Electrodeposition Of Copper In Presence Of Carbohydrates

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ABSTRACT

The rate of electrodeposition of copper plates was determined by measuring cathodic limiting current in absence and in presence of carbohydrates as (Glucose, fructose, mannose, sucrose, lactose and maltose). It is found that the rate of electrodeposition decreases in presence of organic additives by amount ranged from 1.89% to 35.85% depends on the types of additives and their concentrations. The investigated adsorption isotherm indicates that the inhibition fits to the Langmuir adsorption isotherm and Flory-Huggins adsorption isotherm. It is found that the rate of electrodeposition decreases by increasing height and CuSO4 concentrations. Thermodynamic parameters are given and show that electrodeposition process is diffusion controlled. The rate of deposition and its equations are represented as: Sh=9.784 Re0.5017 Sc0.33 for Glucose with an average deviation: ±0.0119%, Sh=9.790 Re0.5017 Sc0.33 for Fructose with an average deviation: ±0.0226%, Sh=9.786 Re0.5017 Sc0.33 for Mannose with an average deviation: ±0.0621%, Sh=9.790 Re0.5016 Sc0.33 for Sucrose with an average deviation: ±0.0234%, Sh=9.790 Re0.5016 Sc0.33 for Lactose with an average deviation: ±0.0075%, Sh=9.799 Re0.5016 Sc0.33 for Maltose with an average deviation: ±0.0126%

KEYWORDS

Electrodeposition; Copper; Carbohydrates; Limiting current; Mass transfer.

INTRODUCTION

Metals are deposited in a very rough or powdery form, when the electrolysis is carried out at limiting current. This seems to be a rather general rule[1] in the case of copper.

The possibility preventing powder formation at the limiting current by means of suitable additives is of interest electroplating[2] and electrometallurgy in general. Some organic substances are used as additives in electroplating, electrowinning and electroforming to improve the quality of electrodeposit, since produce fine grained smooth bright deposit. Although the exact mechanism by which, the organic compound or surface active substance(SAS) added to improve the quality of the electrodeposit is not known, there is a consensus that adsorption of those substances on the metal is involved, where adsorption of those organic compounds on the
cathode surface may block a part of the active electrode area and therefore reduce the limiting current.

In modern electrodeposition practice, it is well known that the addition of even small amounts of certain substances leads to significant changes in the properties and aspect of the deposit. Recent reviews have tried to summarize their different effects. Levelers have the ability to produce deposits relatively thick in small recesses and relatively thin on small protrusions. They act by adsorption at points where otherwise there would be a rapid deposition of the metal[3-8].

Previous studies have shown that SAS reduced the limiting current of uranium[9] and manganese[10] deposit from phosphoric acid and mercury cathode.

The object of this work is to study the effect of carbohydrates as (Glucose, fructose, mannose, sucrose, lactose and maltose) on the rate of electrodeposition. The effects of temperatures were also studied.

**EXPERIMENTAL**

**Chemicals**

Analar grade CuSO$_4$.5H$_2$O and H$_2$SO$_4$ (98% w/w), supplied by BDH Chemicals Ltd., were used for the preparation of the electrolytes. Analar grade (Glucose, fructose, mannose, sucrose, lactose and maltose) supplied by BDH chemicals ltd., were used as organic additives.

**Cell and electrical circuit**

**Using rectangular electrode figure 1(a)**

The cell consisted of a rectangular plastic container (5.1×5×10cm) with electrodes fitting the whole cross section area. The cathode was rectangular copper sheet (10cm height and was 5cm width); the anode was copper sheet with an inter-electrode distance was 5cm. The electrical circuit consists of (6V D.C.). Power supply connected in series with cell along and rheostat and (multi-range digital ameter). A voltameter is connected in parallel with the cell to measure the voltage.

**Using rotating electrode figure 1(b)**

The cathode consisted of copper metal cylinder (1cm) diameter and 10cm length. The unexposed area of the cylinder was covered by epoxy resin. The anode is made of cylindrical copper metal counter electrode of 12cm diameter; it’s acted as the reference electrode by virtue of its high surface area compared to that of cathode.

**Measurement**

Glinostatic polarization curves, from which the limiting current was determined, were constructed by increasing the current stepwise through sliding the rheostat handle towards a lower resistance and measuring the steady state cathode potential against copper references electrode. The copper references electrode was 1cm$^2$ copper sheet, which have the same composition of the cathode material, placed in the cup of luggin tube whose tip was placed at about 1mm far from the cathode surface. To avoid any erroneous readings of the voltage, the values of the limiting current were taken at constant value of the potential.
At the beginning, the bake of the cathode and anode were coated with epoxy resin except at contact with the feed wires; electrode treatment before each run was similar to that previously reported in literature\cite{11,12}.

**RESULTS AND DISCUSSION**

TABLE 1 and figure 2 show the cathodic polarization curve for copper electrodeposition from sulphate solution under the influence of adding different amounts of glucose. It is obvious that in the organic free solution, the current, first increases linearly, then tends to exhibit limiting current plateau with increasing the cathodic potential.

**Effect of electrode height on the limiting current**

shows the effect of the electrode height on the limiting current. The limiting current density decreases with increase the height. In electrodeposition and generally for cathodic deposition of metals, the direction of flow of the hydrodynamic boundary layer is downwards, the thickness of the hydrodynamic boundary layer and the diffusion layer increases in the downward direction, i.e., the resistance to mass transfer increases in the downward direction, accordingly, the local limiting density increases in the upward direction of the anode. This explains why electrodeposition attained at the upper parts of the electrode before the lower parts at the limiting current region. This was confirmed by visual observation during electrodeposition. The average limiting current density decreases with the increase in the height according to the equation:

\[ I \propto \frac{1}{h} \]
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I = C/h 0.3 ± 0.01  \hspace{1cm} (1)

Where C is constant, h is the height and (I) is the limiting current density.

Effect of concentration of CuSO₄ on the limiting current

Table 2: Effect of organic compounds on the percentage inhibition of limiting current at 303K

<table>
<thead>
<tr>
<th>Organic compounds</th>
<th>Cu×10⁴ mol. l⁻¹</th>
<th>(I) Org.</th>
<th>% Inhibition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Glucose</td>
<td>5.500</td>
<td>260</td>
<td>1.886</td>
</tr>
<tr>
<td></td>
<td>11.00</td>
<td>250</td>
<td>5.660</td>
</tr>
<tr>
<td></td>
<td>21.78</td>
<td>240</td>
<td>9.433</td>
</tr>
<tr>
<td></td>
<td>32.36</td>
<td>230</td>
<td>13.21</td>
</tr>
<tr>
<td></td>
<td>42.73</td>
<td>225</td>
<td>15.09</td>
</tr>
<tr>
<td></td>
<td>52.91</td>
<td>215</td>
<td>18.87</td>
</tr>
<tr>
<td>2. Fructose</td>
<td>5.500</td>
<td>230</td>
<td>13.21</td>
</tr>
<tr>
<td></td>
<td>11.00</td>
<td>225</td>
<td>15.09</td>
</tr>
<tr>
<td></td>
<td>21.78</td>
<td>200</td>
<td>24.53</td>
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<tr>
<td></td>
<td>32.36</td>
<td>190</td>
<td>28.30</td>
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<tr>
<td></td>
<td>42.73</td>
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<td>32.08</td>
</tr>
<tr>
<td></td>
<td>52.91</td>
<td>175</td>
<td>33.96</td>
</tr>
<tr>
<td>3. Mannose</td>
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<td>5.660</td>
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<td>16.98</td>
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<tr>
<td></td>
<td>85.47</td>
<td>215</td>
<td>18.87</td>
</tr>
<tr>
<td></td>
<td>105.8</td>
<td>210</td>
<td>20.76</td>
</tr>
<tr>
<td>4. Sucrose</td>
<td>2.90</td>
<td>255</td>
<td>3.773</td>
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<td></td>
<td>5.70</td>
<td>240</td>
<td>9.433</td>
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<tr>
<td></td>
<td>27.8</td>
<td>205</td>
<td>22.64</td>
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<td>5. Lactose</td>
<td>8.720</td>
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<td>83.54</td>
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<td>35.85</td>
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<td>6. Maltose</td>
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<tr>
<td></td>
<td>27.80</td>
<td>200</td>
<td>24.53</td>
</tr>
</tbody>
</table>

Figure 4: The effect of different concentration of CuSO₄ on the limiting current at 303K

Figure 5: The relation between % Inhibition and concentration for different organic compounds at 303K

Effect of organic substance on the limiting current

The limiting current in absence of organic compound (Iₐ) and in presence of organic compound (Iₐorg), is related to the percentage of inhibition by the equation:

\[ \% \text{ Inhibition} = \left( \frac{I_{a} - I_{a\text{org}}}{I_{a}} \right) \times 100 \]  \hspace{1cm} (2)

TABLE 2 and figure 5 show that the percentage inhibition caused by organic compounds ranges from 1.89% to 35.85% for cell using copper anode.

The percentage inhibition was calculated from equation 2 depending on the concentration and type of inhibitor. It is observable that percentage inhibition increased as concentration increased. The order of inhibition was as follow(Fructose>glucose>mannose) for monosaccharide,(Maltose>sucrose>lactose) for disaccharide.

The obtained results show that the presence of organic compound has an inhibiting effect on the kinetics of the copper discharge process, pointed out by the decrease of the exchange current density. The inhibition enhancing due to increasing the organic compound concentration could be related to the strong adsorption of organic compound constituents on the copper electrode surface, which is in agreement with the decay of the current intensity observed on the polarization curves.

The presence of organic compound changes the mechanism of the copper electrodeposition as it can be seen from the decreasing of the cathodic transfer coeff-
icient. A possible explanation for this fact consists in the increasing role of an additional reaction that produces the same chemical species Cu\(^{+}\) as those involved in the rate determining reaction\[15\].

**Adsorption isotherm**

The electrochemical processes on the metal surface are likely to be closely related to the adsorption of the inhibitor\[16\] and the adsorption is known to depend on the chemical structure of the inhibitor\[17-19\]. The adsorption of the inhibitor molecules from aqueous solutions can be regarded as (quasi-substitution) process\[17\] between the organic compound in the aqueous phase, (org.\(_{aq}\)) and water molecules at the electrode surface, (\(H_2O(s)\)).

\[
\text{Org}_{aq} + xH_2O = \text{Org}_{s} + x(H_2O) \tag{3}
\]

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

Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions. The most frequently used isotherms are those of langmuir, frumkin, parsons, temkin, flory-huggins and bockris-swinkels\[20-23\]. All these isotherms are of the general form:

\[
f(\theta, x)e^{-a\theta} = K C \tag{4}
\]

Where \(f(\theta, x)\) is the configuration factor depends essentially on the physical model and assumptions underlying the derivation of the isotherm\[24\]. The mechanism of inhibition of reaction is generally believed to be due to the formation and maintenance of a protective film on the metal surface\[25\].

Inhibitor adsorption characteristics can be estimated by using the Langmuir isotherm given as\[26\]:

\[
K C = \theta / (1 - \theta) \tag{5}
\]

Where \(K\) is the equilibrium constant of adsorption process, \(C\) is the concentration and \(\theta\) is the surface coverage.

The degree of surface coverage(\(\theta\)) at constant temperature was determined from\[27\]:

\[
\theta = (I_b - I_{org}) / I_b \tag{6}
\]

A plot of \((\theta / 1 - \theta)\) vs \((C)\) should yields straight line, Figure 6 shows straight line indicating that all the inhibitors verify Langmuir adsorption isotherm.

Figures 7 show the flory-huggins adsorption isotherm plotted as log \(\theta/C\) vs. log \((1 - \theta)\) for CuS\(_{aq}\)/H\(_2\)S\(_{aq}\) organic compounds 303K yield a straight line with slope \(x\) and intercept log \(xK\). TABLE 3 shows the values of \(x\) and \(K\). The experimental data fits the Flory-Huggins adsorption isotherm which represented by:

\[
\log \theta/C = \log xK + x \log(1 - \theta) \tag{7}
\]

Here \(x\) is the number of water molecules replaced by one molecule of the inhibitor. It is clear that the surface coverage data are useful for discussing adsorption characteristics. The adsorption of inhibitors at metal-solution interface may be due to the formation of either electrostatic or covalent bonding between the adsorbates and the metal surface atoms\[28\].

The free energy of adsorption \(\Delta G_{ads}\) at different concentrations was calculated from the equation\[29\]:

\[
\Delta G_{ads} = RT \ln(55.5 K) \tag{8}
\]

The value 55.5: is the concentration of water in the
The values of (ΔG<sub>ads.</sub>) are given in TABLE 3. In all cases, the (ΔG<sub>ads.</sub>) values are negative and lie in the range of -14.525 to -21.791 kJ/mol. The most efficient inhibitor shows the most negative (ΔG<sub>ads.</sub>) value. This suggests that they are strongly adsorbed on the metal surface. The negative values of (ΔG<sub>ads.</sub>) indicate the spontaneous adsorption of the inhibitor. This usually characteristic of strong interaction with metal surface. It is found that the (ΔG<sub>ads.</sub>) values are more positive than -40 kJ/mol indicating that inhibitors are physically adsorbed on the metal surface. Similar results have also been reported by Talati et al. [30].

**Effect of stirring and applications of dimensional analysis**

The effect of the speed of rotation on the rate of metal deposition can also be used to determine whether the electrodeposition process is diffusion or chemically controlled process. If the rate of electrodeposition increases by the speed of rotation, then the reaction is diffusion controlled. However, if the rate of electrodeposition is independent of rotation, so the reac-
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The angular velocity $\omega$ is given by:

$$\omega = \frac{2\pi \text{rpm}}{60}$$  \hspace{1cm} (9)

Figure 8 gives the relation between the limiting current density $I$ and the angular velocity $\omega$ to the power 0.7 at different concentrations of organic substance at 35°C. Straight lines were obtained and the limiting current density increases by increasing the rotation which indicates that electrodeposition reaction of copper is a diffusion controlled reaction.[31]

The values of $I$ obtained at different temperatures permits the calculation of activation energy $E_a$ according to Arrhenius equation:

$$\log I = E_a / 2.303RT + \log A$$  \hspace{1cm} (10)

The plot of $\log I$ against $1/T$ gave a straight line where $A$ is a pre-exponential factor, $R$ is the gas constant and $T$ is the absolute temperature. The slope of which is proportional to $E_a$. The activation energy of the process is an important parameter for determining the rate controlling step. If the rate controlling step is the diffusion of species in the boundary layer then $E_a$ is generally $\leq 28 \text{kJ/mol}$,[31] while $E_a$ values usually $> 43 \text{kJ/mol}$ when adsorption of species on the reaction surface and subsequent chemical reaction takes place.

TABLE 4 shows that the values of $E_a$ are lower than 43 kJ/mol; characterizing diffusion processes are controlling the electrodeposition reaction. However, the value of $E_a$ of electrodeposition reaction is higher in presence of organic compound. This is attributed to that these compounds partly formed some chemical bond with copper, and this led to the fact that a part of the electrode remain covered even at higher temperature.

Thermodynamic treatment of the reaction:

The value of the enthalpy of activation $\Delta H^*$, entropy of activation $\Delta S^*$ and free energy of activation $\Delta G^*$ can be obtained by using equation:

$$\Delta H^* = E_a - RT$$  \hspace{1cm} (11)

$$\Delta S^*/R = \ln A - \ln (BT_e/h)$$  \hspace{1cm} (12)

$$\Delta G^* = \Delta H^* - \Delta S^*$$  \hspace{1cm} (13)

TABLE 4 shows that the entropy $\Delta S^*$ possesses negative values, indicating a highly ordered organic species in the solution under investigation. From the TABLES it is also noticed that the weak dependence of $\Delta G^*$ on the composition of the organic additives can be attributed largely to the general linear composition between $\Delta H^*$ and $\Delta S^*$ for the given temperature.
The isokinetic relationship

Variation in the rate within a reaction series may be caused by changes in either, or both, the enthalpy or the entropy of activation. The correlation of $\Delta H^*$ with $\Delta S^*$ is a linear relationship may be stated algebraically;

$$\Delta H^* = \beta \Delta S^* + \text{Constant} \quad (14)$$

$$\delta \Delta H^* = \beta \delta \Delta S^* \quad (15)$$

The operator, $\delta$, concerns difference between any two reactions in the series. Substituting from (15) into the familiar relationship:

$$\delta \Delta H^* = \delta \Delta G^* + T \delta \Delta S^*$$

We obtain

$$\beta \delta \Delta S^* = \delta \Delta G^* + T \delta \Delta S^*, \quad (17)$$

It follows that when $\delta \Delta G^*$ equal zero, $\beta$ equals $T$. In other words, the slope in a linear plot of $\Delta H^*$ versus $\Delta S^*$ is the temperature at which all the reactions that conform to the line occur at the same rate, $\beta$ is therefore known as the isokinetic temperature.

The isokinetic temperature $\beta$ were estimated as 289, 281, 290.9, 278.8, 296K. for Fructose, mannose, sucrose, lactose, maltose. These values which are much lower than that of the experimental temperature 298K indicating that the rate of the reactions is entropy controlled$^{[33]}$, But the value of $\beta$ which are much higher than 298K such as 308.9K for glucose indicating that the rate of the reaction is enthalpy controlled process$^{[34]}$.

1. Data correlation

To obtain an over all mass transfer correlation under the present conditions where a rotating cylinder is used the method of dimensional analysis was used. To identify the variables which affect the rate of mass transfer in the electrodeposition reaction, the mechanism of forced convection mass transfer should be recalled first. Forced convection takes place as a result of cylinder rotation. The thickness of this hydrodynamic boundary layer determines the thickness of the diffusion layer across which diffusion of $Cu^{2+}$ from the solution bulk to surface of Cu takes place. The thickness of the hydrodynamic boundary layer at the rotating cylinder and the
diffusion layer are determined by the physical properties of the solution, the geometry of the system (cylinder diameter) and cylinder rotation speed. This picture leads to the equation

$$K = f(\rho, \eta, D, U, d) \quad (18)$$

Where $K$ = mass transfer coefficient, sec$^{-1}$; $\rho$ = is density of bulk, g cm$^{-3}$; $\eta$ = is viscosity of bulk, cm$^2$.sec$^{-1}$; $D$ = is diffusion coefficient, cm$^2$.sec$^{-1}$; $U$ = is cylinder linear velocity ($U=\omega d$); $\omega$ = is angular velocity; $d$ = is diameter of cylinder, cm.

Figures 9 gives the over all correlation for all organic compounds with copper cylinder electrode which correlates by the equation:

$$\log \frac{Sh}{Sc^{0.33}} = \log a + b \log Re \quad (19)$$

The exponents in the equation denotes a highly turbulent flow which agree with the previous mass transfer study in aqueous media.

In our present study, a forced convection mechanism$^{38}$ is obtained which agree very well with the relationship given by Eisenberg et al.$^{32}$ for mass transfer to a rotating cylinder in turbulent flow system.

$$Sh = 0.0791 \ Re^{0.87} Sc^{0.36} \quad (20)$$

Also, our results agree excellently with:

$$Sh = 1.581Re^{0.725} Sc^{0.33} \quad (21)$$

Given by M. Nasser et al.$^{36}$ for mass transfer during cementation using rotating cylinder in an aqueous medium as well as with the equation $Sh = 0.061 Re^{0.833} Sc^{0.33}$ given by Ahmed et al.$^{37}$ for mass transfer during copper cementation from alcoholic water mixtures using rotating cylinder in turbulent system.

The over all correlation for all organic compounds. $Sh = 9.784 Re^{0.5017} Sc^{0.33}$ for Glucose with an average deviation: ±0.0119%, $Sh = 9.790 Re^{0.5017} Sc^{0.33}$ for fructose with an average deviation: ±0.0226%, $Sh = 9.786 Re^{0.5017} Sc^{0.33}$ for mannose with an average deviation: ±0.0621%, $Sh = 9.790 Re^{0.5016} Sc^{0.33}$ for sucrose with an average deviation: ±0.0234%, $Sh = 9.790 Re^{0.5016} Sc^{0.33}$ for lactose with an average deviation: ±0.0075%, $Sh = 9.799 Re^{0.5016} Sc^{0.33}$ for maltose with an average deviation: ±0.0126%

CONCLUSION

It is observed that the rate of electrodeposition in presence of cell using copper anode decreases by adding organic additives. This is attributed to the conductivity of solutions mixture decreases in presence of organic additives, and also viscosities of solutions are higher in presence of organic additives than in blank solutions.

Our results revealed that

i. The average limiting current density decreases by increase the electrode height.

ii. The limiting current density increases as CuSO$_4$ concentration increase.

iii. Organic substances have inhibition effect on the limiting current depending on the concentration and type of inhibitor.

iv. The rate of electrodeposition increases by increasing temperature.

v. When using RCE at 25°C the rate of electrodeposition increases by increasing rotation number.

REFERENCES


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