59.09 1.18×10^{-2} 8.70 6.22 -177.94 59.25 1.48×10^{-2} 9.40 6.92 -176.30 59.46 1.77×10^{-2} 9.05 6.57 -177.96 59.61 Blank 11.76 9.28 -165.77 58.68 1.53×10^{-3} 8.73 6.26 -178.76 59.53 3.04×10^{-3} 11.44 8.96 -170.21 59.69 Ethylamine 4.56×10^{-3} 11.83 9.35 -169.41 59.84 6.11×10^{-3} 11.38 8.90 -171.41 59.98 7.64×10^{-3} 14.21 11.74 -162.97 60.30 9.16×10^{-3} 15.28 12.80 -160.24 60.55 Blank 11.76 9.28 -165.77 58.68 1.26×10^{-3} 9.18 6.70 -175.28 59.93 3.78×10^{-3} 9.18 6.70 -175.28 59.93 3.78×10^{-3} 9.18 6.70 -175.28 59.93 3.78×10^{-3} 9.34 6.86 -175.61 59.19 50.34×10^{-3} 10.43 7.95 -171.39 59.03 3.78×10^{-3} 9.34 6.86 -175.61 59.19 6.30×10^{-3} 11.84 9.37 -168.51 59.58 7.56×10^{-3} 11.66 9.19 -169.65 59.74 Blank 11.76 9.28 -165.77 58.68 2.14×10^{-3} 10.70 8.23 -171.63 59.37 7.56×10^{-3} 11.66 9.19 -169.65 59.74 Blank 11.76 9.28 -165.77 58.68 2.14×10^{-3} 9.79 7.32 -174.30 59.26 Glycine 6.44×10^{-3} 10.57 8.09 -172.39 59.46 8.56×10^{-3} 10.57 8.09 -172.39 59.46 8.56×10^{-3} 10.57 8.09 -172.39 59.46 8.56×10^{-3} 10.25 7.77 -174.27 59.71 1.07×10^{-2} 13.52 11.04 -164.09 59.94 1.28×10^{-2} 14.42 11.94 -161.65 60.11 Blank 11.76 9.28 -165.77 58.68 1.90×10^{-3} 8.48 6.01 -176.92 58.73 3.80×10^{-3} 7.95 5.48 -179.08 58.84 1.90×10^{-3} 8.48 6.01 -176.92 58.73 3.80×10^{-3} 7.95 5.48 -179.08 58.84 1.90×10^{-3} 8.48 6.01 -176.92 58.73 3.80×10^{-3} 7.95 5.48 -179.08 58.84 1.90×10^{-3} 8.48 6.01 -176.92 58.73 3.80×10^{-3} 7.95 5.48 -179.08 58.84 7.60×10^{-3} 7.78 5.31 -179.96 58.94 7.60×10^{-3} 7.78 5.31						
Formamide 8.85×10^{-3} 9.03 6.55 -176.33 59.09 1.18×10^{-2} 8.70 6.22 -177.94 59.25 1.48×10^{-2} 9.40 6.92 -176.30 59.46 1.77×10^{-2} 9.05 6.57 -177.96 59.61 Blank 11.76 9.28 -165.77 58.68 1.53×10^{-3} 8.73 6.26 -178.76 59.53 3.04×10^{-3} 11.44 8.96 -170.21 59.69 Ethylamine 4.56×10^{-3} 11.83 9.35 -169.41 59.84 6.11×10^{-3} 11.38 8.90 -171.41 59.98 7.64×10^{-3} 14.21 11.74 -162.97 60.30 9.16×10^{-3} 15.28 12.80 -160.24 60.55 Blank 11.76 9.28 -165.77 58.68 1.26×10^{-3} 9.18 6.70 -175.28 59.93 2.52×10^{-3} 10.43 7.95 -171.39 59.03 3.78×10^{-3} 9.34 6.86 -175.61 59.19 50.44×10^{-3} 10.70 8.23 -171.63 59.37 6.30×10^{-3} 11.84 9.37 -168.51 59.58 7.56×10^{-3} 11.66 9.19 -169.65 59.74 Blank 11.76 9.28 -165.77 58.68 2.14×10^{-3} 10.70 8.23 -171.63 59.37 6.30×10^{-3} 11.66 9.19 -169.65 59.74 Blank 11.76 9.28 -165.77 58.68 2.14×10^{-3} 9.79 7.32 -174.30 59.26 6.44×10^{-3} 10.57 8.09 -172.39 59.46 8.56×10^{-3} 10.42 10.44 10						
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					-172.18	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Formamide					59.09
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			8.70	6.22		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$						
Ethylamine $\begin{array}{c} 1.53\times 10^{-3} & 8.73 & 6.26 & -178.76 & 59.53 \\ 3.04\times 10^{-3} & 11.44 & 8.96 & -170.21 & 59.69 \\ 4.56\times 10^{-3} & 11.83 & 9.35 & -169.41 & 59.84 \\ 6.11\times 10^{-3} & 11.38 & 8.90 & -171.41 & 59.98 \\ 7.64\times 10^{-3} & 14.21 & 11.74 & -162.97 & 60.30 \\ 9.16\times 10^{-3} & 15.28 & 12.80 & -160.24 & 60.55 \\ \hline \\ & & & & & & & & & & & & & & & & &$		1.77×10^{-2}	9.05	6.57	-177.96	59.61
Ethylamine $\begin{array}{cccccccccccccccccccccccccccccccccccc$				9.28	-165.77	58.68
Ethylamine 4.56×10^{-3} 11.83 9.35 -169.41 59.84 6.11×10^{-3} 11.38 8.90 -171.41 59.98 7.64×10^{-3} 14.21 11.74 -162.97 60.30 9.16×10^{-3} 15.28 12.80 -160.24 60.55 12.80 -160.24 60.55 12.80 1.26×10^{-3} 9.18 6.70 -175.28 59.93 2.52×10^{-3} 10.43 7.95 -171.39 59.03 3.78×10^{-3} 9.34 6.86 -175.61 59.19 5.04×10^{-3} 10.70 8.23 -171.63 59.37 6.30×10^{-3} 11.84 9.37 -168.51 59.58 7.56×10^{-3} 11.66 9.19 -169.65 59.74 11.76 $11.$			8.73	6.26	-178.76	59.53
$\begin{array}{c} 6.11\times 10^{-3} & 11.38 & 8.90 & -171.41 & 59.98 \\ 7.64\times 10^{-3} & 14.21 & 11.74 & -162.97 & 60.30 \\ 9.16\times 10^{-3} & 15.28 & 12.80 & -160.24 & 60.55 \\ \hline \\ Blank & 11.76 & 9.28 & -165.77 & 58.68 \\ 1.26\times 10^{-3} & 9.18 & 6.70 & -175.28 & 59.93 \\ 2.52\times 10^{-3} & 10.43 & 7.95 & -171.39 & 59.03 \\ 3.78\times 10^{-3} & 9.34 & 6.86 & -175.61 & 59.19 \\ 5.04\times 10^{-3} & 10.70 & 8.23 & -171.63 & 59.37 \\ 6.30\times 10^{-3} & 11.84 & 9.37 & -168.51 & 59.58 \\ 7.56\times 10^{-3} & 11.66 & 9.19 & -169.65 & 59.74 \\ \hline \\ Blank & 11.76 & 9.28 & -165.77 & 58.68 \\ 2.14\times 10^{-3} & 8.27 & 5.79 & -178.93 & 58.11 \\ 4.28\times 10^{-3} & 9.79 & 7.32 & -174.30 & 59.26 \\ \hline \\ Glycine & 6.44\times 10^{-3} & 10.57 & 8.09 & -172.39 & 59.46 \\ 8.56\times 10^{-3} & 10.25 & 7.77 & -174.27 & 59.71 \\ 1.07\times 10^{-2} & 13.52 & 11.04 & -164.09 & 59.94 \\ 1.28\times 10^{-2} & 14.42 & 11.94 & -161.65 & 60.11 \\ \hline \\ Blank & 11.76 & 9.28 & -165.77 & 58.68 \\ 1.90\times 10^{-3} & 8.48 & 6.01 & -176.92 & 58.73 \\ 3.80\times 10^{-3} & 7.95 & 5.48 & -179.08 & 58.84 \\ \hline \\ Acetonitrile & 5.70\times 10^{-3} & 7.78 & 5.31 & -179.96 & 58.94 \\ 7.60\times 10^{-3} & 9.27 & 6.79 & -175.52 & 59.10 \\ 9.50\times 10^{-3} & 10.54 & 8.06 & -171.75 & 59.25 \\ \hline \end{array}$			11.44	8.96	-170.21	59.69
$\begin{array}{c} 7.64 \times 10^{-3} & 14.21 & 11.74 & -162.97 & 60.30 \\ 9.16 \times 10^{-3} & 15.28 & 12.80 & -160.24 & 60.55 \\ \hline \\ Blank & 11.76 & 9.28 & -165.77 & 58.68 \\ 1.26 \times 10^{-3} & 9.18 & 6.70 & -175.28 & 59.93 \\ 2.52 \times 10^{-3} & 10.43 & 7.95 & -171.39 & 59.03 \\ 3.78 \times 10^{-3} & 9.34 & 6.86 & -175.61 & 59.19 \\ 5.04 \times 10^{-3} & 10.70 & 8.23 & -171.63 & 59.37 \\ 6.30 \times 10^{-3} & 11.84 & 9.37 & -168.51 & 59.58 \\ 7.56 \times 10^{-3} & 11.66 & 9.19 & -169.65 & 59.74 \\ \hline \\ Blank & 11.76 & 9.28 & -165.77 & 58.68 \\ 2.14 \times 10^{-3} & 8.27 & 5.79 & -178.93 & 58.11 \\ 4.28 \times 10^{-3} & 9.79 & 7.32 & -174.30 & 59.26 \\ \hline \\ Glycine & 6.44 \times 10^{-3} & 10.25 & 7.77 & -174.27 & 59.71 \\ 1.07 \times 10^{-2} & 13.52 & 11.04 & -164.09 & 59.94 \\ 1.28 \times 10^{-2} & 14.42 & 11.94 & -161.65 & 60.11 \\ \hline \\ Blank & 11.76 & 9.28 & -165.77 & 58.68 \\ 1.90 \times 10^{-3} & 8.48 & 6.01 & -176.92 & 58.73 \\ 3.80 \times 10^{-3} & 7.95 & 5.48 & -179.08 & 58.84 \\ \hline \\ Acetonitrile & 5.70 \times 10^{-3} & 7.78 & 5.31 & -179.96 & 58.94 \\ 7.60 \times 10^{-3} & 9.27 & 6.79 & -175.52 & 59.10 \\ 9.50 \times 10^{-3} & 10.54 & 8.06 & -171.75 & 59.25 \\ \hline \end{array}$	Ethylamine	4.56×10^{-3}	11.83	9.35	-169.41	59.84
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		6.11×10^{-3}				
$\begin{array}{c} \text{Blank} & 11.76 & 9.28 & -165.77 & 58.68 \\ 1.26 \times 10^{-3} & 9.18 & 6.70 & -175.28 & 59.93 \\ 2.52 \times 10^{-3} & 10.43 & 7.95 & -171.39 & 59.03 \\ 3.78 \times 10^{-3} & 9.34 & 6.86 & -175.61 & 59.19 \\ 5.04 \times 10^{-3} & 10.70 & 8.23 & -171.63 & 59.37 \\ 6.30 \times 10^{-3} & 11.84 & 9.37 & -168.51 & 59.58 \\ 7.56 \times 10^{-3} & 11.66 & 9.19 & -169.65 & 59.74 \\ \hline \\ Blank & 11.76 & 9.28 & -165.77 & 58.68 \\ 2.14 \times 10^{-3} & 8.27 & 5.79 & -178.93 & 58.11 \\ 4.28 \times 10^{-3} & 9.79 & 7.32 & -174.30 & 59.26 \\ \hline \\ Glycine & 6.44 \times 10^{-3} & 10.57 & 8.09 & -172.39 & 59.46 \\ 8.56 \times 10^{-3} & 10.25 & 7.77 & -174.27 & 59.71 \\ 1.07 \times 10^{-2} & 13.52 & 11.04 & -164.09 & 59.94 \\ 1.28 \times 10^{-2} & 14.42 & 11.94 & -161.65 & 60.11 \\ \hline \\ Blank & 11.76 & 9.28 & -165.77 & 58.68 \\ 1.90 \times 10^{-3} & 8.48 & 6.01 & -176.92 & 58.73 \\ 3.80 \times 10^{-3} & 7.95 & 5.48 & -179.08 & 58.84 \\ \hline \\ Acetonitrile & 5.70 \times 10^{-3} & 7.78 & 5.31 & -179.96 & 58.94 \\ 7.60 \times 10^{-3} & 9.27 & 6.79 & -175.52 & 59.10 \\ 9.50 \times 10^{-3} & 10.54 & 8.06 & -171.75 & 59.25 \\ \hline \end{array}$		7.64×10^{-3}	14.21	11.74	-162.97	60.30
2-Methoxy ethanol $ \begin{array}{c} 1.26 \times 10^{-3} & 9.18 & 6.70 & -175.28 & 59.93 \\ 2.52 \times 10^{-3} & 10.43 & 7.95 & -171.39 & 59.03 \\ 3.78 \times 10^{-3} & 9.34 & 6.86 & -175.61 & 59.19 \\ 5.04 \times 10^{-3} & 10.70 & 8.23 & -171.63 & 59.37 \\ 6.30 \times 10^{-3} & 11.84 & 9.37 & -168.51 & 59.58 \\ 7.56 \times 10^{-3} & 11.66 & 9.19 & -169.65 & 59.74 \\ \hline \\ Blank & 11.76 & 9.28 & -165.77 & 58.68 \\ 2.14 \times 10^{-3} & 8.27 & 5.79 & -178.93 & 58.11 \\ 4.28 \times 10^{-3} & 9.79 & 7.32 & -174.30 & 59.26 \\ \hline \\ Glycine & 6.44 \times 10^{-3} & 10.57 & 8.09 & -172.39 & 59.46 \\ 8.56 \times 10^{-3} & 10.25 & 7.77 & -174.27 & 59.71 \\ 1.07 \times 10^{-2} & 13.52 & 11.04 & -164.09 & 59.94 \\ 1.28 \times 10^{-2} & 14.42 & 11.94 & -161.65 & 60.11 \\ \hline \\ Blank & 11.76 & 9.28 & -165.77 & 58.68 \\ 1.90 \times 10^{-3} & 8.48 & 6.01 & -176.92 & 58.73 \\ 3.80 \times 10^{-3} & 7.95 & 5.48 & -179.08 & 58.84 \\ \hline \\ Acetonitrile & 5.70 \times 10^{-3} & 7.78 & 5.31 & -179.96 & 58.94 \\ 7.60 \times 10^{-3} & 9.27 & 6.79 & -175.52 & 59.10 \\ 9.50 \times 10^{-3} & 10.54 & 8.06 & -171.75 & 59.25 \\ \hline \end{array}$		9.16×10^{-3}	15.28	12.80	-160.24	60.55
$ \begin{array}{c} \text{2-Methoxy} \\ \text{ethanol} \\ \end{array} \begin{array}{c} 2.52 \times 10^{-3} \\ 3.78 \times 10^{-3} \\ 5.04 \times 10^{-3} \\ 6.30 \times 10^{-3} \\ 7.56 \times 10^{-3} \\ 11.84 \\ 9.37 \\ 7.56 \times 10^{-3} \\ 11.84 \\ 9.37 \\ -168.51 \\ 59.58 \\ 7.56 \times 10^{-3} \\ 11.66 \\ 9.19 \\ -169.65 \\ 59.74 \\ \end{array} \\ \begin{array}{c} \text{Blank} \\ 2.14 \times 10^{-3} \\ 4.28 \times 10^{-3} \\ 9.79 \\ 1.07 \times 10^{-2} \\ 13.52 \\ 11.04 \\ 1.07 \times 10^{-2} \\ 1.28 \times 10^{-3} \\ 1.76 \\ 9.28 \\ -165.77 \\ 58.68 \\ -178.93 \\ 58.11 \\ 4.28 \times 10^{-3} \\ 8.27 \\ 5.79 \\ -178.93 \\ 58.11 \\ 4.28 \times 10^{-3} \\ 10.57 \\ 8.09 \\ -172.39 \\ 59.46 \\ 8.56 \times 10^{-3} \\ 10.25 \\ 7.77 \\ -174.27 \\ 59.71 \\ 1.07 \times 10^{-2} \\ 13.52 \\ 11.04 \\ -164.09 \\ 59.94 \\ 1.28 \times 10^{-2} \\ 14.42 \\ 11.94 \\ -161.65 \\ 60.11 \\ \end{array} \\ \begin{array}{c} \text{Blank} \\ 11.76 \\ 9.28 \\ -165.77 \\ 58.68 \\ 1.90 \times 10^{-3} \\ 3.80 \times 10^{-3} \\ 7.95 \\ 5.48 \\ -179.08 \\ 58.84 \\ \end{array} \\ \begin{array}{c} \text{Acetonitrile} \\ 5.70 \times 10^{-3} \\ 7.60 \times 10^{-3} \\ 9.27 \\ 6.79 \\ -175.52 \\ 59.10 \\ 9.50 \times 10^{-3} \\ 10.54 \\ \hline \end{array} \\ \begin{array}{c} \text{10.43} \\ 7.95 \\ -171.39 \\ -175.52 \\ 59.10 \\ -175.52 \\ 59.10 \\ -171.75 \\ 59.25 \\ \end{array}$		Blank	11.76	9.28	-165.77	58.68
ethanol 3.78 × 10 ⁻³ 9.34 6.86 -175.61 59.19 5.04×10^{-3} 10.70 8.23 -171.63 59.37 6.30×10^{-3} 11.84 9.37 -168.51 59.58 7.56×10^{-3} 11.66 9.19 -169.65 59.74 Blank 11.76 9.28 -165.77 58.68 2.14×10^{-3} 8.27 5.79 -178.93 58.11 4.28×10^{-3} 9.79 7.32 -174.30 59.26 Glycine 6.44×10^{-3} 10.57 8.09 -172.39 59.46 8.56×10^{-3} 10.25 7.77 -174.27 59.71 1.07×10^{-2} 13.52 11.04 -164.09 59.94 1.28×10^{-2} 14.42 11.94 -161.65 60.11 Blank 11.76 9.28 -165.77 58.68 1.90×10^{-3} 8.48 6.01 -176.92 58.73 3.80×10^{-3} 7.95 5.48 -179.08 58.84 Acetonitrile 5.70×10^{-3} 7.78 5.31 -179.96 58.94 7.60×10^{-3} 9.27 6.79 -175.52 59.10 9.50 $\times 10^{-3}$ 10.54 8.06 -171.75 59.25		1.26×10^{-3}	9.18	6.70	-175.28	59.93
ethanol $\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 Mathavy	2.52×10^{-3}	10.43	7.95	-171.39	59.03
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		3.78×10^{-3}	9.34	6.86	-175.61	59.19
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Culation			8.23	-171.63	59.37
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		6.30×10^{-3}	11.84	9.37	-168.51	59.58
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		7.56×10^{-3}	11.66	9.19	-169.65	59.74
Glycine $ \begin{array}{c} 4.28 \times 10^{-3} & 9.79 & 7.32 & -174.30 & 59.26 \\ 6.44 \times 10^{-3} & 10.57 & 8.09 & -172.39 & 59.46 \\ 8.56 \times 10^{-3} & 10.25 & 7.77 & -174.27 & 59.71 \\ 1.07 \times 10^{-2} & 13.52 & 11.04 & -164.09 & 59.94 \\ 1.28 \times 10^{-2} & 14.42 & 11.94 & -161.65 & 60.11 \\ \hline & Blank & 11.76 & 9.28 & -165.77 & 58.68 \\ 1.90 \times 10^{-3} & 8.48 & 6.01 & -176.92 & 58.73 \\ 3.80 \times 10^{-3} & 7.95 & 5.48 & -179.08 & 58.84 \\ Acetonitrile & 5.70 \times 10^{-3} & 7.78 & 5.31 & -179.96 & 58.94 \\ 7.60 \times 10^{-3} & 9.27 & 6.79 & -175.52 & 59.10 \\ 9.50 \times 10^{-3} & 10.54 & 8.06 & -171.75 & 59.25 \\ \end{array} $			11.76	9.28	-165.77	58.68
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		2.14×10^{-3}	8.27	5.79	-178.93	58.11
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		4.28×10^{-3}	9.79	7.32	-174.30	59.26
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Glycine	6.44×10^{-3}	10.57	8.09	-172.39	59.46
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		8.56×10^{-3}	10.25	7.77	-174.27	59.71
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		1.07×10^{-2}	13.52	11.04	-164.09	59.94
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1.28×10^{-2}	14.42	11.94	-161.65	60.11
Acetonitrile $\begin{array}{cccccccccccccccccccccccccccccccccccc$	Acetonitrile	Blank	11.76	9.28	-165.77	58.68
Acetonitrile 5.70×10^{-3} 7.78 5.31 -179.96 58.94 7.60×10^{-3} 9.27 6.79 -175.52 59.10 9.50×10^{-3} 10.54 8.06 -171.75 59.25		1.90×10^{-3}	8.48	6.01	-176.92	58.73
7.60×10^{-3} 9.27 6.79 -175.52 59.10 9.50 × 10 ⁻³ 10.54 8.06 -171.75 59.25		3.80×10^{-3}	7.95	5.48	-179.08	58.84
9.50×10^{-3} 10.54 8.06 -171.75 59.25		5.70×10^{-3}	7.78	5.31	-179.96	58.94
		7.60×10^{-3}	9.27	6.79	-175.52	59.10
		9.50×10^{-3}	10.54	8.06	-171.75	59.25
1.14×10^{-2} 11.41 8.93 -169.61 59.47		1.14×10^{-2}	11.41	8.93	-169.61	59.47

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Thermodynamic activated functions were obtained by applying Arhenuis and transition state equation [32]:

$$ln I_1 = -E_a/RT + ln A$$
 (14)

where A is a pre-exponential factor related to concentration, steric effects, metal surface characteristics, R is the molar gas constant and T is the absolute temperature. Values of E_a that have derived from the slopes of the Arrhenius plots are given in Table-6.

$I_1 = (RT/Nh) \exp \Delta S^*/R \exp -\Delta H^*/RT$

where I_l is limiting current, E_a is apparent activation energy, R is the molar gas constant, T is absolute temperature, A is frequency factor, ΔH^* is the enthalpy of activation, ΔS^* is the entropy of activation, A is the Avogadro A number.

From Table-6, its observed that E_a for solution containing additives is lower than that of free solution, hence supports the phenomena of chemical adsorption [5].

Many researches also reported the activation energy in the presence of additive molecules was lower than that of absolute of them, where it was attributed to the chemical nature of interaction between additives molecules and metal surface. It is also noticed that ΔH^* value is +ve which reflects that the endothermic nature, refining reaction also emphasizing copper deposition rate increase with increasing temperature [32].

The value of ΔS^* are large and negative both in absence and presence of organic compounds, which implies that the activated complex in the rate determining step represent association rather than dissociation step indicated that a decrease in disorder on going from reactant to activated complex [17,33,34].

Conclusions

The values of inhibition efficiency of Cu deposition, increase with increasing inhibitor concentrations and decrease slightly with temperature.

- Addition of organic compounds did not change the diffusion controlled mechanism of Cu deposition to a charge transfer controlled mechanism.
- The adsorption of all inhibitors on copper cathode obeys Temkin, Florry-Huggins and kinetic adsorption isotherms.
- The values of both K_{ads} and ΔG_{ads} indicated that all studied inhibitors are strongly adsorbed on copper surface.
- The activation energy values for copper electrodeposition in the inhibited solutions are higher than that for the uninhibited solutions indicating good inhibitor characteristics associating with physical mechanism.

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