

## The Use of Rotating Cylinder Electrode to Study the Effect of 1,3-Dihydroxypropane on the Production of Copper Powder

H. M. A. Soliman<sup>\*,a</sup> and H. H. Abdel-Rahman<sup>b</sup>

<sup>a</sup> Institute of New Materials and Advanced Technologies, Mubarak City for Scientific Research and Technology Applications, New Borg El-Arab City, P.O. Box 21934 Alexandria, Egypt

<sup>b</sup> Chemistry Department, Faculty of Science, Alexandria University, P.O. Box 426, Ibrahimia 21321, Alexandria, Egypt

O efeito de diferentes concentrações de 1,3-diidroxiopropano (DHP) na eletrodeposição de cobre a partir de soluções de sulfato de cobre acidificado, tem sido estudado em diferentes temperaturas e velocidades de rotação. A eletrodeposição de cobre foi obtida sobre um eletrodo de cilindro rotatório (RCE) de cobre puro. A porcentagem de inibição, P, no cobre eletrodepositado foi 0,00-92,91%, dependendo das variáveis experimentais. P depende da temperatura e fração molar de DHP, enquanto a rotação não mostrou nenhuma influência. Os valores da energia de ativação do processo de eletrodeposição,  $E_a$ , encontrados, foram menores do que  $28 \text{ kJ mol}^{-1}$ , indicando que o processo é controlado por difusão. As correlações da transferência de massa global, nas presentes condições, têm sido obtidas usando-se o método de análise dimensional. Os dados foram válidos para  $80 < \text{Sh}$  ( $\text{Sh} = \text{número de Sherwood}$ )  $< 3970$ ,  $290 < \text{Sc}$  ( $\text{Sc} = \text{número de Schmidt}$ )  $< 59284$  and  $271 < \text{Re}$  ( $\text{Re} = \text{número de Reynolds}$ )  $< 52705$  e os resultados concordaram com os estudos prévios de transferência de massa para cilindros rotatórios em regimes de fluxo turbulento. Determinação experimental da velocidade crítica da solução foi obtida para branco e solução de DHP a 20% (v/v) em 298 K. O efeito do tempo, quantidade de DHP, temperatura e velocidade de rotação nas mudanças morfológicas do cobre em pó eletrodepositado, bem como a composição do depósito e tamanho de partícula, têm sido estudados. Vários tamanhos de partículas, no intervalo de 60,5 a 203,4 nm foram obtidos e caracterizados por EDS e XRD, tendo-se encontrado que as partículas eram de cobre puro com pequena quantidade de oxigênio. Diferentes topografias provaram que a razão da eletrodeposição de cobre aumenta com o aumento do tempo, temperatura e velocidade de rotação. Além disso, foi provado que a razão da eletrodeposição decresce pela adição de DHP à solução. Entretanto, os resultados obtidos por SEM apoiaram aqueles obtidos por medidas eletroquímicas. A estrutura morfológica do pó de cobre depositado da solução a 20% (v/v) de DHP em 1000 rpm e 298 K foi notável, agregados cristalinos arredondados com espaços vazios.

The effect of different concentrations of 1,3-dihydroxypropane (DHP) on the electrodeposition of copper powder from acidified copper sulphate solution has been studied at different temperatures and different speeds of rotation. Copper powder was electrodeposited onto rotating cylinder electrode (RCE) that made of pure copper. The inhibition percentage, P, in the electrodeposited copper powder was 0.00 – 92.91%, depending on the experimental variables. P was affected by temperature and mole fraction of DHP, while rotation did not show any influence whatsoever. Values of the activation energy of electrodeposition process,  $E_a$ , were found to be less than  $28 \text{ kJ mol}^{-1}$  indicating diffusion controlled process. The overall mass transfer correlations under the present conditions have been obtained using the dimensional analysis method. The data were valid for  $80 < \text{Sh}$  ( $\text{Sh} = \text{Sherwood number}$ )  $< 3970$ ,  $290 < \text{Sc}$  ( $\text{Sc} = \text{Schmidt number}$ )  $< 59284$  and  $271 < \text{Re}$  ( $\text{Re} = \text{Reynolds number}$ )  $< 52705$  and the results agreed with the previous studies of mass transfer to rotating cylinders in turbulent flow regimes. Experimental determination of the solution critical velocity was obtained for blank and 20% (v/v) DHP solutions at 298 K. The effect of time, DHP content, temperature and the speed of rotation on the morphological changes of the electrodeposited copper powder as well as deposits composition and particle size have been studied. Various particle sizes ranged 60.5 – 203.4 nm were obtained, characterized by EDS and XRD and found to be pure copper with small amount of oxygen. Different topographs proved that the rate of copper electrodeposition increased by increasing time, temperature and the speed of rotation. In addition, they proved that the deposition rate decreased by adding DHP to the solution. Therefore, the results obtained by SEM supported those results obtained by electrochemical measurements. The morphological structure of deposited copper powder from 20% (v/v) DHP at 1000 rpm and 298K was unique, rounded-crystalline aggregates with voids.

**Keywords:** 1,3-dihydroxypropane, copper powder, electrodeposition, rotating cylinder electrode

\* e-mail: hsolman@link.net

## Introduction

The use of RCE, as a cathode reaction surface for metal electrodeposition or metal extraction, has proved successful for a wide range of applications.<sup>1</sup> The RCE provides high rates of mass transport due to high rates of convective-diffusion in turbulent flow,<sup>2</sup> as stated by Eisenberg *et al.*<sup>3</sup> who found the relationship  $Sh = 0.079 Re^{0.7} Sc^{0.356}$  to hold for the range  $100 < Re < 100,000$ .

Copper is an intermediate metal,<sup>4</sup> which has medium exchange current density ( $10^{-5}$  to  $1 \text{ mA cm}^{-2}$ ) and deposits at medium polarization. It deposits in very rough or powdery form when electrodeposition is carried out at the limiting current density. An addition agent is defined as any material, which is added to an electroplating bath for the specific purpose of modifying the physical properties of the deposit. Relatively small amounts of addition agent have large effect on the physical properties of deposits such as brightness, smoothness, hardness and ductility. Most addition agents are organic compounds,<sup>5,6</sup> but, occasionally, inorganic materials are employed.<sup>7</sup> Organic solvents are also employed in the electrodeposition of metals that cannot be electrodeposited directly from aqueous solutions.<sup>8,9</sup> The importance of these media lies in the fact that changing their composition can vary their physicochemical properties. Bright copper has been electrodeposited from aqueous ammonia solutions.<sup>10</sup> Electrodeposition of copper has been studied in presence of ethanol, n-propanol, iso-propanol and tert-butanol,<sup>11</sup> and methanol, ethylene glycol and glycerol.<sup>12</sup> Electrodeposition of nickel from mixed baths,<sup>13</sup> and from nonaqueous baths,<sup>14</sup> led to some promising results. In the case of mixed solvent bath, the change in physicochemical properties of the deposit is attributed to the change in solvent composition. Moreover, the effect of aprotic constituent, dielectric constant and state of solvation of ions to be electrodeposited can easily vary by simply changing the composition of the mixed solvents. During electrodeposition studies of copper and nickel from water-methanol bath,<sup>15</sup> the change in electronic state of metal ion was attributed to the structural changes of solvent.

Compromising between the mass production and particle size is a challenging task in the industry of metallic powders and, given that, the microstructure and morphology of the electrodeposited metal are affected by the state of solvation; therefore, this work aims to investigate copper powder electrodeposition from acidified solutions of copper sulphate mixed with different contents of DHP under forced convection regime. Such investigation included change in temperature, rotation speed of RCE, and concentration of DHP. In addition, it aims to study the SEM topographs and EDS analysis to support the experimental measurements and to shed more light on copper powder production. Overall, this study is concerned

with all possibilities to generate new ideas for understanding and prediction of the electrode and cell geometries through dimensionless correlations to reach the optimum conditions useful in the industry of copper powder.

## Experimental

All chemicals were Analar grade and supplied by BDH chemicals Ltd. Solutions were prepared with water of resistivity  $15\text{-M}\Omega \text{ cm}$ , which was obtained from a MilliRo/MilliQ water purification system. Copper sulphate concentration and content were checked by the iodine-thiosulphate method.<sup>11</sup> The density and viscosity for all solutions, Table S1 (see Supplementary Information), were measured at 298, 303, 308 and 313K.<sup>11</sup>

A standard glass type cell with a polypropylene lid was used in all experiments.<sup>16</sup> The solution volume was 1000 mL. The polypropylene lid contained four inlets, which were used for working electrode WE immersion, luggin probe (reference electrode RE: saturated calomel electrode, SCE), counter electrode CE (copper) and thermometer to measure the temperature.

A 99.99% purity copper cylindrical sample was used as WE. This sample was rotated at controlled rates by an analytical rotator model A.S.R. made by PINE Instrument Company. The cylindrical samples of copper had dimensions of 8 mm height and 12 mm diameter. The specimens were lightly abraded with 1200 grade silicon carbide paper, washed with distilled water, acetone and deionised water and dried in a cool air stream prior to use. The anode CE, was machined from high purity (99.99%), commercially available copper. In order to ensure a correct control of the specimen rotation rate and the correct recording of potentials, regular checking of the rotation rate was carried out.

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  $1.67 \text{ mV s}^{-1}$ , which considered being suitable for copper electrodeposition.<sup>4</sup>

### Cathodic polarization

The variables used in this investigation were rotation speed (0 – 1000 rpm), temperature (298 – 313 K), and blank solution ( $0.1 \text{ mol L}^{-1} \text{ CuSO}_4$  and  $1.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ ) without and with DHP 10 - 60% (v/v) with a sweep range of 700 mV.

### Determination of the critical velocity

In these experiments, cathodic polarisation was used. The temperature was 298 K in all experiments and additive's concentration was 20% (v/v) DHP besides the blank solution. The rotation range was 1500 to 7000 rpm. The experimental procedure and set up were similar to cathodic polarisation.

### Morphology and composition analyses

An AMRAY 1810 Scanning Electron Microscope (SEM) was used to examine the surface topography of specimens after experiment, while Energy Dispersive X-ray Analysis (EDS) was used for elemental analyses. The specimens were examined through an acceleration potential of 20 KeV; the specimens were coated with carbon to avoid electron charging of the surface since the surface film may not be electrically conductive.

Two types of specimens were prepared to examine the surface topography. The first type of specimens was used for free convection experiments, while the second type was used for forced convection ones. The free convection specimens were made of copper rods that were cut into small pieces of dimensions 0.8 cm height and 1.2 cm diameter; while those used for forced convection were made of copper cylinders with 0.8 cm in height and 1.2 cm in diameter. For all specimens, the surfaces for SEM analyses were polished with series of silicon carbide paper grades in the range 120 – 1200  $\mu\text{m}$ , then with 3  $\mu\text{m}$  diamond paste followed by 1  $\mu\text{m}$  diamond paste on a polishing wheel. After washing with deionised water and degreasing in acetone, warm air was blown over the surface. These specimens were stored in a desiccator over silica gel prior to use.

X-ray Diffraction (XRD) measurement for copper powder was carried out using a Shimadzu XRD-7000 X-ray Diffractometer with Cu-K $\alpha$ 1 radiation operated at 40 kV and 30 mA, with a scan speed of 2 $\theta$  min<sup>-1</sup>.

Temperature, 298 – 313 K; DHP content, 0 – 60% (v/v); rotation rate, 0 - 1000 rpm; and time, 10 - 30 min, were the different variables that have been employed to study the surface analysis by EDS and XRD identification measurements.

## Results and Discussion

### Cathodic polarisation

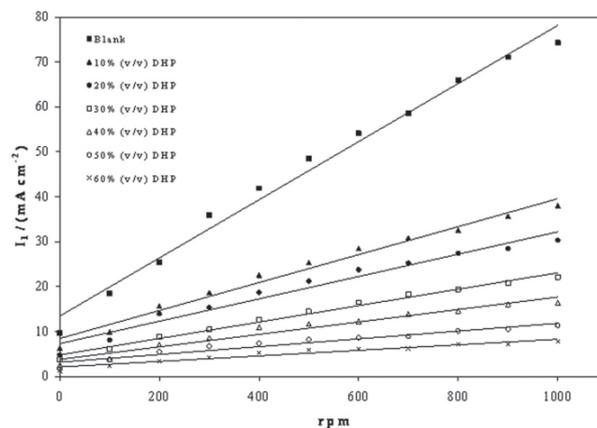
Values of the limiting current densities,  $I_l$ , for all solutions at different rotations and different temperatures using copper anode are given in Table S2 (see Supplementary Information).

Noticeably, the limiting current density decreases with increasing DHP mole fraction and increases by increasing temperature. The increase of mass transport under forced or turbulent conditions may refer to elevation in solution temperature,<sup>2</sup> roughness of the deposit and/or the increase in agitation. Equation 1 was used to calculate the mass transfer coefficients,  $k$ , for DHP solutions.

$$k = \frac{I_l}{nFC_0} \quad (1)$$

where  $n$  = number of electrons involved in the reaction,  $F$  = Faraday constant = 96500 (C mol<sup>-1</sup>,  $C = A \text{ s}$ ),  $C_0$  = bulk concentration of copper sulphate (mol cm<sup>-3</sup>).

It is clear in Table S2 and in Figure 1 that the limiting current density increases with increasing the speed of rotation, which proves that the electrodeposition process of copper in presence of DHP as well as in aqueous media is diffusion-controlled reaction.



**Figure 1.** Variation of limiting current density,  $I_l$ , with the speed of rotation, rpm, at 298K.

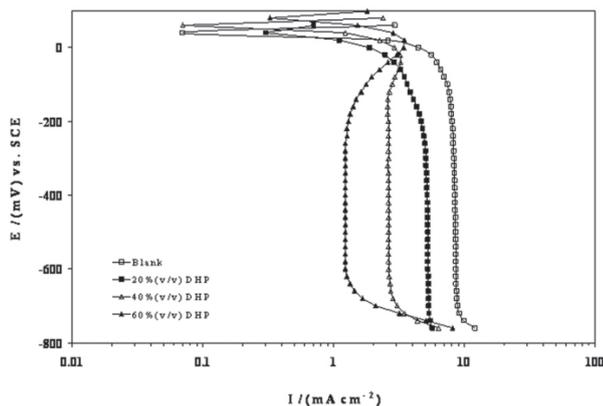
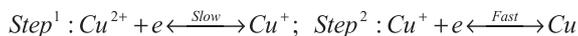
The percentage of inhibition,  $P$ , was calculated from equation 2.  $P$  caused by DHP was in the range of 0.00 - 92.91% depending on the concentration of DHP as well as the temperature.

$$P = \frac{I_{l_{\text{blank}}} - I_{l_{\text{DHP}}}}{I_{l_{\text{blank}}}} \times 100 \quad (2)$$

Table S3 (see Supplementary Information) gives the values of  $P$ , which shows that  $P$  increased as the mole fraction of DHP,  $X$ , increased, but it was not affected by rotation. This indicates that the rotation factor has little effect on the adsorption process and the decrease in mass transfer coefficient in this case is attributable to the increase in the interfacial viscosity,<sup>16</sup> which caused by the adsorption of alcohol molecules at the cylinder surface with their non-polar ends, while the polar ones are directed towards solution.

Figure 2 shows the cathodic polarisation curves for copper powder that electrodeposited from acid-sulphate solution with

variable amounts of DHP at 298 K and zero rpm as an example. It is obvious that in alcohol-free solution the current at the beginning increases linearly, then as the cathodic potential increases it tends to exhibit limiting current plateau. The reduction of copper ions takes place through two steps:<sup>17</sup>



**Figure 2.** Typical potential – current curves obtained at 298K, no rotation, and different DHP contents.

It was assumed that the first step in this process occurred slowly and the rate was controlled by the equilibrium between  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  at the electrode surface. However, addition of alcohol to the sulphate solution increases the cathodic polarisation and decreases the value of the limiting current density. The observed changes in the cathodic polarisation in the presence of DHP suggest that it acts as an inhibitor, which is confirmed by the observation, at any given overpotential, the current density for copper deposition from solutions containing DHP is always lower than that for the blank solution. This inhibition effect may be due to the adsorption of alcohol molecules on the cathode surface and/or the complexation of  $\text{Cu}^{2+}$  with alcohol molecules. It is known that in acidic media,  $\text{Cu}^{2+}$  can complex with alcohol molecules via the alcohol hydroxyl groups and exists as a cationic complex.<sup>17</sup>

### Adsorption isotherms

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. All these isotherms are of the general form:

$$f(\theta, x) \exp(-a\theta) = K_e C \quad (3)$$

where  $\theta$  is the surface coverage,  $K_e$  is the equilibrium constant,  $C$  is the concentration of the electrolyte and  $f(\theta, x)$  is the

configurational factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm. The mechanism of electrodeposition inhibition is generally believed to be due to the formation and maintenance of an adsorbed film on the metal surface.

The surface coverage,  $\theta$ , can be determined using the following equation:

$$\theta = 1 - \frac{I_{\text{DHP}}}{I_{\text{Blank}}} \quad (4)$$

where  $I_{\text{DHP}}$  and  $I_{\text{Blank}}$  are the limiting current densities in case of solvent and blank solutions; respectively.

Values of the equilibrium constant were computed and listed in Table S4 (see Supplementary Information) using Langmuir isotherm:

$$K_e C = \frac{\theta}{1 - \theta} \quad (5)$$

When  $\log \frac{\theta}{1 - \theta}$  was plotted versus  $\log C$ , straight lines were obtained with slopes nearly equal unity, which proves the fact that the adsorption of DHP on copper surface obeys the Langmuir adsorption isotherm. As a result, this leads to the suggestion that the adsorbed molecules do not interact with each other. In addition, straight lines were obtained when  $\theta$  was plotted versus  $\log C$  at different temperatures, indicating that the adsorption of DHP on copper surface follows Temkin's adsorption isotherm as well.

The free energy of adsorption,  $\Delta G_{\text{ads}}$ , at different temperatures was calculated and listed in Table S5 (see Supplementary Information) using the following equation:

$$K_e = \frac{1}{55.5} \exp\left[\frac{-\Delta G_{\text{ads}}}{RT}\right] \quad (6)$$

The value of 55.5 is the concentration of water in solution expressed in  $\text{mol L}^{-1}$ . The negative sign of  $\Delta G_{\text{ads}}$  values indicates the spontaneous adsorption of DHP molecules, which is usually characteristic for strong interaction with metal surface. From Table S5, values of  $\Delta G_{\text{ads}}$  are more positive than  $-40 \text{ kJ mol}^{-1}$ , indicating physical adsorption on metal surface.

### Thermodynamic treatment of the results

To investigate the mechanism of the electrodeposition process, the activation energies,  $E_a$ , of the process were calculated from the values of the limiting current density in absence and in presence of DHP at different temperatures according to Arrhenius equation:

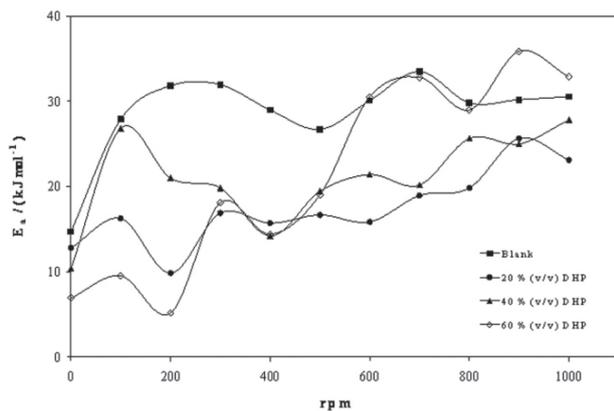
$$\ln(I_1) = \ln(A) - \frac{E_a}{R} \frac{1}{T} \quad (7)$$

where  $A$  is a pre-exponential factor related to concentration, steric effects, metal surface characteristics, etc;  $R$  is the molar gas constant and  $T$  is the absolute temperature.

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

Values of activation energy,  $E_a$ , as well as the rest of thermodynamic parameters, enthalpy of activation,  $\Delta H^*$ , entropy of activation,  $\Delta S^*$ , and free energy of activation,  $\Delta G^*$ , were calculated and listed in Table S6 (see Supplementary Information).

Table S6 shows that all  $E_a$  values are lower than  $43 \text{ kJ mol}^{-1}$ ; characterizing diffusion processes are controlling the electrodeposition reaction. Figure 3 is a presentation of controlling the particle size as a parameter of two variables; the composition of DHP and the speed of rotation. As it is shown in Figure 3, the highest composition of DHP does not mean the lowest  $E_a$  value and vice versa. This last observation is also applicable for forced convection regime.

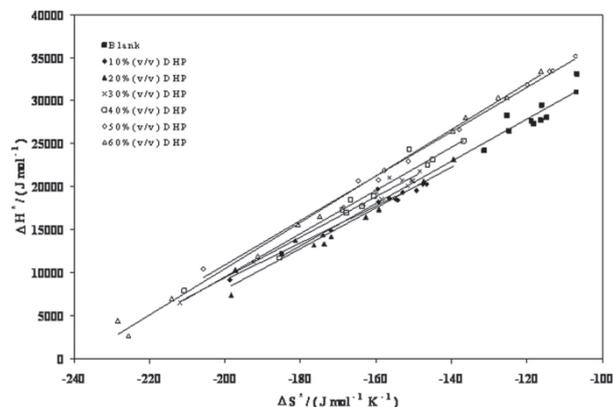


**Figure 3.** Variation of activation energy,  $E_a$  ( $\text{kJ mol}^{-1}$ ), with the speed of rotation, rpm, at 298K.

From Table S6, it is also noticed that the weak dependence of  $\Delta G^*$  on the composition of the organic solvent can be attributable largely to the general linear compensation between  $\Delta H^*$  and  $\Delta S^*$  for the given temperature. The non linear variation of  $\Delta S^*$  with the mole fraction is a criterion of specific solvation where random distribution is not valid in the absence of strong hydrogen bonding between the molecules of water and the organic solvent.<sup>18</sup>

The plots of  $\Delta H^*$  versus  $\Delta S^*$ , Figure 4, for different solvent compositions at different speeds of rotation were found to be linear. The values of isokinetic temperature,  $\beta$ , were computed from the slope of such

plots and found to be in the range  $214.3 - 269.0 \text{ K}$  indicating that mass transfer rate is entropy controlled,<sup>19</sup> where the solute-solvent interaction plays an important role in the rate determining step.



**Figure 4.** Variation of enthalpy of activation,  $\Delta H^*$  ( $\text{kJ mol}^{-1}$ ), with the entropy of activation,  $\Delta S^*$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ).

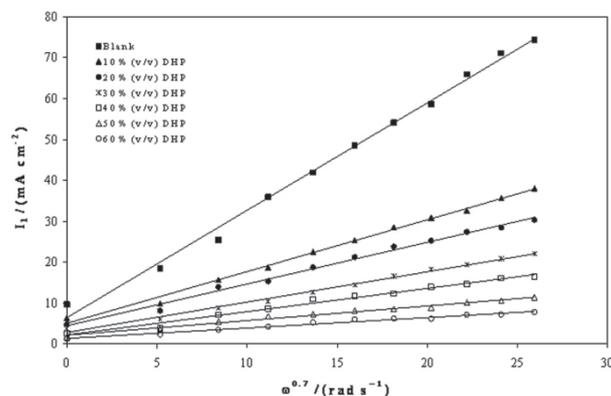
#### Effect of rotation

The angular velocity,  $\omega$ , is given by equation 8:

$$\omega = \frac{2\pi \text{rpm}}{60} \quad (8)$$

Figure 5 shows the relation between the limiting current density and the angular velocity to a power 0.7 at 298 K and different compositions of DHP. Straight lines were obtained and the limiting current density increases by increasing rotation, which indicates that the electrodeposition process of copper in presence of DHP as well as in aqueous media is diffusion-controlled reaction.

The diffusion coefficient of  $\text{Cu}^{2+}$  ions,  $D$ , in different solutions was determined from the values of limiting current density, as shown in Table S7 (see Supplementary Information), using Eisenberg equation:<sup>3</sup>



**Figure 5.** Variation of the limiting current density,  $I_l$ , with the angular velocity to a power 0.7,  $\omega^{0.7}$ , at 298K using different DHP contents.

$$I_1 = 0.0791 n F C_b U^{0.7} d_i^{-0.3} \nu^{-0.344} D^{0.644} \quad (9)$$

where  $C_b$  is the bulk concentration ( $\text{mol cm}^{-3}$ ),  $U$  is the peripheral velocity  $= \omega r$  in  $\text{cm rad s}^{-1}$  ( $r$  is the radial distance in  $\text{cm}$ ) or  $U=2\pi\omega r$  in  $\text{cm s}^{-1}$ ,  $d_i$  is the characteristic length for the rotating cylinder in  $\text{cm}$ , and  $\nu$  is the kinematic viscosity in stoke ( $\nu = \eta/\rho$ ,  $\eta$  is the viscosity in  $\text{g cm}^{-1} \text{s}^{-1}$  and  $\rho$  is the density in  $\text{g cm}^{-3}$ ).

The diffusion coefficient;  $D$ , of  $\text{Cu}^{2+}$  ions in solutions containing alcohols decreases due to the increase in the interfacial viscosity,  $\eta$  in accordance with de Stokes-Einstein equation:<sup>20</sup>

$$\frac{\eta D}{T} = \text{const.} \quad (10)$$

The present results agree with the polarographic studies conducted in solutions containing surfactants where it was found that the diffusion current decreases in the presence of surfactants.<sup>21,22</sup>

Table S7 illustrates the slight decrease in the values of the diffusion coefficient,  $D$ , in presence of DHP, which indicate that DHP hinders the diffusion of cupric ions from the bulk to the outer limit of the electrode double layer. A possible explanation is that DHP is a polar molecule with interfacial activity that could change the composition and the properties of the double layer on the electrode surface. Thus, DHP molecules replace the water molecules on the metallic surface, forming an adsorbed superficial film. This would increase the electrolyte viscosity and lower the dielectric constant at the electrode/electrolyte interface.<sup>23</sup> Consequently, hydrated metal ions or complex ions approach the surface with increased difficulty to enable charge transfer.

It was noted in a previous review,<sup>24</sup> that mass transport to an inner RCE in turbulent flow system may be described by empirical dimensionless correlations of the form:

$$\text{Sh} = a \text{Re}^b \text{Sc}^c \quad (11)$$

where  $\text{Sh}$ ,  $\text{Re}$  and  $\text{Sc}$  are the Sherwood ( $\text{Sh}=kl/D$ ), Reynolds ( $\text{Re}=lU/\nu$ ) and Schmidt ( $\text{Sc}=\nu/D$ ) numbers; respectively and  $a$  and  $b$  are empirical constants,  $c = 0.33$ ; indicating forced convection regime.<sup>1</sup> Table S8 (see Supplementary Information) summarizes the values of dimensionless groups ( $\text{Sh}$ ,  $\text{Sc}$  and  $\text{Re}$ ) at all experimental conditions. By plotting  $\log\left[\frac{\text{Sh}}{\text{Sc}^{0.33}}\right]$  against  $\log(\text{Re})$ , a straight line was obtained its slope gave the constant  $b$  while the intercept offered the other constant  $a$ , Table S9 (see Supplementary Information). Values of constants  $a$  and  $b$  depend on:<sup>24</sup> (i) the type of roughness, (ii) the degree of roughness, and (iii) the electrolyte composition,

temperature and the morphology of the deposits.

In this study, a forced convection mechanism is obtained which agrees very well with the relationship  $\text{Sh} = 0.0791 \text{Re}^{0.7} \text{Sc}^{0.356}$  given by Eisenberg *et al.*,<sup>25</sup> for mass transfer to a rotating cylinder in turbulent flow system and exponents in all equations denote a highly turbulent flow, which agrees with the previous mass transfer study in aqueous media.<sup>26</sup> Also, results at hand agree excellently with  $\text{Sh} = 1.581 \text{Re}^{0.725} \text{Sc}^{0.33}$  given by Mamdouh *et al.*,<sup>27</sup> for mass transfer during cementation using rotating cylinder in an aqueous medium as well as with the equation  $\text{Sh} = 0.061 \text{Re}^{0.833} \text{Sc}^{0.33}$  given by Ahmed *et al.*,<sup>28</sup> for mass transfer during copper cementation from alcoholic-water mixtures using rotating cylinder in turbulent system.

#### Determination of the critical velocity

To evaluate whether the limiting current increases indefinitely with increasing the speed of rotation or there is a limit for such increase, two solutions were chosen, one of them was the blank solution and the other was 20% (v/v) DHP. Polarizations were carried out at high speeds of rotation and 298 K. Figure 6 shows the relation between the limiting current density and the angular velocity,  $\omega$ , to a power 0.7 for blank and 20% (v/v) DHP solutions at 298 K and high speeds of rotation. It is shown in Table S10 (see Supplementary Information) that the critical velocity in case of blank solution in the range of 5000 – 6000 rpm with average critical limiting current density of 148.91  $\text{mA cm}^{-2}$ , while for 20% (v/v) DHP solution it was 5500 – 7000 rpm with average limiting current density of 101.34  $\text{mA cm}^{-2}$ . Currently, it is clear that the presence of DHP in the medium increases the critical velocity and decreases the critical limiting current density. This leads to conclude that the presence of DHP in copper electrodeposition bath will offer a faster surface diffusion process compared with electron

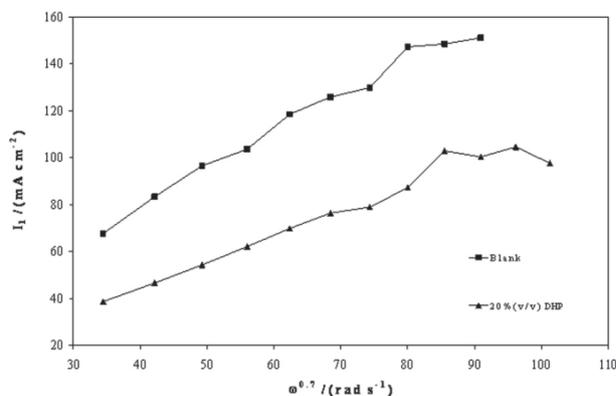


Figure 6. Variation of the limiting current density,  $I_1$ , with the angular velocity to a power 0.7,  $\omega^{0.7}$ , at high speeds of rotation and 298K.

transfer and as a result the formation of adatoms and both crystal lattices and surface features will be well formed.<sup>29</sup> It can be noticed from Figure 6 that the limiting current density increases by increasing rotation until we reach a certain region at which the current keeps almost constant, this is again the region of the critical velocity. Then the data at high speeds of rotation can be correlated by the equation,  $Sh = 0.1022Re^{0.705} Sc^{0.33}$  as previously shown.

From the previous study concerning the electrodeposition process of copper powder in acidified solutions of copper sulphate and in the presence of DHP using the rotating cylinder electrode (RCE) the data were valid for  $80 < Sh < 3970$ ,  $290 < Sc < 59284$  and  $271 < Re < 52705$ .

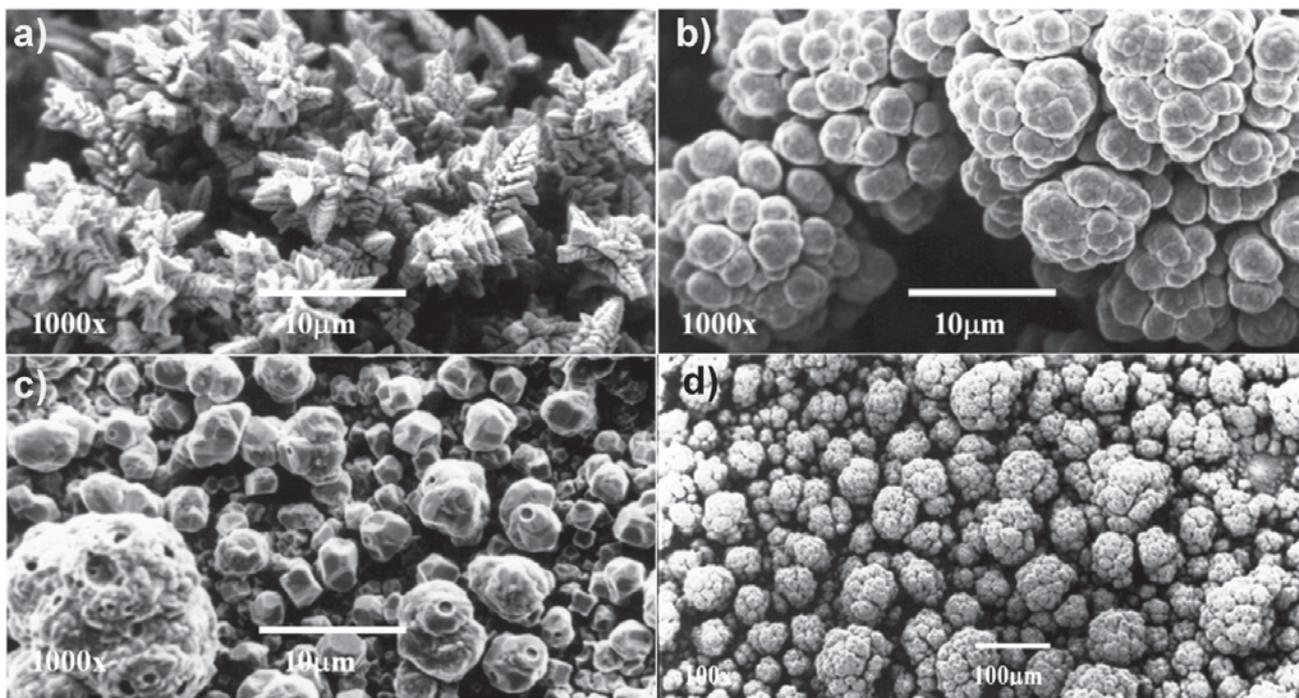
#### *Morphology and composition analyses*

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 powder must be characterised by 3-D nucleation.<sup>7</sup> The phenomenon of dendritic growth,<sup>29</sup> may occur if the rate of the electrodeposition process is partially diffusion controlled, so, on a microrough surface, the rate of deposition at surface peaks will be greater than that at troughs. These surface non-uniformities, therefore, become more pronounced resulting, eventually, in the formation of macrorough

deposits. The phenomenon of dendritic growth may also be related to differences in the rate of diffusion at different points on a surface. In the case of macrospiral growth, for instance, spherical diffusion to the tip of the spiral results in a higher rate of mass transport to this point and this may lead to dendritic growth.

All experiments were proceeded at 298 K with duration time of 20 minutes using copper anode and copper was electrodeposited onto copper cylinder with variation in the speed of rotation between 200 and 1000 rpm. Although it was stated,<sup>30</sup> that an increase in copper ion concentration or in agitation will increase the particles size and obscures their dendritic character, it was found dramatic changes occurred when rotation started, dendrite nodules were formed with high degree of discontinuity as well as very rough deposits as in case of blank solution at 200 rpm, Figure 7a.

Contrary to Figure 7a at 200 rpm, grape-like aggregates were formed with low degree of discontinuity at 1000 rpm in case of blank solution, as shown in Figure 7b. Figure 7c represents the third type of morphology in this study in case of 20% (v/v) DHP at 1000 rpm, which is rounded-crystalline aggregates with voids. The main reason for voids formation is attributable to the swelling effect that correlates with the liberation of gases.<sup>31</sup> This structure is considered as a unique surface feature in this study, although case of 10% (v/v) DHP tends to give similar structure.



**Figure 7.** Electrodeposited copper in case of blank solution after 20 minutes a) at  $25 - 26 \text{ mA cm}^{-2}$ , 298K and 200 rpm, b) at  $74 - 75 \text{ mA cm}^{-2}$ , 298K and 1000 rpm, c) at  $30 - 31 \text{ mA cm}^{-2}$ , 298K and 1000 rpm, and d) at  $54 - 55 \text{ mA cm}^{-2}$ , 298K and 600 rpm.

At 600 rpm for all solutions, except 20% (v/v) DHP, a transient structure between dendrite nodules and grape-like aggregates was formed, which means that the region between 200 – 600 rpm is considered as a transient region with mixed deposition mechanisms as shown in Figure 7d in case of blank solution.

High current densities or high cathodic overpotentials, accompanied by fast stirring rates can adversely affect electrodeposition process resulting in brittle deposits, which can comprise occlusions of additives and/or foreign materials.<sup>32</sup> Figure 8 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 powder under different conditions for all solutions was mainly pure copper (80.24 at.%) and oxygen (19.37 at.%) with tiny percentage of silicon and carbon, which may be due to the occlusion of foreign materials,<sup>32</sup> 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 Figure 8 might caused by the oxidation of a negligible part of the deposit due to the high voltage used in the analysis. Figure 9 represents the distribution of both copper and oxygen in the produced powder under different conditions, showing the mutual homogeneous distribution of copper and oxygen.

XRD patterns of the deposited copper powder are presented in Figure 10 as an example. This exhibits polycrystalline copper in as deposited state with (111) as prominent plane parallel to the substrate. According to the standard PDF card (No. 04-0836),<sup>33</sup> all of the

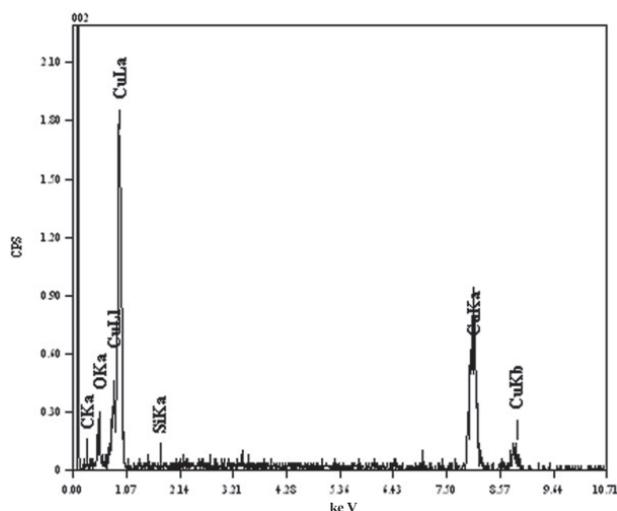


Figure 8. Deposit EDS analysis at different experimental conditions.

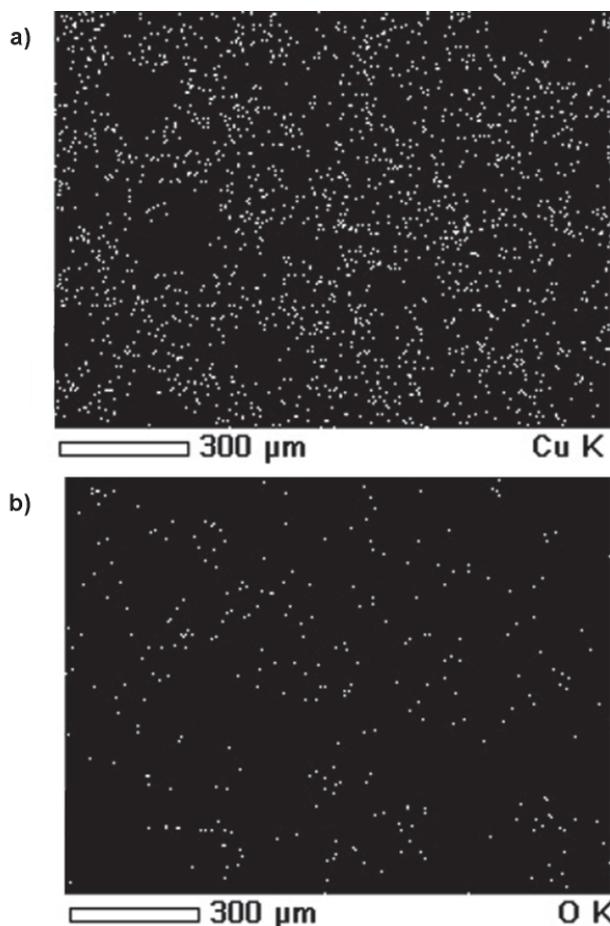


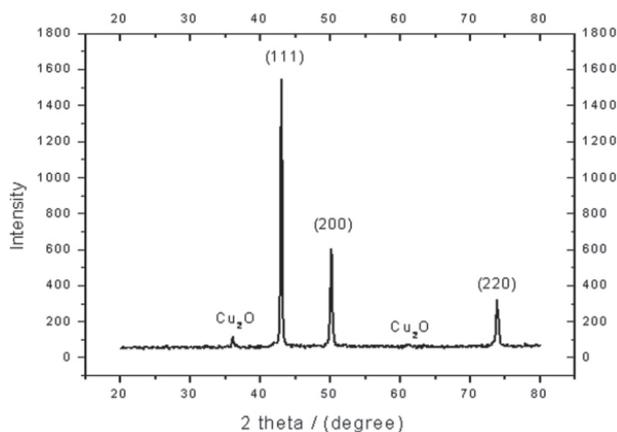
Figure 9. Atomic distribution of a) Cu K and b) O K.

detected peaks are indexed as those from the cubic crystal [space group  $Fm\bar{3}m$  (225)] with small two peaks that patterned for  $Cu_2O$ . The average particle size was calculated using Scherrer's equation:

$$D = \frac{0.9\lambda}{B \cos \theta_B} \quad (1)$$

where  $D$  is the particle size in nm,  $\lambda$  is the wave length of X-ray radiation source (Cu  $K\alpha_1$ ,  $\lambda = 1.54056$ ),  $B$  is the full-width at half maximum and  $\theta$  is the angle.

The average particle size of copper powder electrodeposited in absence of DHP was ranged between 127 nm at 1000 rpm and 132.8 nm at 0 rpm, except at 600 rpm which was 83.8 nm, supporting the hypothesis of transient mechanism at that rotation speed. Contrary to the blank solution, the average particle size in presence of DHP was 60.5 nm at all rotation speeds and all concentrations, except at 1000 rpm and 20% (v/v) DHP which was 203.4 nm, proving the unique structure of the deposited copper powder from that concentration.



**Figure 10.** XRD patterns of as deposited Cu powder at different experimental conditions.

## Conclusions

From the previous study concerning the electro-deposition process of copper powder in acidified solutions of copper sulphate and in the presence of DHP using the rotating cylinder electrode (RCE) the data were valid for  $80 < Sh < 3970$ ,  $290 < Sc < 59284$  and  $271 < Re < 52705$  with overall dimensionless correlation of  $Sh = 0.1022Re^{0.705} Sc^{0.33}$ . Addition of DHP to the sulphate electrodeposition bath increases the cathodic polarisation and decreases the value of the limiting current density, while it increases with increasing temperature and the speed of rotation. The percentage of inhibition,  $P$ , was in the range 0.00 - 92.91% depending on the concentration of DHP as well as the temperature. The adsorption of DHP on copper surface was found to be physical adsorption and obeyed both Langmuir and Temkin adsorption isotherms. The mass transfer rate was found to be entropy controlled with diffusion process controlling the electrodeposition. The range of the critical velocity in case of blank solution was 5000 – 6000 rpm with average critical limiting current density of  $148.91 \text{ mA cm}^{-2}$ , while it was 5500 – 7000 rpm for 20% (v/v) DHP solution with average limiting current density of  $101.34 \text{ mA cm}^{-2}$ .

3-D dendritic structures were formed when the electrodeposition was carried out at the limiting current density with various particle sizes ranged 60.5 – 203.4 nm. EDS elemental analysis and XRD diffraction patterns indicated that the formed powder was mainly copper (80.24 at.%) and oxygen (19.37 at.%) with traces of carbon (0.35 at.%) and silicon (0.04 at.%). The morphological structure of deposited copper from 20% (v/v) DHP at 1000 rpm and 298K was unique, rounded-crystalline aggregates with voids.

## Supplementary Information

Tables S1 to S10 are available free of charge as PDF file at <http://jbcs.sbg.org.br>

## References

- Gabe, D.R.; Walsh, F.C.; *J. Appl. Electrochem.* **1983**, *13*, 3.
- Gabe, D.R.; Walsh, F.C.; *The Reinhardt Schuhmann International Symposium on Innovative Technology and Reactor Design in Extraction Metallurgy*, Colorado Springs, Colorado, USA, 1986, p. 775.
- Eisenberg, M.; Tobias, C.W.; Wilke, C.R.; *J. Electrochem. Soc.* **1954**, *101*, 306.
- Winand, R.; *Application of Polarisation Measurements in the Control of Metal Deposition*, Warren, I. H., ed., Elsevier Science Publishers: Amsterdam, 1984, p. 47.
- Muresan, L.; Varvara, S.; Maurin, G.; Dorneanu, S.; *Hydrometallurgy* **2000**, *54*, 161.
- Kelly, J.J.; Tian, C.Y.; West, A.C.; *J. Electrochem. Soc.* **1999**, *146*, 2540.
- Andersen, T.N.; Pitt, C.H.; Livingston, L.S.; *J. Appl. Electrochem.* **1983**, *13*, 429.
- Biallazor, S.; Lisowska-Oleksiak, A.; *J. Appl. Electrochem.* **1990**, *20*, 590.
- Kumbhar, P.P.; Lokhande, C.D.; *Ind. J. Chem. Technol.* **1994**, *1*, 194.
- Ibrahim, M.A.M.; *Plat. Surf. Finish.* **2000**, *87*, 67.
- Selim, I.Z.; El-Sobki, K.M.; Khedr, A.A.; Soliman, H.M.A.; *Bull. Electrochem. Ind.* **2000**, *16*, 315.
- Soliman, H.M.A.; *Medium Effect on Mass Transfer Coefficient in Electrodeposition Process of Copper from Acidic Copper Sulfate Solutions*, Ph.D. Thesis submitted for Faculty of Science, Alexandria University, Egypt, 1998.
- Tikoo, P.K.; Singh, V.B.; Sultan, S.; *Plat. Surf. Finish.* **1984**, *71*, 64.
- Bahadur, L.; Singh, V.B.; Tikoo, P.K.; *J. Electrochem. Soc.* **1981**, *128*, 2518.
- Srivastava, H.K.; Tikoo, P.K.; *Surf. Coat. Technol.* **1987**, *31*, 343.
- Selim, I.Z.; Ahmed, A.M.; Khedr, A.A.; Soliman, H.M.A.; *Bull. Electrochem. Ind.* **2001**, *17*, 27.
- Abd El Rehim, S.S.; Sayyah, S.M.; El Deeb, M.M.; *Appl. Surf. Sci.* **2000**, *165*, 249.
- Ismail, A.M.; El-Naggar, G.A.; Ahmed, A.M.; *Bull. Electrochem. Ind.* **2001**, *17*, 385.
- El Shazly, Sh.A.; Massoud, S.S.; Zaghloul, A.A.; Mohamed, M.T.; Amira, M.F.; *Bull. Soc. Chim.* **1989**, *6*, 780.
- Taha, A.A.; Sallam, S.H.; Ahmed, A.M.; *Anti-Corros. Methods Mater.* **1994**, *41*, 10.
- Issa, I.M.; Ghoneim, M.M.; El-Samahy, A.A.; Tharwat, M.; *Electrochim. Acta* **1972**, *17*, 1251.

- 22 Beck, T.R.; Alkire, R.C.; *J. Electrochem. Soc.* **1979**, *126*, 1662.
- 23 Franklin, T.C.; Williams, T.; Narayan, T.S.N.; Guhl, R.; Hair, G.; *J. Electrochem. Soc.* **1997**, *144*, 3064.
- 24 Gabe, D.R.; Wilcox, G.D.; *J. Appl. Electrochem.* **1998**, *28*, 759.
- 25 Eisenberg, M.; Tobias, C.W.; Wilke, C.R.; *J. Electrochem. Soc.* **1955**, *102*, 415.
- 26 Pickett, D.; *Electrochemical Reactor Design*, Elsevier: Amsterdam, 1977, p. 110.
- 27 Nasser, A. Mamdoh; Fadalli, Olfat A.; Sedahmed, Gomaa H.; *Metallkde* **1989**, *80*, 60.
- 28 Abdel-Rahman, Hanaa H.; *Kinetic Studies of Cementation of Copper on Rotating Zinc Cylinder in Aqueous and Mixed Solvents*, Ph.D. Thesis submitted for Faculty of Science, Alexandria University, Egypt, 1998.
- 29 Pletcher, D.; Walsh, F.C.; *Industrial Electrochemistry*, Chapman and Hall, 1989, p. 216.
- 30 Russev, D.R.; *J. Appl. Electrochem.* **1981**, *11*, 177.
- 31 Walker, R.; Duncan, S.J.; *Surf. Coat. Technol.* **1986**, *27*, 137.
- 32 Hope, G.A.; Brown, G.M.; Schweinsberg, D.P.; Shimizu, K.; Kobayashi, K.; *J. Appl. Electrochem.* **1995**, *25*, 890.
- 33 *Natl. Bur. Stand. (U.S.)* **1953**, *Circ.539*, 1 15.

Received: July 26, 2005

Published on the web: May 16, 2006

## The Use of Rotating Cylinder Electrode to Study the Effect of 1,3 Dihydroxypropane on the Production of Copper Powder

H.M.A. Soliman<sup>\*a</sup> and H.H. Abdel-Rahman<sup>b</sup>

<sup>a</sup> Institute of New Materials and Advanced Technologies, Mubarak City for Scientific Research and Technology Applications, New Borg El-Arab City, P.O. Box 21934 Alexandria, Egypt

<sup>b</sup> Chemistry Department, Faculty of Science, Alexandria University, P.O. Box 426, Ibrahimia 21321, Alexandria, Egypt

**Table S1.** Viscosities and densities for all solutions at different temperatures

	Temperature, T (K)	Viscosity, $\eta$ (poise)	Density, $\rho$ (g cm <sup>-3</sup> )
Blank, 0% (v/v) DHP	298	0.01084	1.09928
	303	0.00972	1.09647
	308	0.00879	1.09365
	313	0.00800	1.09084
10% (v/v) DHP	298	0.01129	1.10656
	303	0.01013	1.10373
	308	0.00915	1.10090
	313	0.00833	1.09807
20% (v/v) DHP	298	0.01304	1.11484
	303	0.01169	1.11199
	308	0.01056	1.10913
	313	0.00961	1.10628
30% (v/v) DHP	298	0.01543	1.12810
	303	0.01384	1.12522
	308	0.01250	1.12233
	313	0.01138	1.11945
40% (v/v) DHP	298	0.01879	1.13638
	303	0.01685	1.13348
	308	0.01523	1.13057
	313	0.01386	1.12766
50% (v/v) DHP	298	0.02334	1.14865
	303	0.02093	1.14571
	308	0.01892	1.14277
	313	0.01721	1.13984
60% (v/v) DHP	298	0.02964	1.15793
	303	0.02658	1.15497
	308	0.02402	1.15200
	313	0.02186	1.14904

\* e-mail: hsolman@link.net

**Table S2.** Values of the limiting current density,  $I_l$  (mA cm<sup>-2</sup>), for all solutions at different temperatures and different speeds of rotation

	rpm	298 K	303 K	308 K	313 K		rpm	298 K	303 K	308 K	313 K	
Blank, 0% (v/v) DHP	0	9.70	10.80	11.76	12.93	30% (v/v) DHP (cont.)	600	16.50	19.12	22.15	26.49	
	100	18.51	26.01	30.82	33.78		700	18.33	21.05	23.94	27.58	
	200	25.41	35.73	37.01	54.00		800	19.36	23.39	26.28	30.66	
	300	35.88	45.52	55.40	66.77		900	20.77	24.22	27.66	32.70	
	400	41.89	53.51	61.62	74.48		1000	22.08	26.35	29.42	34.59	
	500	48.51	60.88	64.67	84.45		40% (v/v) DHP	0	2.56	2.59	2.80	3.12
	600	54.12	71.92	80.61	99.41			100	3.89	5.75	6.20	6.73
	700	58.63	73.78	96.56	109.97			200	7.11	7.64	9.18	10.51
	800	65.92	82.96	98.05	118.30			300	8.62	9.39	10.79	12.62
	900	71.07	87.87	111.13	125.64			400	10.93	12.27	12.93	14.58
1000	74.27	96.34	112.74	135.79	500	11.74		12.79	14.44	17.14		
10% (v/v) DHP	0	6.32	6.92	7.27	7.99	600		12.27	14.33	16.05	18.71	
	100	9.93	11.95	13.16	15.50	700		13.91	15.80	17.45	20.78	
	200	15.68	18.12	19.36	22.29	800		14.61	17.00	20.50	23.83	
	300	18.69	21.98	24.90	27.97	900		16.09	18.26	22.67	25.62	
	400	22.57	26.97	29.52	34.48	1000	16.44	18.78	23.65	27.68		
	500	25.34	30.97	34.52	39.06	50% (v/v) DHP	0	1.65	1.72	1.84	2.13	
	600	28.55	33.69	37.68	43.23		100	3.68	4.17	4.91	5.74	
	700	30.86	36.89	41.71	46.43		200	5.47	5.50	7.51	8.34	
	800	32.57	40.58	45.16	51.26		300	6.73	7.67	9.60	10.29	
	900	35.68	43.16	48.57	55.08		400	7.32	8.06	10.50	11.59	
1000	38.02	46.05	51.33	59.76	500		8.20	8.76	10.54	11.87		
20% (v/v) DHP	0	4.82	5.08	5.75	6.09		600	8.59	9.81	12.27	14.91	
	100	8.13	8.89	10.13	11.03		700	8.90	10.76	13.64	17.22	
	200	13.94	14.44	15.65	16.79		800	10.13	11.63	15.27	20.03	
	300	15.31	16.48	18.59	21.17		900	10.51	12.72	16.42	20.93	
	400	18.72	19.26	22.07	25.11	1000	11.35	13.46	16.46	23.89		
	500	21.20	24.34	26.55	29.46	60% (v/v) DHP	0	1.23	1.23	1.30	1.40	
	600	23.77	26.18	29.12	32.27		100	2.35	2.56	2.78	2.80	
	700	25.21	29.59	32.00	36.91		200	3.45	3.65	3.72	3.83	
	800	27.38	30.53	34.27	40.39		300	4.23	4.35	5.53	5.77	
	900	28.45	33.07	37.58	47.38		400	5.27	5.43	6.24	6.86	
1000	30.33	34.54	39.49	47.71	500		5.97	6.17	6.93	8.67		
30% (v/v) DHP	0	3.76	3.89	4.10	4.49		600	6.21	6.62	8.15	11.19	
	100	6.13	6.27	6.48	8.17		700	6.21	8.39	10.17	11.77	
	200	8.85	9.85	12.26	13.63		800	7.11	8.53	10.54	12.35	
	300	10.44	13.64	13.85	16.61		900	7.18	9.55	12.62	14.13	
	400	12.68	16.40	17.05	19.38	1000	7.76	11.40	13.44	14.84		
	500	14.40	17.33	19.57	22.78							

**Table S3.** Values of the percentage of inhibition (P) for all solutions at different temperatures and different speeds of rotation

	rpm	298 K	303 K	308 K	313 K		rpm	298 K	303 K	308 K	313 K					
10% (v/v) DHP	0	34.82	35.89	38.20	38.18	40% (v/v) DHP	0	73.62	75.99	76.16	75.87					
	100	46.34	54.04	57.31	54.11		100	78.98	77.90	79.88	80.08					
	200	38.29	49.29	47.70	58.73		200	72.00	78.62	75.19	80.53					
	300	47.91	51.72	55.04	58.11		300	75.98	79.37	80.52	81.10					
	400	46.12	49.59	52.09	53.71		400	73.90	77.08	79.01	80.43					
	500	47.75	49.14	46.62	53.75		500	75.80	78.99	77.67	79.71					
	600	47.24	53.16	53.25	56.51		600	77.34	80.07	80.09	81.18					
	700	47.36	50.00	56.80	57.78		700	76.27	78.58	81.93	81.10					
	800	50.59	51.09	53.94	56.67		800	77.83	79.51	79.09	79.86					
	900	49.80	50.88	56.29	56.16		900	77.37	79.22	79.60	79.61					
20% (v/v) DHP	1000	48.81	52.20	54.48	55.99	1000	77.87	80.50	79.02	79.61	50% (v/v) DHP	0	83.01	84.10	84.35	83.53
	0	50.34	52.94	51.10	52.93	100	80.11	83.97	84.08	83.01						
	100	56.10	65.80	67.13	67.34	200	78.48	84.60	79.72	84.56						
	200	45.13	59.58	57.72	68.92	300	81.25	83.14	82.67	84.59						
	300	57.32	63.79	66.44	68.30	400	82.52	84.94	82.96	84.45						
	400	55.30	64.01	64.18	66.29	500	83.09	85.61	83.70	85.94						
	500	56.30	60.02	58.95	65.12	600	84.13	86.36	84.78	85.01						
	600	56.07	63.60	63.87	67.54	700	84.82	85.42	85.87	84.35						
	700	57.00	59.89	66.86	66.43	800	84.64	85.98	84.43	83.07						
	800	58.46	63.20	65.05	65.86	900	85.21	85.52	85.22	83.34						
30% (v/v) DHP	900	59.96	62.37	66.18	62.29	1000	84.71	86.03	85.40	82.41	60% (v/v) DHP	0	87.34	88.63	88.95	89.18
	1000	59.17	64.15	64.98	64.86	100	87.32	90.16	90.98	91.72						
	0	61.27	63.96	65.14	65.30	200	86.44	89.78	89.95	92.91						
	100	66.87	75.89	78.99	75.83	300	88.21	90.44	90.02	91.36						
	200	65.16	72.43	66.87	74.76	400	87.42	89.86	89.87	90.79						
	300	70.91	70.03	75.00	75.12	500	87.69	89.86	89.29	89.74						
	400	69.74	69.36	72.33	73.98	600	88.53	90.80	89.88	88.74						
	500	70.32	71.54	69.74	73.03	700	89.41	88.62	89.47	89.30						
	600	69.51	73.42	72.52	73.35	800	89.21	89.72	89.25	89.56						
	700	68.74	71.47	75.21	74.92	900	89.89	89.13	88.64	88.76						
800	70.63	71.81	73.20	74.08	1000	89.55	88.17	88.08	89.07							
900	70.77	72.44	75.11	73.98												
1000	70.27	72.65	73.91	74.53												

**Table S4.** Values of the equilibrium constant of adsorption ( $K_e$ ) of DHP on copper at different temperatures and different speeds of rotation

rpm	298 K	303 K	308 K	313 K
0	0.27	0.29	0.30	0.31
100	0.49	0.73	0.84	0.72
200	0.31	0.54	0.50	0.81
300	0.53	0.61	0.77	0.83
400	0.48	0.57	0.65	0.69
500	0.51	0.52	0.49	0.68
600	0.48	0.63	0.66	0.83
700	0.47	0.56	0.81	0.85
800	0.55	0.60	0.71	0.81
900	0.54	0.60	0.81	0.76
1000	0.52	0.66	0.75	0.80

**Table S5.** Values of free energy of adsorption ( $\Delta G_{ads}$ ) for DHP on copper at different temperatures and different speeds of rotation

Solution	rpm	- $\Delta G_{ads}$ (kJ mol <sup>-1</sup> )				Solution	rpm	- $\Delta G_{ads}$ (kJ mol <sup>-1</sup> )			
		298 K	303 K	308 K	313 K			298 K	303 K	308 K	313 K
Blank, 0 % (v/v) DHP	0	9.20	9.47	9.88	10.04	40 % (v/v) DHP		17.23	17.93	18.23	18.71
10 % (v/v) DHP		12.51	12.98	13.00	13.41	50 % (v/v) DHP		18.88	19.64	19.64	20.00
20 % (v/v) DHP		14.61	15.15	15.53	15.80	60 % (v/v) DHP		20.26	21.22	21.30	21.33
30 % (v/v) DHP		16.73	17.33	17.64	17.89	Blank, 0 % (v/v) DHP	600	10.49	10.94	11.82	12.11
40 % (v/v) DHP		18.67	19.19	19.55	19.71	10 % (v/v) DHP		13.17	13.69	14.69	14.88
50 % (v/v) DHP		19.98	20.62	21.05	21.45	20 % (v/v) DHP		15.43	16.02	16.77	17.00
60 % (v/v) DHP		10.39	11.34	11.87	11.73	30 % (v/v) DHP		17.08	17.70	18.54	18.70
Blank, 0 % (v/v) DHP	100	13.08	14.33	14.72	14.98	40 % (v/v) DHP		19.01	19.44	19.86	19.87
10 % (v/v) DHP		15.22	16.59	17.32	17.13	50 % (v/v) DHP		20.48	20.62	21.18	21.48
20 % (v/v) DHP		17.47	17.60	18.20	18.53	60 % (v/v) DHP		10.81	11.05	11.52	12.00
30 % (v/v) DHP		18.20	19.16	19.50	19.61	Blank, 0 % (v/v) DHP	700	13.32	14.04	14.48	14.81
40 % (v/v) DHP		19.98	21.03	21.62	22.22	10 % (v/v) DHP		15.65	16.06	16.50	16.89
50 % (v/v) DHP		9.57	10.86	10.88	12.22	20 % (v/v) DHP		17.30	17.84	18.07	18.49
60 % (v/v) DHP		11.99	13.66	13.69	15.17	30 % (v/v) DHP		18.97	19.56	19.57	19.62
Blank, 0 % (v/v) DHP	200	15.03	16.14	15.73	16.98	40 % (v/v) DHP		20.43	20.91	21.12	21.55
10 % (v/v) DHP		16.53	17.71	17.51	18.60	50 % (v/v) DHP		10.74	11.02	11.76	11.94
20 % (v/v) DHP		17.95	19.28	18.74	19.91	60 % (v/v) DHP		13.47	13.95	14.61	14.41
30 % (v/v) DHP		19.78	20.92	21.32	22.66	Blank, 0 % (v/v) DHP	800	15.67	16.14	16.76	16.87
40 % (v/v) DHP		10.55	11.11	11.64	12.15	10 % (v/v) DHP		17.24	17.80	18.15	18.45
50 % (v/v) DHP		13.20	14.11	14.64	15.10	20 % (v/v) DHP		19.08	19.47	19.73	19.67
60 % (v/v) DHP		15.69	15.84	16.74	17.03	30 % (v/v) DHP		20.61	20.75	20.97	21.34
Blank, 0 % (v/v) DHP	300	17.04	17.82	18.30	18.70	40 % (v/v) DHP		10.64	11.16	11.58	11.92
10 % (v/v) DHP		18.38	19.01	19.24	19.92	50 % (v/v) DHP		13.39	14.15	14.47	14.70
20 % (v/v) DHP		20.18	21.11	21.34	22.10	60 % (v/v) DHP		15.61	16.16	16.60	16.95
30 % (v/v) DHP		10.37	10.90	11.33	11.68	Blank, 0 % (v/v) DHP	900	17.31	18.00	18.06	18.45
40 % (v/v) DHP		13.00	14.13	14.39	14.86	10 % (v/v) DHP		18.99	19.57	19.76	19.50
50 % (v/v) DHP		15.55	15.76	16.39	16.88	20 % (v/v) DHP		20.52	20.51	20.83	21.42
60 % (v/v) DHP		16.77	17.48	18.06	18.58	30 % (v/v) DHP		9.20	9.47	9.88	10.04
Blank, 0 % (v/v) DHP	400	18.59	19.35	19.29	19.89	40 % (v/v) DHP		12.51	12.98	13.00	13.41
10 % (v/v) DHP		20.00	20.95	21.29	21.92	50 % (v/v) DHP		14.61	15.15	15.53	15.80
20 % (v/v) DHP		10.53	10.85	10.77	11.69	60 % (v/v) DHP		16.73	17.33	17.64	17.89
30 % (v/v) DHP		13.10	13.71	13.82	14.73	Blank, 0 % (v/v) DHP	1000	18.67	19.19	19.55	19.71
40 % (v/v) DHP		15.61	16.03	16.07	16.75	10 % (v/v) DHP		19.98	20.62	21.05	21.45
50 % (v/v) DHP		17.02	17.76	17.86	18.47	20 % (v/v) DHP		10.39	11.34	11.87	11.73
60 % (v/v) DHP		18.69	19.48	19.43	20.20	30 % (v/v) DHP		13.08	14.33	14.72	14.98
Blank, 0 % (v/v) DHP	500	20.06	20.95	21.14	21.60	40 % (v/v) DHP		15.22	16.59	17.32	17.13
10 % (v/v) DHP		10.48	11.26	11.45	11.98	50 % (v/v) DHP		17.47	17.60	18.20	18.53
20 % (v/v) DHP		13.08	14.09	14.35	15.01	60 % (v/v) DHP		18.20	19.16	19.50	19.61
30 % (v/v) DHP		15.52	16.26	16.42	16.79						

**Table S6.** Electrodeposition average thermodynamic parameters within the temperature range 298 – 313 K for DHP solutions at different speeds of rotation

	rpm	$E_a$ (kJ mol <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Blank, 0% (v/v) DHP	0	14.7	12.2	-185.1	68.7
10% (v/v) DHP		11.7	9.0	-198.9	69.9
20% (v/v) DHP		12.8	8.9	-197.5	70.6
30% (v/v) DHP		9.1	7.3	-212.2	71.3
40% (v/v) DHP		10.4	8.6	-211.0	72.3
50% (v/v) DHP		13.0	8.6	-206.0	73.4
60% (v/v) DHP		6.9	6.9	-228.6	74.2
Blank, 0% (v/v) DHP	100	27.9	25.4	-134.7	66.5
10% (v/v) DHP		22.2	18.5	-159.7	68.5
20% (v/v) DHP		16.3	25.4	-181.5	69.2
30% (v/v) DHP		13.7	13.3	-192.6	70.0
40% (v/v) DHP		26.8	14.8	-151.4	70.5
50% (v/v) DHP		23.2	12.6	-164.9	71.0
60% (v/v) DHP		9.5	2.8	-214.3	72.4
Blank, 0% (v/v) DHP	200	31.8	29.3	-119.1	65.7
10% (v/v) DHP		17.4	16.5	-172.2	67.4
20% (v/v) DHP		9.9	19.6	-198.6	68.0
30% (v/v) DHP		23.5	17.6	-156.6	68.8
40% (v/v) DHP		21.0	14.3	-166.9	69.4
50% (v/v) DHP		24.4	20.0	-157.9	70.1
60% (v/v) DHP		5.2	14.9	-225.7	71.6
Blank, 0% (v/v) DHP	300	32.0	29.4	-116.3	65.0
10% (v/v) DHP		20.7	16.1	-159.5	66.9
20% (v/v) DHP		16.9	20.0	-174.2	67.6
30% (v/v) DHP		21.9	18.1	-160.1	68.3
40% (v/v) DHP		19.8	15.5	-169.1	69.0
50% (v/v) DHP		23.3	15.6	-159.5	69.5
60% (v/v) DHP		18.1	12.6	-180.9	70.8
Blank, 0% (v/v) DHP	400	29.0	26.5	-124.9	64.6
10% (v/v) DHP		21.1	15.9	-156.5	66.4
20% (v/v) DHP		15.7	22.3	-176.6	67.1
30% (v/v) DHP		20.4	18.3	-163.4	67.8
40% (v/v) DHP		14.2	14.5	-185.8	68.4
50% (v/v) DHP		25.4	14.6	-151.7	69.2
60% (v/v) DHP		14.4	19.3	-191.5	70.4
Blank, 0% (v/v) DHP	500	26.7	24.2	-131.5	64.3
10% (v/v) DHP		21.8	16.4	-153.1	66.1
20% (v/v) DHP		16.7	21.9	-172.0	66.7
30% (v/v) DHP		23.2	17.8	-153.2	67.5
40% (v/v) DHP		19.4	18.6	-167.9	68.2
50% (v/v) DHP		20.1	23.2	-168.8	69.1
60% (v/v) DHP		19.0	18.4	-175.1	70.0
Blank, 0% (v/v) DHP	600	30.1	27.6	-119.0	63.9
10% (v/v) DHP		21.0	16.1	-154.9	65.8
20% (v/v) DHP		15.9	19.1	-173.9	66.4
30% (v/v) DHP		24.3	18.6	-148.7	67.2
40% (v/v) DHP		21.4	18.4	-160.7	68.0
50% (v/v) DHP		29.1	27.2	-138.1	68.7
60% (v/v) DHP		30.5	21.6	-136.4	69.6
Blank, 0% (v/v) DHP	700	33.5	30.9	-107.1	63.7
10% (v/v) DHP		20.9	16.9	-154.5	65.6
20% (v/v) DHP		19.0	24.9	-162.9	66.2
30% (v/v) DHP		21.0	17.6	-158.7	67.0
40% (v/v) DHP		20.2	16.2	-163.9	67.7
50% (v/v) DHP		34.3	25.0	-120.1	68.5
60% (v/v) DHP		32.8	26.7	-127.8	69.3
Blank, 0% (v/v) DHP	800	29.8	27.3	-118.4	63.5
10% (v/v) DHP		22.8	19.4	-147.7	65.4
20% (v/v) DHP		19.8	22.4	-159.4	66.0
30% (v/v) DHP		23.2	17.0	-150.8	66.7
40% (v/v) DHP		25.7	17.9	-145.1	67.4
50% (v/v) DHP		35.9	24.9	-114.2	68.2
60% (v/v) DHP		29.0	24.2	-139.9	69.2

Table S6. cont.

	rpm	$E_a$ (kJ mol <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Blank, 0% (v/v) DHP	900	30.2	27.7	-116.6	63.3
10% (v/v) DHP		22.1	21.2	-149.5	65.2
20% (v/v) DHP		25.7	28.7	-139.6	65.8
30% (v/v) DHP		23.2	19.5	-150.5	66.6
40% (v/v) DHP		25.0	21.5	-146.5	67.2
50% (v/v) DHP		36.0	24.9	-113.3	68.1
60% (v/v) DHP		35.9	25.4	-116.4	68.9
Blank, 0% (v/v) DHP	1000	30.5	28.0	-114.9	63.1
10% (v/v) DHP		22.7	17.6	-146.7	65.0
20% (v/v) DHP		23.1	29.2	-147.6	65.7
30% (v/v) DHP		22.6	17.6	-151.8	66.4
40% (v/v) DHP		27.8	20.6	-136.9	67.1
50% (v/v) DHP		37.6	22.2	-107.3	67.9
60% (v/v) DHP		32.9	24.0	-125.5	68.7

Table S7. Values of diffusion coefficient (D) for all mixtures at different temperatures

	rpm	298 K D/(cm <sup>2</sup> s <sup>-1</sup> x10 <sup>-5</sup> )	303 K D/(cm <sup>2</sup> s <sup>-1</sup> x10 <sup>-5</sup> )	308 K D/(cm <sup>2</sup> s <sup>-1</sup> x10 <sup>-5</sup> )	313 K D/(cm <sup>2</sup> s <sup>-1</sup> x10 <sup>-5</sup> )
Blank, 0% (v/v) DHP	100	1.280	1.866	2.305	2.530
	200	1.016	1.439	1.441	2.468
	300	0.987	1.348	1.735	2.208
	400	0.918	1.268	1.497	1.914
	500	0.904	1.216	1.266	1.825
	600	0.879	1.291	1.463	1.928
	700	0.842	1.136	1.637	1.908
	800	0.873	1.179	1.450	1.848
	900	0.864	1.134	1.550	1.785
	1000	0.825	1.167	1.413	1.796
10% (v/v) DHP	100	0.451	0.568	0.626	0.769
	200	0.432	0.510	0.537	0.636
	300	0.365	0.443	0.511	0.582
	400	0.358	0.446	0.486	0.590
	500	0.336	0.433	0.487	0.561
	600	0.332	0.405	0.457	0.539
	700	0.317	0.395	0.453	0.509
	800	0.298	0.396	0.443	0.514
	900	0.302	0.383	0.437	0.505
	1000	0.297	0.378	0.424	0.512
20% (v/v) DHP	100	0.355	0.386	0.449	0.488
	200	0.387	0.386	0.415	0.440
	300	0.288	0.305	0.349	0.406
	400	0.288	0.284	0.333	0.387
	500	0.274	0.321	0.348	0.390
	600	0.268	0.295	0.330	0.368
	700	0.249	0.301	0.323	0.384
	800	0.245	0.273	0.310	0.382
	900	0.228	0.272	0.315	0.430
	1000	0.225	0.260	0.304	0.388
30% (v/v) DHP	100	0.249	0.244	0.243	0.332
	200	0.208	0.232	0.309	0.347
	300	0.173	0.247	0.240	0.303
	400	0.171	0.241	0.243	0.282
	500	0.163	0.206	0.236	0.284
	600	0.166	0.197	0.234	0.295
	700	0.165	0.193	0.224	0.265
	800	0.155	0.197	0.224	0.270
	900	0.152	0.183	0.213	0.263
	1000	0.149	0.186	0.209	0.256

**Table S7.** cont.

	rpm	298 K D/(cm <sup>2</sup> s <sup>-1</sup> x10 <sup>-5</sup> )	303 K D/(cm <sup>2</sup> s <sup>-1</sup> x10 <sup>-5</sup> )	308 K D/(cm <sup>2</sup> s <sup>-1</sup> x10 <sup>-5</sup> )	313 K D/(cm <sup>2</sup> s <sup>-1</sup> x10 <sup>-5</sup> )
40% (v/v) DHP	100	0.136	0.236	0.252	0.272
	200	0.164	0.173	0.218	0.256
	300	0.142	0.153	0.180	0.219
	400	0.150	0.170	0.175	0.200
	500	0.132	0.142	0.163	0.202
	600	0.116	0.139	0.157	0.190
	700	0.119	0.137	0.151	0.189
	800	0.111	0.133	0.168	0.202
	900	0.113	0.130	0.173	0.199
	1000	0.104	0.121	0.165	0.200
50% (v/v) DHP	100	0.140	0.160	0.196	0.237
	200	0.121	0.116	0.178	0.200
	300	0.108	0.125	0.168	0.178
	400	0.090	0.099	0.141	0.157
	500	0.084	0.088	0.111	0.128
	600	0.074	0.086	0.116	0.149
	700	0.066	0.084	0.115	0.158
	800	0.070	0.082	0.119	0.172
	900	0.065	0.083	0.117	0.163
	1000	0.066	0.081	0.105	0.178
60% (v/v) DHP	100	0.158	0.085	0.091	0.088
	200	0.137	0.069	0.068	0.067
	300	0.122	0.059	0.081	0.082
	400	0.102	0.060	0.071	0.078
	500	0.095	0.058	0.066	0.089
	600	0.084	0.053	0.069	0.108
	700	0.075	0.065	0.083	0.099
	800	0.079	0.057	0.076	0.092
	900	0.074	0.060	0.088	0.100
	1000	0.074	0.071	0.087	0.096

**Table S8a.** Dimensionless groups used in dimensional analysis for all solutions at 298 and 303 K

	rpm	298 K			303 K		
		Sh=kl/D	Sc=v/D	Re=IU/v	Sh=kl/D	Sc=v/D	Re=IU/v
Blank, 0% (v/v) DHP	100	92	771	705	83	475	784
	200	162	971	1409	148	616	1568
	300	217	1000	2114	202	658	2351
	400	272	1075	2818	252	699	3135
	500	320	1091	3523	299	729	3919
	600	368	1122	4228	332	687	4703
	700	416	1172	4932	388	780	5486
	800	451	1129	5637	420	752	6270
	900	491	1142	6342	462	782	7054
	1000	538	1196	7046	493	760	7838
10% (v/v) DHP	100	131	2262	681	126	1614	757
	200	217	2364	1362	212	1798	1514
	300	306	2797	2042	296	2070	2272
	400	377	2853	2723	361	2059	3029
	500	450	3037	3404	426	2117	3786
	600	514	3077	4085	496	2265	4543
	700	582	3225	4765	558	2326	5301
	800	653	3429	5446	612	2320	6058
	900	706	3383	6127	672	2395	6815
	1000	764	3437	6808	728	2429	7572

Table S8a. cont.

	rpm	298 K $Sh=kl/D$	$Sc=v/D$	$Re=IU/\nu$	303 K $Sh=kl/D$	$Sc=v/D$	$Re=IU/\nu$
20% (v/v) DHP	100	137	3291	594	137	2722	661
	200	215	3023	1189	223	2723	1322
	300	317	4060	1783	323	3446	1983
	400	388	4062	2377	405	3700	2644
	500	462	4270	2971	453	3278	3305
	600	529	4357	3566	531	3569	3966
	700	605	4703	4160	586	3490	4627
	800	668	4782	4754	666	3844	5288
	900	744	5121	5348	725	3859	5949
	1000	805	5202	5943	793	4045	6610
30% (v/v) DHP	100	147	5483	508	153	5040	565
	200	254	6583	1016	254	5306	1130
	300	361	7922	1524	329	4974	1695
	400	443	8009	2032	407	5111	2260
	500	526	8375	2540	503	5979	2825
	600	595	8264	3048	581	6256	3391
	700	664	8302	3556	651	6372	3956
	800	745	8815	4064	710	6254	4521
	900	814	8981	4572	792	6735	5086
	1000	883	9159	5080	847	6623	5651
40% (v/v) DHP	100	170	12139	420	145	6302	467
	200	259	10099	840	264	8605	935
	300	362	11645	1261	366	9701	1402
	400	434	11008	1681	432	8763	1870
	500	532	12563	2101	537	10463	2337
	600	633	14308	2521	615	10690	2804
	700	699	13912	2941	689	10861	3272
	800	786	14903	3362	765	11217	3739
	900	847	14593	3782	836	11407	4207
	1000	939	15826	4202	923	12240	4674
50% (v/v) DHP	100	157	14565	342	156	11415	380
	200	269	16733	684	283	15767	761
	300	372	18837	1026	366	14614	1141
	400	486	22573	1368	488	18513	1521
	500	581	24140	1710	593	20729	1902
	600	691	27402	2052	679	21195	2282
	700	801	30637	2394	764	21723	2662
	800	862	28991	2736	845	22242	3043
	900	960	31091	3078	915	22006	3423
	1000	1032	30937	3419	994	22612	3804
60% (v/v) DHP	100	139	16218	271	180	27130	302
	200	238	18633	543	314	33190	604
	300	329	20976	814	443	39275	906
	400	429	25135	1086	536	38119	1208
	500	514	26880	1357	637	39764	1510
	600	611	30512	1629	747	43491	1812
	700	708	34115	1900	774	35566	2114
	800	762	32281	2172	887	40101	2416
	900	849	34620	2443	947	38227	2718
	1000	912	34448	2715	964	32599	3020

**Table S8b.** Dimensionless groups used in dimensional analysis for all solutions at 308 and 313 K

% (v/v) DHP	rpm	308 K			313 K		
		$Sh=kl/D$	$Sc=v/D$	$Re=IU/\nu$	$Sh=kl/D$	$Sc=v/D$	$Re=IU/\nu$
Blank, 0% (v/v) DHP	100	80	349	865	80	290	948
	200	153	557	1730	131	297	1896
	300	191	463	2595	180	332	2844
	400	246	536	3460	232	383	3792
	500	305	634	4325	276	402	4740
	600	329	549	5190	308	380	5688
	700	352	491	6055	344	384	6636
	800	404	554	6920	382	397	7584
	900	428	518	7785	420	411	8533
	1000	476	568	8650	451	408	9481
10% (v/v) DHP	100	125	1328	836	120	987	916
	200	215	1549	1671	209	1193	1832
	300	291	1628	2507	287	1303	2748
	400	362	1709	3343	349	1287	3664
	500	423	1709	4179	415	1351	4580
	600	492	1818	5014	479	1407	5496
	700	550	1836	5850	544	1489	6412
	800	608	1876	6686	596	1477	7328
	900	664	1905	7522	651	1501	8244
	1000	722	1960	8357	697	1483	9160
20% (v/v) DHP	100	135	2124	730	135	1782	800
	200	225	2297	1459	228	1974	1599
	300	318	2731	2189	311	2139	2399
	400	396	2861	2918	387	2243	3198
	500	455	2736	3648	451	2231	3998
	600	527	2889	4377	523	2361	4798
	700	592	2952	5107	574	2266	5597
	800	659	3068	5836	632	2278	6397
	900	712	3022	6566	658	2021	7196
	1000	776	3138	7296	734	2241	7996
30% (v/v) DHP	100	159	4577	624	147	3060	684
	200	237	3607	1247	235	2933	1367
	300	344	4642	1871	327	3353	2051
	400	420	4593	2495	411	3608	2734
	500	496	4728	3118	479	3578	3418
	600	564	4755	3742	537	3450	4101
	700	639	4983	4366	621	3832	4785
	800	702	4984	4989	677	3759	5468
	900	775	5232	5613	742	3867	6152
	1000	840	5332	6237	807	3973	6836
40% (v/v) DHP	100	147	5346	516	148	4515	565
	200	251	6177	1032	245	4796	1131
	300	357	7466	1548	344	5615	1696
	400	442	7710	2063	434	6133	2262
	500	530	8280	2579	506	6081	2827
	600	609	8565	3095	588	6466	3392
	700	688	8892	3611	656	6497	3958
	800	727	8007	4127	703	6074	4523
	900	782	7783	4643	768	6170	5088
	1000	857	8172	5159	825	6133	5654
50% (v/v) DHP	100	150	8465	420	144	6364	460
	200	252	9295	840	249	7568	920
	300	341	9858	1259	345	8486	1380
	400	444	11723	1679	442	9645	1840
	500	565	14860	2099	555	11831	2300
	600	633	14304	2519	597	10133	2761
	700	706	14348	2939	652	9580	3221
	800	767	13931	3358	693	8756	3681
	900	837	14139	3778	769	9293	4141
	1000	938	15800	4198	801	8486	4601
800	832	27562	2666	800	20655	2922	
900	856	23683	2999	845	19060	3287	
1000	927	24087	3333	922	19793	3653	

**Table S8b.** Dimensionless groups used in dimensional analysis for all solutions at 308 and 313 K

% (v/v) DHP	rpm	308 K			313 K		
		$Sh=kl/D$	$Sc=v/D$	$Re=IU/v$	$Sh=kl/D$	$Sc=v/D$	$Re=IU/v$
100	181	22797	333	190	21614	365	
	200	328	30803	667	339	28244	731
	300	409	25872	1000	420	23213	1096
	400	523	29266	1333	522	24242	1461
	500	630	31754	1666	584	21484	1826
	600	701	30046	2000	618	17609	2192
	700	734	25221	2333	711	19250	2557

**Table S9.** Dimensionless correlation constants a and b under all studies conditions

	298 K	303 K	308 K	313 K
Constant <i>a</i>				
Blank, 0% (v/v) DHP	0.1010	0.0993	0.0996	0.0982
10% (v/v) DHP	0.1031	0.1026	0.1025	0.1014
20% (v/v) DHP	0.1036	0.1042	0.1036	0.1046
30% (v/v) DHP	0.1058	0.1063	0.1065	0.1052
40% (v/v) DHP	0.1084	0.1055	0.1060	0.1060
50% (v/v) DHP	0.1058	0.1064	0.1055	0.1074
60% (v/v) DHP	0.1063	0.1124	0.1138	0.1157
Constant <i>b</i>				
Blank, 0% (v/v) DHP	0.7044	0.7051	0.7038	0.7044
10% (v/v) DHP	0.7052	0.7046	0.7041	0.7046
20% (v/v) DHP	0.7059	0.7044	0.7044	0.7023
30% (v/v) DHP	0.7054	0.7037	0.7027	0.7033
40% (v/v) DHP	0.7040	0.7066	0.7049	0.7040
50% (v/v) DHP	0.7096	0.7078	0.7074	0.7039
60% (v/v) DHP	0.7096	0.7029	0.7000	0.6970

**Table S10.** Values of the limiting current density ( $I_l$ ), angular velocity ( $\omega$ ), kinematic viscosity ( $\nu$ ), diffusion coefficient ( $D$ ), and dimensionless groups used in dimensional analysis for blank and 20% (v/v) DHP at high speeds of rotation and 298K

	$I_l$ (mA cm <sup>-2</sup> )	rpm	$\omega$	$\nu$ (stoke)	$D$ (cm <sup>2</sup> s <sup>-1</sup> x 10 <sup>5</sup> )	$Sh=kl/D$	$Sc=v/D$	$Re=IU/v$		
Blank, 0% (v/v) DHP	67.57	1500	157.1	0.0098616	0.458	912	2086	11294		
	83.32	2000	209.4		0.464	1110	2060	15059		
	96.50	2500	261.8		0.457	1305	2090	18823		
	103.55	3000	314.2		0.419	1530	2284	22588		
	118.50	3500	366.5		0.436	1679	2191	26352		
	125.85	4000	418.9		0.415	1877	2307	30117		
	129.87	4500	471.2		0.383	2097	2497	33882		
	147.25	5000	523.6		0.415	2194	2304	37646		
	148.46	5500	576.0		0.379	2422	2523	41411		
	151.03	6000	628.3		0.354	2638	2700	45176		
	20% (v/v) DHP	38.62	1500		157.1	0.012545	0.186	1242	4973	11294
		46.51	2000		209.4		0.181	1532	5094	15059
		54.30	2500		261.8		0.181	1793	5105	18823
		62.02	3000		314.2		0.182	2031	5062	22588
69.81		3500	366.5	0.185	2249		4981	26352		
76.33		4000	418.9	0.184	2475		5014	30117		
78.91		4500	471.2	0.171	2762		5412	33882		
87.20		5000	523.6	0.178	2931		5197	37646		
102.85		5500	576.0	0.207	2967		4461	41411		
100.31		6000	628.3	0.181	3307		5098	45176		
104.62		6500	680.7	0.177	3525		5209	48940		
97.60		7000	733.0	0.147	3970		6289	52705		