

Effect of 1,3-dihydroxypropane on copper electrorefining process

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The effect of different concentrations of 1,3-DiHydroxyPropane (DHP) on the electrorefining of copper from acidified copper sulphate solution has been studied at different temperatures. The inhibition percent in the electrodeposited copper was in the range of 0.00 to 89.18 depending on the temperature and the mole fraction of DHP. Values of the activation energy of electrodeposition process, E_a , were found to be less than 28 kJ.mol^{-1} indicating diffusion-controlled process. The effect of time, DHP content and temperature on the morphological changes of the electrodeposited copper as well as on the deposit composition have been examined. Different topographs proved that the rate of copper electrodeposition increased by increasing electrodeposition time and temperature. In addition, it was proved that the deposition rate decreased by adding DHP to the solution with finer grain particulate size, especially at 30 % (v/v) DHP that was as low as 700 nm of round-particulates. Thus, in electrodeposition process, the results obtained by SEM supported those obtained by measuring the limiting current.

تم دراسة تأثير تركيزات مختلفة من كحول ٣،١ ثنائي هيدروكسي البروبان على عملية تنقية النحاس من محلول كبريتات النحاس المحمض بحمض الكبريتيك وتمت الدراسة عند درجات حرارية مختلفة ووجد أن نسبة إعاقة عملية ترسيب النحاس تتراوح من صفر حتى ٨٩% وتعتمد على درجة الحرارة والكسر الجزيئي للكحول كما وجد أن قيم طاقة التنشيط (E_a) لعملية الترسيب أقل من ٢٨ كيلو جول لكل مول وهذا يدل على أن العملية السابقة تتحكم فيها عملية الانتشار. وتم دراسة تأثير الزمن وكمية الكحول ودرجة الحرارة على التغيرات الناتجة في السطح وعلى تركيب الراسب وتم الحصول على عدة صور تدل على أن معدل الترسيب يزداد بالزمن وبالحرارة ويقل بإضافة الكحول وتم تدعيم تلك النتائج التي تم الحصول عليها بواسطة قياس التيار المحدد لتلك العمليات بالميكروسكوب الإلكتروني الماسح (SEM).

Keywords: Copper, Electrorefining process, 1, 3-Dihydroxypropane, Natural convection

1. Introduction

Natural convection arises due to the buoyancy forces, which are caused by a local variation in the solution density [1-2]. The buoyancy forces arise, in particular, in the metal electrodeposition, because the solution density near the electrode becomes lower than that in the bulk solution. Under the action of the buoyancy forces, the liquid near the electrode surface rises up forming a thin boundary layer of variable thickness δ_d . In contrast to the forced convection, the natural convection is induced by the diffusion and migration of ionic fluxes themselves. In its turn the generated liquid motion changes the space distribution of the ionic concentration in the near- electrode region. As a result, a complex pattern arises due to the interaction of diffusion, migration and hydrodynamic fields.

Copper is one of the metals that most extensively used in industry as a base to further formation of metallic films because of its intrinsic properties. Electrodeposition is one of the methods most generally employed to obtain metallic films of adequate thickness, porosity-free structure and good adhesion [3-4]. Electrodeposited copper films have been widely investigated with respect to their morphological characteristics, electrical properties and corrosion resistance [5-6] but less attention has been paid to their mechanical behaviour and its relation to electrodeposition parameters by controlling variables such as current density, applied current signal, temperature, bath composition, etc.

The microstructure and morphology of electrodeposited copper are affected by the state of solvation; therefore, this work aims to investigate copper electrodeposition process

from acidified solutions of copper sulphate mixed with different contents of DHP under natural convection regime. Such investigation included changes in temperature and solvent's content. In addition, it aims to study the SEM topographs and EDS analysis to support the experimental measurements and to shed more light on the mechanism of this electrodeposition process.

2. Experimental techniques

2.1. Materials

- Analar grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and H_2SO_4 (98% w/w) supplied by BDH Chemicals Ltd. were used for the preparation of the electrolytes of 0.1M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 1.5M H_2SO_4 , while 1,3-dihydroxypropane supplied by Lancaster Chemicals Ltd. was used as organic solvent to modify the medium.
- Potassium iodide and potassium thiosulphate supplied by BDH Chemicals Ltd. were used to check the concentration of copper sulphate.
- Ethanol and acetone were used for washing the specimen after it was mechanically polished-washed with distilled water.

2.2. Preparation of solutions

- Solutions were prepared with water of resistivity of 18-M Ω .cm, which was obtained from a MilliRo/ MilliQ water purification system.
- CuSO_4 concentration and content was checked by the iodine-thiosulphate method [7].

2.3. Measurements

The Potentiostat was Ministat Precision Potentiostat made by Thompson Electrochem. Ltd. coupled to a Chemical Electronics (Birtley) Ltd. Sweep Generator and controlled by an 8086 Personal Computer via an Advantech PCL-718 Lab Card and a PCLD-780 wiring terminal board. In this system the Advantech Labtech Aquire software was used.

All electrochemical experiments and polarization curves were carried out using a

potentiodynamic method. The sweep rate in all experiments was 1.67 mV.s⁻¹.

The limiting current density was measured using a standard glass-type cell [7] with solution volume of 1000 ml. The cell lid contained four inlets, which were used for working electrode, WE, immersion (a 99.99% purity rectangular copper plate of 1 x 5 cm in dimensions), a glass luggin probe attached to a reference electrode, RE, (saturated calomel electrode, SCE), counter electrode, CE, (a 99.99% purity copper plate with similar dimensions as those of the cathode) and thermometer to measure the temperature.

At the beginning, electrodes were mechanically polished with different grades of silicon carbide papers (120, 800, and 1200) and washed with distilled water and degreased by acetone. The backside of the cathode and anode were masked with Lacomit coating.

2.4. SEM microscopy and EDS analysis

Scanning Electron Microscope-EDS, AMRAY 1810, was used for elemental analysis. The specimens were examined through an acceleration potential of 20 KeV; the specimens were coated with carbon to avoid electron charging of the surface and to enhance the electrical conductivity of the electrodeposited films.

The specimens [7] were made of copper rods that were cut into small pieces, of dimensions 0.8-cm height and 1.2-cm diameter. Specimens were attached to PVC holders and were polished with series of silicon carbide paper grades in the range 120 – 1200 μm , then with 3 μm diamond paste followed by 1 μm diamond paste on a polishing wheel. Then after washing with deionised water and degreasing in acetone, warm air was blown over the surface and stored in a desiccator over silica gel prior to use.

3. Results and discussion

Fig. 1 shows the potential – current curves at 25°C and different contents of DHP.

The mass transfer coefficient, k , was calculated using the equation:

Table 1
Values of the limiting current density (i_l) and mass transfer coefficient (k) of 1,3-DihydroxyPropane (DHP) solutions at different temperatures on using copper anode

Solution	Limiting current density (i_l), mA.cm ⁻²				Mass transfer coefficient ($k \times 10^5$), cm.s ⁻¹			
	298K	303K	308K	313K	298K	303K	308K	313K
Blank	9.70	10.80	11.76	12.93	50.2	56.0	60.9	67.0
10 % (vol.) DHP	6.32	6.92	7.27	7.99	32.7	35.9	37.7	41.4
20 % (vol.) DHP	4.82	5.08	5.75	6.09	24.9	26.3	29.8	31.5
30 % (vol.) DHP	3.76	3.89	4.10	4.49	19.5	20.2	21.2	23.2
40 % (vol.) DHP	2.56	2.59	2.80	3.12	13.3	13.4	14.5	16.2
50 % (vol.) DHP	1.65	1.72	1.84	2.13	8.5	8.9	9.5	11.0
60 % (vol.) DHP	1.23	1.23	1.30	1.40	6.4	6.4	6.7	7.2

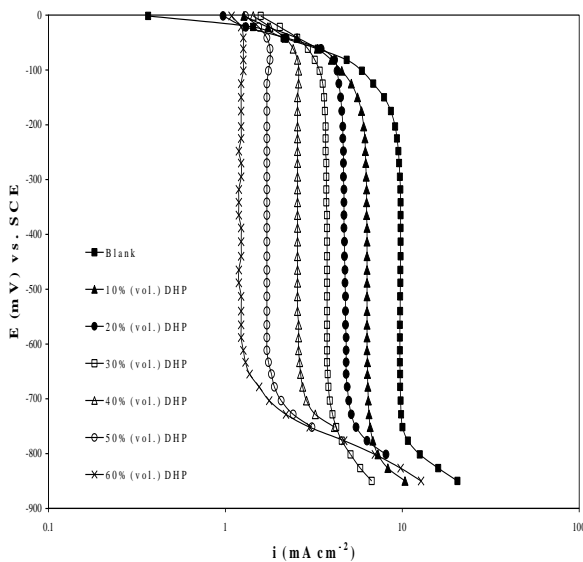


Fig.1. Typical potential – current curves obtained at 298K and different concentrations of 1,3-dihydroxypropane.

$$k = \frac{i_l}{nFC_o} \tag{1}$$

where: k = mass transfer coefficient (cm.s⁻¹), i_l = limiting current density (A.cm⁻²), n = number of electrons involved in the reaction, F =Faraday constant = 96484.6 (coulomb.mol⁻¹, coulomb = A.s), C_o = bulk concentration of copper sulphate (mol.cm⁻³).

Table 1 gives the measured limiting current densities and the calculated values of mass transfer coefficient at different temperatures and solvent’s content. Fig. 2 gives an idea about the relation between the limiting current density and the mole fraction of DHP at different temperatures. It is obvious

from fig. 2 that the limiting current density decreases with increasing the concentration of DHP, which is, probably, due to the decrease in the diffusivity and activity of Cu²⁺ ions as a result of the variation in viscosity of the mixture, solvation and/or dielectric constant. Due to that variation, ions are hydrodynamically combined with a few solvent molecules forming shapes that resemble small rigid spheres. The influence of such electrically uncharged spheres on the solution viscosity has been discussed by Einstein. The increase in viscosity is proportional to the concentration and total volume of such spheres.

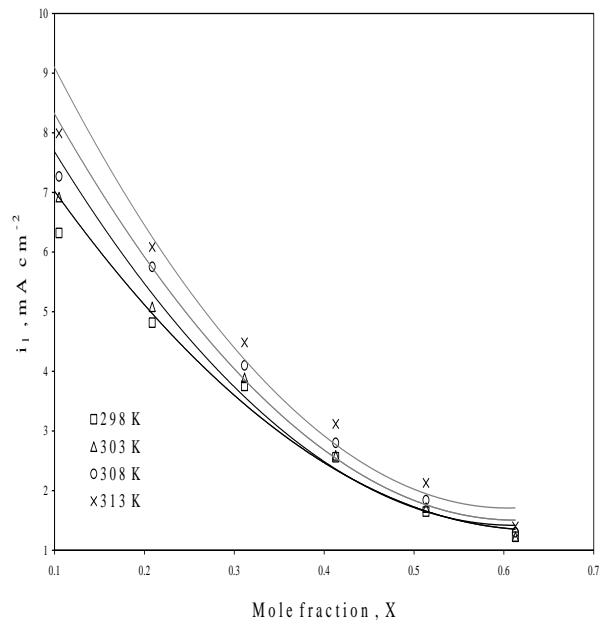


Fig. 2. Effect of the mole fraction (X) of 1,3-dihydroxypropane on the limiting current density at different temperatures.

3.1. Effect of DHP content on the limiting current

In fig. 2, the limiting current density decreases with increasing the concentration of DHP and, from a practical point of view, it is recommended that a relatively high alcohol percent is needed to inhibit deposition of metal. If the limiting current density in absence of alcohol is $(i_1)_b$ and in presence of alcohol is $(i_1)_s$, then the percentage of inhibition can be calculated from the equation:

$$\% \text{ inhibition} = \frac{(i_1)_b - (i_1)_s}{(i_1)_b} \times 100. \quad (2)$$

Table 2 shows that the inhibition percent caused by DHP ranges between 0.00 and 89.18 depending on the concentration of DHP. It is found that the limiting current density decreases with increasing the concentration of alcohol; this is in agreement with the findings of other author who worked within the same concentration range on using other cathode geometries [8]. The decrease in the limiting current density with increasing the concentration of alcohol is attributed to the decrease in the diffusion layer thickness which represents the resistance to the rate of mass transfer of copper ions from the bulk solution to the cathode surface [7].

An explanation for the decrease in the rate of copper electrodeposition may be referred to hydrogen bonds bounding within water molecules. Also, the results obtained in case of alcohol are interpreted on the basis that metal surface is preferentially covered by alcohol molecules. In the present case, the rate of copper electrodeposition agreed with the work obtained by other authors [7]. The decrease in mass transfer coefficient or the rate of electrodeposition is attributed to: alcohol increases the local solution viscosity at the cathode surface with a consequent decrease in the diffusivity of copper ions, and increasing alcohol concentration inhibits the natural convection flow arising from the density difference between bulk solution and solution at the electrode surface due to the

repulsion forces between the cathode surface and OH groups of the alcohol [9].

3.2. Solvent effect on mass transport

Copper deposition is known to be a diffusion controlled reaction whose rate is determined by the rate of mass transfer of Cu^{2+} ions to the cathode. Solvent can affect the rate of mass transfer by variations in viscosity, density, dielectric constant and solvation. It also affects the diffusivity and activity of copper ions.

The change in viscosity affects the mass transport of the electroactive species to the cathode surface. Consequently, when current is controlled by the rate of mass transport of the electroactive species, viscosity change affects the current density of the electrode reaction at a given potential, i.e., it affects the limiting current density at which copper is deposited. This can be understood easily from Stokes-Einstein equation and the expression of diffusion limiting current density or diffusion-controlled transition time. The Stokes-Einstein equation is

$$D = \frac{RT}{N} \frac{1}{6\pi\eta r}, \quad (3)$$

where D and r are the diffusion coefficient and the radius of the electroactive species in solution; respectively. While, μ is the viscosity coefficient of the solvent. On the other hand, the expression of the diffusion limiting current density under natural convection at vertical electrodes is given by Ahmed [10].

The other effect to be considered is the change in the solvent structure in the vicinity of ions caused by their electric field, which, however, strongly screened by solvating solvent molecules, is strong enough to disorganize the solvent structure.

Another effect of solvent on the mass transport is that the species which exist in solution may change by addition of solvent with a consequent alteration in the activity of the electroactive species. For example, Cu^{2+} ion is solvated with water molecule to form $\text{Cu}(\text{HOH})_n^{2+}$ in an aqueous solution, whereas in organic alcohol it forms $\text{Cu}(\text{ROH})_m^{2+}$, m may or may not equal n . This change also affects the

Table 2

The relation between the percentage inhibition (P) and mole fraction (X) of 1,3-DiHydroxyPropane (DHP) solutions at different temperatures on using copper anode

Solution	Mole fraction, X , (mole l ⁻¹)	Inhibition %, P			
		298K	303K	308K	313K
10 % (vol.) DHP	0.11	34.8	35.9	38.2	38.2
20 % (vol.) DHP	0.22	50.3	52.9	51.1	52.9
30 % (vol.) DHP	0.32	61.3	64.0	65.1	65.3
40 % (vol.) DHP	0.43	73.6	76.0	76.2	75.9
50 % (vol.) DHP	0.53	83.0	84.1	84.3	83.5
60 % (vol.) DHP	0.63	87.3	88.6	89.0	89.2

mass transport of electroactive species by affecting the activity of the Cu^{2+} ions, but in many cases this cannot be separated from the effect of viscosity of solvent. The change of ion from $\text{Cu}(\text{HOH})_n^{2+}$ to $\text{Cu}(\text{ROH})_m^{2+}$ may also change the diffusivity of copper ions owing to the change in the ionic size [10].

In water-organic solvent mixtures, the variation of physicochemical properties of medium with the composition percent has an important role in controlling electrodeposition process. It has been found that electrodeposition is inhibited by the organic alcohol and the percentage of inhibition has been found to increase with increasing organic solvent concentration [11]. These results were interpreted on the basis of the fact that these types of electrodeposition are controlled by diffusion of Cu^{2+} ions from bulk solution to metal surface. The increase in the viscosity of the medium with the increase in composition percent of organic solvent leads to a remarkable decrease in mass transfer coefficient, table 1.

In this study, the aspect of dependence of the rate of electrodeposition on the concept of water interaction is considered. Table 2 shows that the addition of DHP to acidified CuSO_4 solution has a noticeable effect on reducing activity of the medium. This has been attributed to the change in the state of solvation of Cu^{2+} ions and to the increase in the proton affinity of water. On adding alcohol to water, the acidity strongly decreases due to the breakdown of the open tetrahedral structure of water [7]. This concept explains the decrease in the rate of electrodeposition with addition of alcohol to a purely aqueous medium, especially in case of alcohol which is more basic. Further addition of alcohol would not influence the tetrahedral structure of

water to the same extent. It has been reported that [12] the dielectric constants of alcohol-water mixtures decrease with increasing alcohol content. According to the electrostatic theory, the association of an electrolyte in a solvent containing hydroxyl group appears to increase with increasing ionic size.

The effect of solvent is due to: (a) stabilization of the ion pairs due to the hydrogen bond contains in the alcohol, and (b) solvation of ions [13] leading to a decrease in the diffusion coefficient values.

The participation of alcohol molecules in the ion-pairs formation equilibrium should involve both steric and columbic effects. On the basis of this approach, the structure modification of the alcoholic polymers generated by the added solvents should result in a variable influence of alcohol molecules on ion-pairs association of CuSO_4 .

When a higher alcohol is chosen as the solvent system, the pattern of ionic association of hydroxyl solvent may be investigated without such complication as 3 D-structure effects. The rate of mass transfer increases as the dielectric constant increases. This can be explained on the basis of increasing ionic mobility with increasing dielectric constant and, hence, the chance to form ion-pair decreases.

3.3. Effect of dielectric constant

The plot of $\log(i)$ against the reciprocal of the dielectric constant of the medium, $1/D$, over the whole range of solvent composition shows no region of linearity, (fig. 3). The absence of linearity suggests a large differential effect of solvent structure acting on the initial and transition states. This was shown

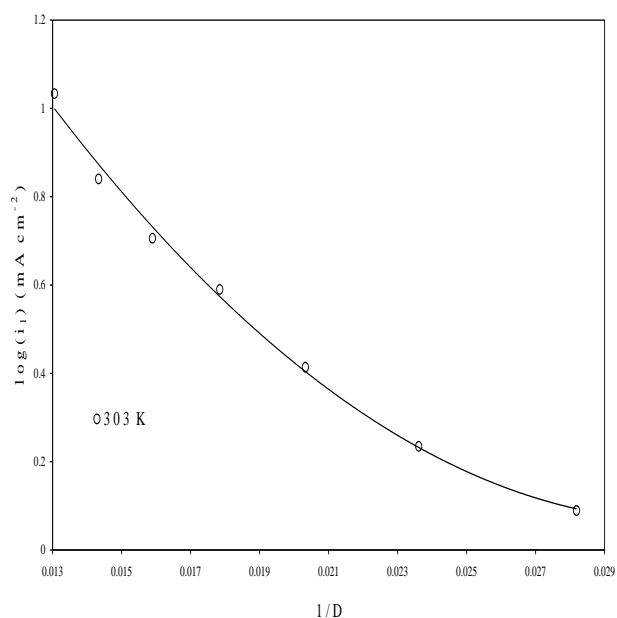


Fig. 3. Variation of limiting current density with reciprocal of dielectric constant at 303K.

from the extension of the equation of Laidler and Landskroener [14], which allows changes in solvent structure with varying solvent composition.

3.4. Limiting current and water concentration

The limiting current was found to increase with water concentration, and, hence, water plays an important role in the kinetics of this reaction. The plot of $\log(i_l)$ against $\log[H_2O]$, fig. 4, gave two linear portions separated by a sharp boundary at water concentration of 25.12 mol.l^{-1} . This behavior indicates that the internal structure of the medium suffers serious changes [14] on adding organic solvent and reflects the formation of two regions of different medium internal structures, which explains their different behavior towards hydrolysis. In the first region, which is the region of higher water concentration, the limiting current density decreases with progressive addition of solvent. This can be explained in terms of three factors: (a) the decrease in water concentration; (b) the decrease in the fraction of the free water molecules due to the fact that addition of solvent causes the water tetrahedral structure

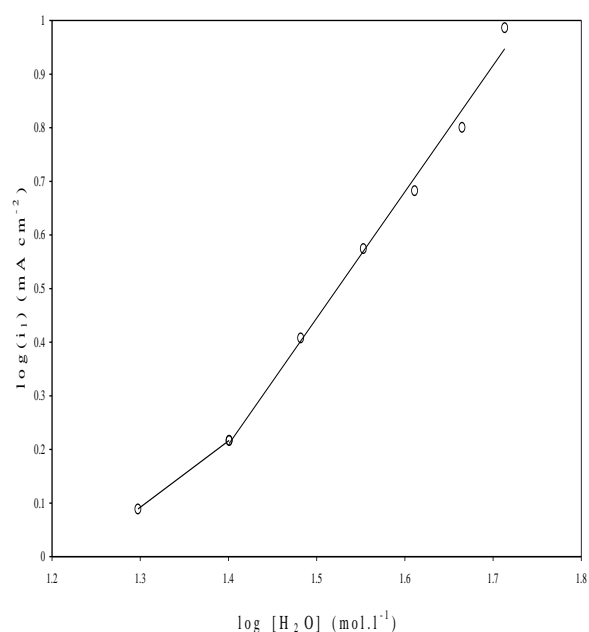


Fig. 4. Variation of limiting current density with water concentration.

to be gradually broken by interposition of organic solvent molecules and hydrogen bonding between water molecules to be replaced by hydrogen bonding between water and solvent molecules; and (c) the increase of the hydroxide ion affinity of the medium by the gradual addition of solvent due to the increase in its preferential solvation. From fig. 4, the slope of the line gives the number of water molecules involved in the formation of the activated complex. The slope of the line in water rich region is 2.357. In the region of low water concentration, the decrease in the limiting current density is less pronounced than in the previous region and the slope of the line is 1.236. This may be due to the fact that the organic solvent is present in excess to water and hydrogen bonding between the organic solvent molecules begins to predominate, and after the tetrahedral structure of water has been largely broken, further addition of solvent molecules, although resulting in a decrease in water concentration will be hydrogen-bonded with each other and will have little effect on the free water molecules.

3.5. Variation of kinetics parameters of activation with solvent composition

From integrated form of the Arrhenius equation:

$$\ln \dot{u} = -E_a/RT + \ln A, \quad (4)$$

where R is the gas constant ($8.314 \text{ kJ}\cdot\text{mol}^{-1}$), E_a is the activation energy and A is the frequency factor.

Values of E_a are given in tables 3. The activation energy of the process E_a , is an important parameter for determining the rate controlling step. If the rate-controlling step [8] is the diffusion of aqueous species in the boundary layer then E_a is generally $\leq 28 \text{ kJ}\cdot\text{mol}^{-1}$, while E_a usually $> 43 \text{ kJ}\cdot\text{mol}^{-1}$ if adsorption of species on the reaction surface and subsequent chemical reaction takes place.

Variation of kinetic parameters of activation with solvent composition were calculated by applying the least square method as given in table 3 and represented in fig. 5 as a function of the mole fraction of the co-solvent. It is obvious that ΔG^* increases with increasing solvent's contents.

The change of ΔH^* and ΔS^* with mole fraction is not [14] linear, which indicate specific solvation effects. The entropy and enthalpy of activation revealed maximum at $X = 0.2-0.5$. Also a sharp minimum in the entropy and enthalpy of activation was also observed at $X \sim 0.1-0.35$.

The highly negative ΔS^* values, support the formation of a highly restricted transition state. The strong electrostriction developed in the activated state restricts the random motion of solvent molecules in the neighborhood of the activated species causing a loss of entropy.

Table 3 shows that all E_a values are less than $28 \text{ kJ}\cdot\text{mol}^{-1}$, indicating that the electrodeposition reaction is diffusion-controlled process.

The ΔS^* values decrease with addition of solvent, because more pronounced structure around the Cu^{2+} ions occurs in solvent-water mixtures than in pure water.

The isokinetic temperature, calculated from the slope of ΔH^* versus ΔS^* plot was found to be 180.35 K as shown in fig. 6.

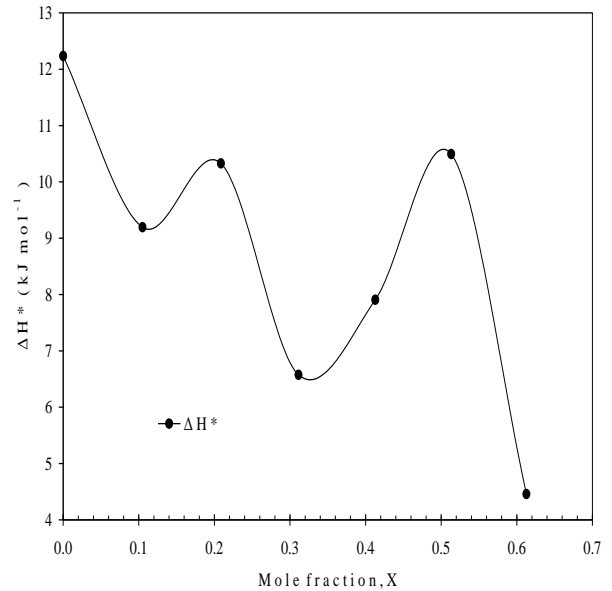


Fig. 5-a.

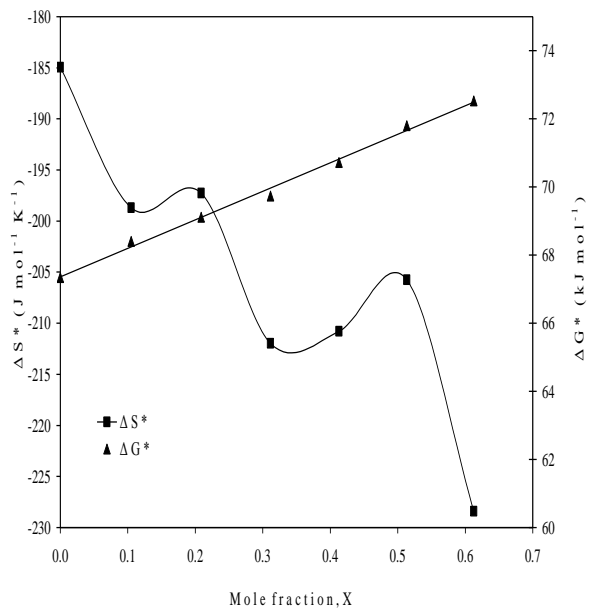


Fig. 5-b.

Fig. 5. Dependence of the activation kinetics parameters on the composition of 1,3-dihydroxypropane – water mixtures.

indicating that this deposition reaction is entropy controlled [15] where the solute-solvent interaction plays an important role in the rate determining step.

Table 3
Electrodeposition average kinetics parameters within the temperature range 298 – 313K for DHP solutions

Solution	E_a (kJ mole ⁻¹)	ΔH^\ddagger (kJ mole ⁻¹)	ΔS^\ddagger (J mole ⁻¹ K ⁻¹)	ΔG^\ddagger (kJ mole ⁻¹)
Blank	14.7	12.2	-185	67.3
10 % (vol.) DHP	11.7	9.2	-199	68.4
20 % (vol.) DHP	12.8	10.3	-197	69.1
30 % (vol.) DHP	9.1	6.6	-212	69.7
40 % (vol.) DHP	10.4	7.9	-211	70.7
50 % (vol.) DHP	13.0	10.5	-206	71.8
60 % (vol.) DHP	6.9	4.5	-228	72.5

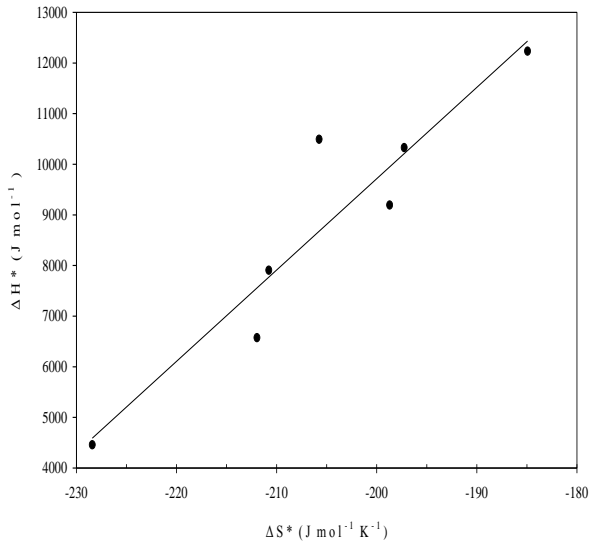


Fig. 6. Variation of ΔH^\ddagger with ΔS^\ddagger to calculate the isokinetic temperature for 1,3-dihydroxypropane – water mixtures.

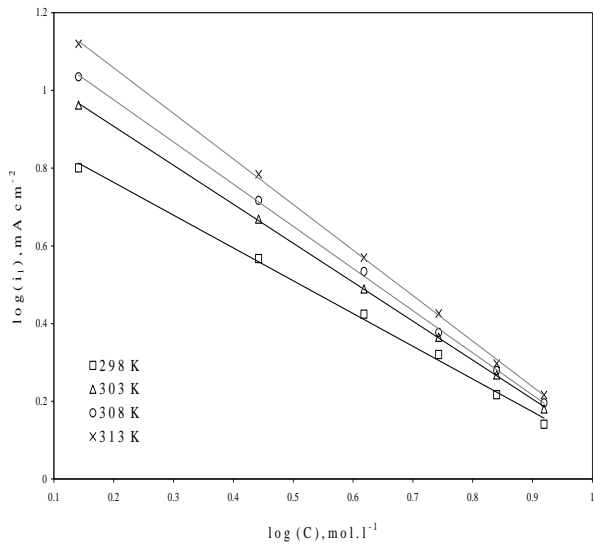


Fig. 7-a.

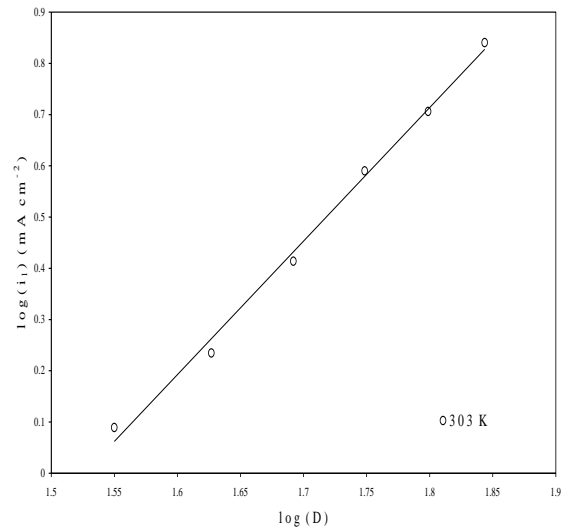


Fig. 7-b.

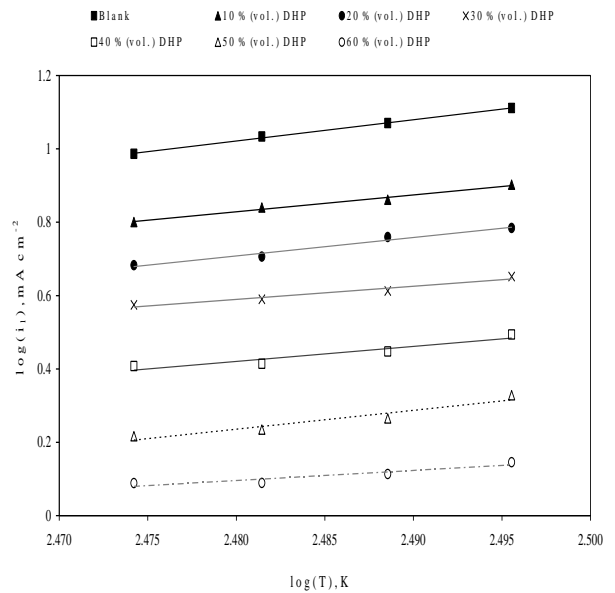


Fig. 7-c

Fig. 7. The relation between $\log(i_1)$ and $\log C$, $\log D$ and $\log T$.

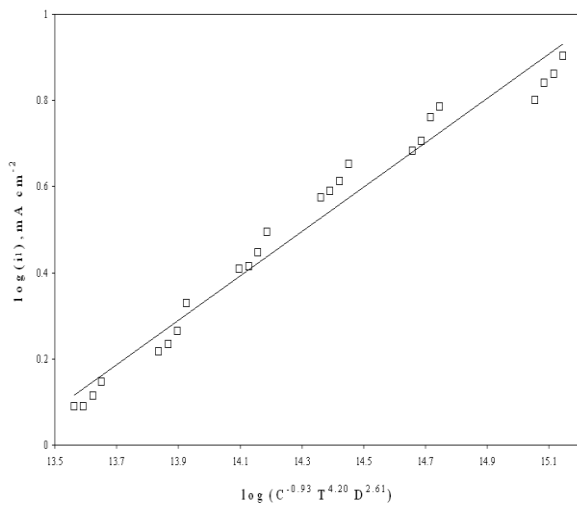


Fig. 8. Overall mass transfer correlation.

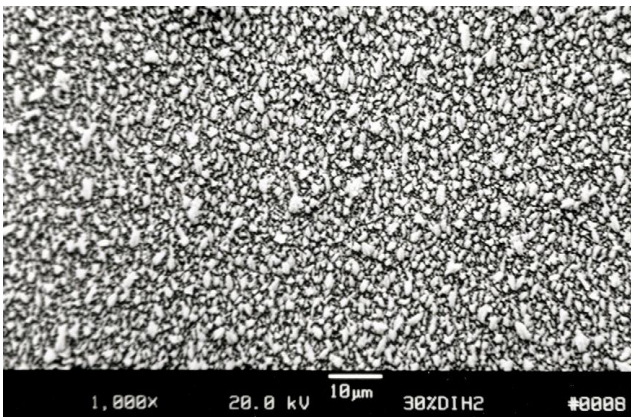


Fig. 9-a.. Electrodeposited copper from 30 % (v/v) DHP solution at 298 K after 20 minutes.

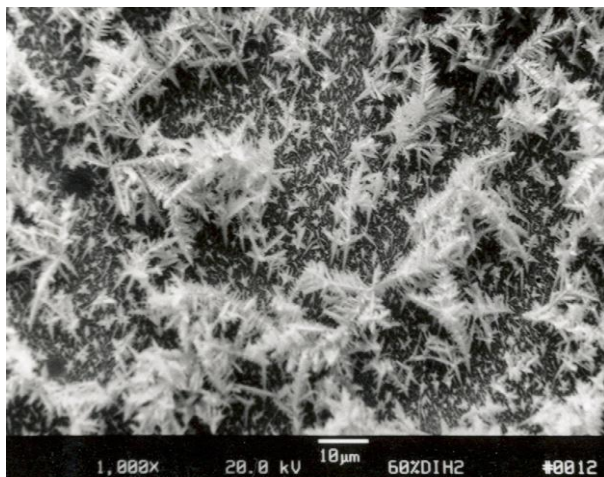


Fig. 9-b. Electrodeposited copper from 60 % (v/v) DHP solution at 298 K after 20 minutes.

3.6. Overall mass transfer

Figs. 7-a. 7-c show, the relation between $\log(i_l)$ and $\log C$, $\log D$ and $\log T$; respectively. Where C is the concentration of the solvent, D is the dielectric constant and T is the temperature. The correlation of the three figures can be represented by the following relations:

$$i_l \propto C^{-0.93}$$

$$i_l \propto D^{2.60}$$

$$i_l \propto T^{4.19}$$

Fig. 8 Illustrates the overall correlation, which is given by the following equation:

$$i_l = 1.50 \times 10^{-7} (C^{-0.93} D^{2.61} T^{4.20})^{3.26}, \quad (5)$$

which proves that flow is natural convection [10].

3.7. Scanning electron microscopy (SEM) and EDS analysis

The morphology of electrodeposited copper from acidic baths on poly or single crystal copper electrodes with and/or without additives has been widely studied [16-17] and the results in this work were essentially similar. Since the concern was mainly the production of copper powder, all experiments were carried out at the limiting current that was determined for each solution, so it is expected that the morphologies of electrodeposited copper must be characterised by 3-D nucleation [18].

Electrodeposition time (10 – 30 minutes), DHP content [0 – 60 % (v/v)], and electrodeposition temperature (298 – 313 K) were the different examined variables affecting the morphology and the composition of the electrodeposited copper.

As expected, the effect of electrodeposition time did not change the main features of the deposited copper, while it increased the rate of deposition reflecting a similar trend to that of the limiting current density.

The content of DHP was the second variable in this investigation, and all experiments were proceeded at 298K and duration time of 20 minutes. In this case, copper was deposited in very smooth and compact form up to 30 % (v/v) DHP with the

formation of round-particulates of the size range 700 nm – 3.5 μm as shown in fig. 9-a, while the deposited copper from solutions of 40 – 60 % (v/v) DHP was rough and discontinuous with the formation of needle-particulates of the size range 4.5 – 15 μm as shown in fig. 9-b.

Temperature is an important factor in the electrodeposition of metals [19]. Deposited copper from blank solution did not lose its compactness with the formation of needle-clusters that contain many cloves of the size range 5 – 30 μm for each clove as shown in fig. 10-a. In case of 20% (v/v) DHP the deposited copper was discontinuous and loose with trees of nodular-clusters with clove size 1 – 11 μm as in fig. 10-b.

Fig. 11 gives the EDS analysis for some chosen specimens that represent most of the experimental conditions. The analysis indicated that the composition of the electrodeposited copper under different conditions for all solutions was pure copper with tiny percentage of silicon, carbon and oxygen, which may be due to the occlusion of foreign materials [11] on one hand. On the other hand, the presence of silicon could be attributable to the attendance of some glass leftover from another specimen, while carbon is referable to the coating of specimen with carbon before the analysis. In addition, oxygen peak in fig. 11 might be caused by the oxidation of a negligible part of the deposit due to the high voltage used in the analysis.

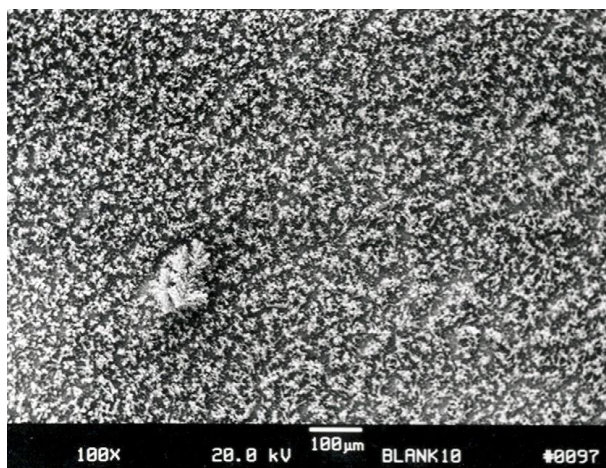


Fig. 10-a. Electrodeposited copper from blank solution at 313 K after 20 minutes.

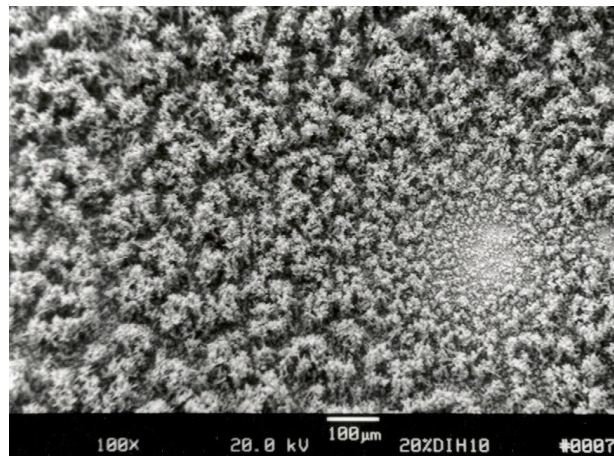


Fig. 10-b. Electrodeposited copper from 20 % (v/v) DHP solution at 313 K after 20 minutes.

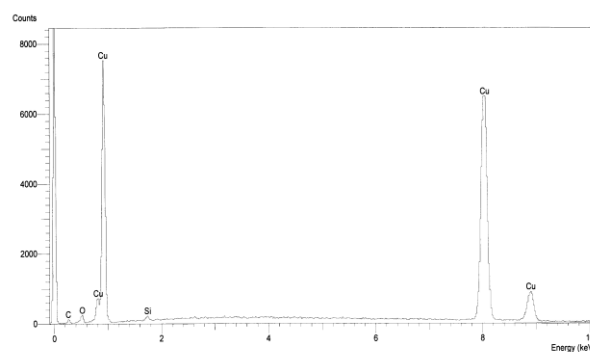


Fig. 11. EDS analysis of the deposits in case of blank, 10 60 % (v/v) DHP at 298 K and after 20 minutes.

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