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Diffusion Coefficient of Cupric Ion in a Copper Electrorefining Electrolyte Containing Nickel and Arsenic

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Abstract

Diffusion and convection are the main modes of mass transport that occur during copper electrorefining. Diffusion determines the rate of copper transfer across the diffusion layer, which in turn, affects the dissolution of the anode and deposition on the cathode. The diffusion coefficient of cupric ion ($D_{Cu(II)}$) is a typical property that can be defined from the limiting current density (j_{lim}) values. In this work, the limiting current densities were measured for 24 different synthetic copper electrolytes over a temperature range of 50–70 °C using a rotating disc electrode (RDE). From this data, a model for j_{lim} and the corresponding models for $D_{Cu(II)}$ were constructed using Levich (Model L), Koutecký-Levich (Model K) and mixed-control Newman equations (Model M). The models for j_{lim} and $D_{Cu(II)}$ were designed, refined and analyzed using the modeling and design tool MODDE, with the temperature, copper, nickel, arsenic and sulfuric acid concentrations as variables. Results from this research show for the first time that an increase in arsenic concentration has a reciprocal effect on the $D_{Cu(II)}$ under copper electrorefining conditions. Furthermore, the models were validated with 11 industrial electrorefining electrolytes with known compositions. Model L ($D_{Cu(II)}$ based on Levich equation) was shown to provide the highest correlation with the industrial solutions when compared to the other models (Model K and M) considered and previously published diffusion coefficient models. Overall, this work provides an explanation for the previously observed data variances in the literature, investigates for the first time the combined effect of parameters on $D_{Cu(II)}$ value in industrial copper electrolysis and clarifies the effect of arsenic on the $D_{Cu(II)}$ of copper electrorefining electrolytes.

Keywords: copper electrorefining electrolyte; diffusion coefficient; cupric ion; arsenic impurities

Nomenclature

A	area of the working electrode disc
c_0	bulk concentration
D	diffusion coefficient
F	Faraday's constant
I_K	activation-limited current
I_L	diffusion-limited current
I_{lim}	limiting current
j_K	activation-limited current density

j_L	diffusion-limited current density
j_{lim}	limiting current density
j_0	exchange current density
rpm	revolutions per minute
δ_H	hydrodynamic boundary layer
δ_N	diffusion boundary layer
v	kinematic viscosity
ω	angular velocity

1. Introduction

The effects of the impurities on industrial copper electrorefining electrolytes have become increasingly important due to the use of increasingly impure ores (Forsén et al., 2017; Jafari et al., 2017; Kalliomäki et al., 2017). In particular, the level of arsenic within such processes has grown leading to higher levels of As incorporation in copper anodes (Moats et al., 2016). The composition of such anodes has a significant impact on the amount of impurities within the electrolytes (Moats et al., 2007, 2016; Schlesinger et al., 2011), which in turn affects the physicochemical properties and overall energy efficiency of the process. For example, the amount of arsenic in 2003 was 790 ppm per anode and 5.5 g/dm^3 in electrolyte on average; in 2010 these values had increased to 1010 ppm and 6.9 g/dm^3, whereas by 2016 As content had further increased to 1480 ppm and 8.9 g/dm^3, respectively (Moats et al., 2016). At the same time, annual copper production has also grown steadily (ICSG World Copper Factbook, 2017), as production levels of refined copper have risen from 10.69 Mt (1991), to 22.87 Mt (2015). Based on 2016 values, approximately 64% of copper is produced from primary ores by fire-refining and electrorefining, and approximately 18% by leaching, solid extraction and electrowinning (Brininstool, 2017; Forsén et al., 2017). The rest of the copper is produced from secondary copper ores, and processed by directly melting or by electrorefining (Brininstool, 2017; Forsén et al., 2017).

In industrial copper electrorefining, the mass transport of copper ions is the limiting factor of the process (Jarjoura et al., 2003) with the primary types of mass transfer present in the electrorefining process being diffusion and convection - migration has only a minor effect on the process (Schab and Hein, 1992). Of these, diffusion has been determined to have the most dominant effect on the mass transport that occurs at the electrode surfaces (Schab and Hein, 1992).

The diffusion coefficient of cupric ion ($D_{\mathrm{Cu(II)}}$) is a typical physico-chemical property of copper electrolyte (Subbaiah and Das, 1989) which, with other physico-chemical properties like conductivity, density and viscosity (Price and Davenport, 1980, 1981), can significantly affect the energy consumption as well as dissolution and deposition of copper in the electrorefining process (Moats et al., 2000). Diffusion determines the rate at which copper transfers across the Nernst boundary layer (diffusion layer) and therefore affects the dissolution of the copper anode and deposition of copper on the cathode (Aromaa, 2007; Moats et al., 2000). Lowest energy consumption can be obtained when both the diffusion coefficient (Moats et al., 2000) and electrical conductivity are high (Price and Davenport, 1980), whilst viscosity is low (Moats et al., 2000). In practice, these properties can be strongly influenced through adjustment of the composition and temperature of the copper electrolyte.

Under electrorefining conditions an increase in temperature results in a parallel increase in $D_{Cu(II)}$ (Jarjoura et al., 2003; Moats et al., 2000; Subbaiah and Das,1989), whereas conversely, an increase in Cu, H_2SO_4 (Moats et al., 2000; Subbaiah and Das, 1989) or Ni (Jarjoura et al., 2003) concentration has been reported to lead to a decrease in the diffusion coefficient value. Until now, the effect of arsenic on the diffusion coefficient in copper electrorefining electrolyte has not been determined, although previous research has shown that increase in arsenic, nickel and copper concentrations increase viscosity (Price and Davenport, 1981).

Various methods can be used in order to define $D_{Cu(II)}$, including chronoamperometry, polarography, and diaphragm cell (Quickenden and Jiang, 1984; Quickenden and Xu, 1996), in this work however, the focus has been on using the rotating disc electrode (RDE) technique. The RDE technique is a hydrodynamic method, in which convection is generated via electrode rotation and by using this technique, a limiting current density can be attained through cathodic polarization of the rotating working electrode (Bard and Faulkner, 2001). The limiting current density relates to the highest rate of reaction possible in a mass-transfer controlled system, while it is still exclusively under mass transfer control and from this value the diffusion coefficient can be determined (Aromaa, 2007). In previous studies (Jarjoura et al., 2003; Moats et al., 2000; Subbaiah and Das, 1989) the $D_{Cu(II)}$ has been defined using the Levich equation (Jarjoura et al., 2003) which does not take into account activation polarization, in contrast to the Koutecký-Levich (2) and mixed-control Newman (3) equations (Quickenden and Xu, 1996). In general, the use of the Levich equation for the determination of the $D_{Cu(II)}$ as well as the measurement accuracy has been criticized as it neglects the effects of activation polarization, which can cause inaccuracy in the results. This was highlighted in the work by Quickenden and Xu who recommend use of the mixed-control Eq. (3), for the most precise determination of $D_{Cu(II)}$ (Quickenden and Xu, 1996).

$$I_L = 0.62 \cdot \mathrm{n}\mathrm{F}A \cdot \mathrm{D}^{2/3} \cdot \omega^{1/2} \cdot v^{-1/6} \cdot c_0 \tag{1}$$

$$1/I_{\mathrm{lim}} = 1/I_K + 1/I_L = 1/I_K + 1 / (0.62 \cdot n\mathrm{F}A \cdot \mathrm{D}^{2/3} \cdot \omega^{1/2} \cdot \mathrm{v}^{-1/6} \cdot c_0) \tag{2}$$

$$1/I_{\mathrm{lim}} = 1/I_K + (1 + 0.298\,(\mathrm{D}/v)^{1/3} + 0.14514\,(\mathrm{D}/v)^{2/3}) / (0.62 \cdot n\mathrm{F}A \cdot \mathrm{D}^{2/3} \cdot \omega^{1/2} \cdot v^{-1/6} \cdot c_0) \tag{3}$$

where I_{lim} is the limiting current, I_L the diffusion-limited and I_K the activation-limited cathodic current (in amps), n is the number of transferred electrons in the reaction, F is Faraday's constant, A is the area of the working electrode disc (cm^2), D is the diffusion coefficient (cm^2/s), ω is angular velocity (1/s), v is kinematic viscosity (cm^2/s) and c_0 is the concentration of metal (Cu(II)) ions (mol/cm^3) (Moats et al., 2000).

In this work, the main diffusible ion in the test electrolytes is Cu(II) based on the standard electrode potentials and potential ranges used in the analysis. Since the standard reduction potential of Ni(II) is 587 mV lower than that of Cu(II), Ni is not reduced and thus does not diffuse to the surface under the investigated conditions (Aromaa, 2007). The standard reduction potentials of Bi(III), As(III/V) and Sb(III/V) ions or their oxides - as well as Cu(I) ions - are closer to the Cu(II) reduction potential (Aromaa, 2007; Schlesinger et al., 2011). Nevertheless, the concentrations of Bi and Sb ions present in the electrolyte solutions are too low to affect the results and Cu(I) concentration is also minimal as the reduction reaction of Cu(II) to Cu(I) is slow, whereas that of Cu(I) to Cu relatively rapid in contrast. The concentrations of these elements in the electrolytes are presented closer in experimental section. In addition, although As may potentially deposit on the RDE based on the related standard electrode potentials (Aromaa, 2007; Schlesinger et al., 2011; Dewalens, 1975), the potential range, at 50 °C 0.200 ± 0.010V (NHE), where As(III) may co-deposit with Cu on the electrode (Dewalens, 1975), is distinguishable from the potential range where the limiting current density (j_{lim}) is determined.

The diffusion coefficient of cupric ion ($D_{\mathrm{Cu(II)}}$) has not been extensively researched under copper electrorefining conditions and there are only a few literature studies, the results of which vary significantly (Jarjoura et al., 2003; Moats et al., 2000; Subbaiah and Das,1989). Of these, only the work by Jarjoura et al. (2003) takes into account the presence of nickel ions as a typical impurity, whereas the effect of arsenic, present in the process due to increasingly impure raw materials (Moats et al., 2016), has been generally neglected. Only Hiskey and Maeda (2003) briefly researched the effect of arsenic on $D_{\mathrm{Cu(II)}}$ using cyclic voltammetry but they did not have enough wide-ranging data to allow for a clear determination of its influence. Furthermore, previous studies have not investigated the probable combined effects of the parameters and their impact on the overall physico-chemical properties of the electrorefining process.

The objectives of this work were to define the $D_{\mathrm{Cu(II)}}$ from RDE experiment limiting current densities and to construct mathematical models for j_{lim} and the corresponding $D_{\mathrm{Cu(II)}}$ as a function of temperature, and copper, nickel, arsenic and sulfuric acid concentrations. Additionally, it was investigated whether there were any combined effects, with a particular focus on finding an explanation for the previously observed data variance in the literature (Jarjoura et al., 2003; Moats et al., 2000; Subbaiah and Das, 1989). The j_{lim} and corresponding $D_{\mathrm{Cu(II)}}$ data was analyzed using the modeling and design tool MODDE 8, (MKS Data Analytics Solution) and the resultant models (Models L, K, M) were validated with 11 industrial electrorefining electrolyte samples provided by Boliden Harjavalta. All measurements were performed within the temperature range and using synthetic electrolytes compositions typically employed in copper refineries, although the synthetic electrolytes investigated did not include any deposition controlling additives like glue, thiourea, Avitone A or chloride (Aromaa, 2007; Moats et al., 2007; Moats et al., 2016).

2. Experimental

The synthetic copper electrolytes used in this work contained varying amounts of copper, nickel, arsenic and sulfuric acid (Table 1). The chemicals used were copper sulfate ($CuSO_4 \cdot 5\ H_2O$, min. 98%, VWR Chemicals), nickel sulfate ($NiSO_4 \cdot 6\ H_2O$, min. 98%, VWR Chemicals), sulfuric acid (H_2SO_4, 95–98%, Sigma-Aldrich), and distilled water. For the synthetic electrolytes with arsenic, a combination of arsenic trioxide (As_2O_3 99.5%, Alfa Aesar, Thermo Fisher Scientific GmbH) with

H_2O_2 (30%, for analysis, Merck KGaA) was used to oxidize As(III) to As(V) in order to enhance aqueous dissolution. Additionally, 11 industrial electrolytes with known composition (Table 2) from electrorefining plant at Boliden Harjavalta were investigated in order to validate the models. The industrial electrolytes were filtered before the tests to ensure a homogenous electrolyte composition.

Multivariate data analysis, design of experiments (DOE) and sensitivity analysis of the models were carried out using the modeling and design tool MODDE 8 (MKS Data Analytics Solutions AB). For the data analysis and design of experiments the experimental defining factors, responses and levels of the factors outlined in Table 1, were used. In contrast, for the sensitivity analysis the variables were changed one by one from their mean values, with the percentage change in $D_{Cu(II)}$ determined as a function of the variables.

Table 1
Copper electrorefining electrolyte factors and their levels investigated in the experimental work.

Factor	**Level**	**Unit**
[Cu]	40; 50; 60	g/dm^3
[H_2SO_4]	130; 145; 160; 175; 180; 190; 200; 205; 220	g/dm^3
[Ni]	0; 10; 20	g/dm^3
[As]	0; 15; 30; 45	g/dm^3
T	50; 60; 70	°C

Table 2
Concentrations of the industrial copper electrorefining electrolytes (Sample 1–11) investigated in the experimental work.

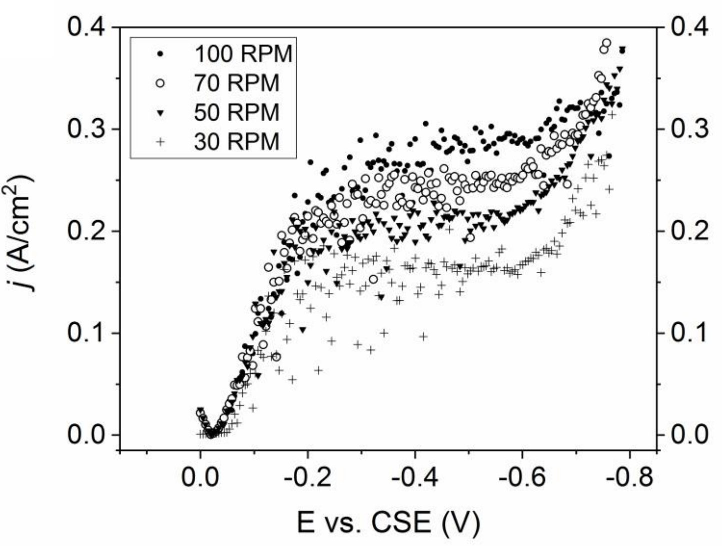
	Concentrations, g/dm^3										
	Sample										
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
[Cu]	62.59	57.07	54.09	42.91	39.66	44.46	45.98	54.36	44.62	46.66	48.93
[H_2SO_4]	153	135	153	175.6	174.8	172.2	162.0	160.1	156.2	162.8	151.9
[Ni]	17.3	15.54	11.07	17.91	16.39	15.95	15.58	15.11	16.32	12.19	18.69
[As]	15.3	15.3	10.7	11.63	11.41	10.65	11.23	12.35	13.34	7.99	15.02
[Sb]	0.323	0.571	0.291	0.031	0.044	0.049	0.054	0.168	0.153	0.240	0.131
[Se]	0.013	<0.004	<0.004	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
[Te]	0.027	<0.004	<0.004	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
[Pb]	0.025	0.044	0.046	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
[Bi]	0.069	<0.004	<0.004	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
[Ag]	0.007	<0.004	<0.004	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
[Ba]	0.011	0.009	0.008	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

The limiting current density was measured using cathodic linear sweep voltammetry with a rotating disc electrode (RDE) apparatus (Model 616, Princeton Applied Research), jacketed three-electrode cell (0.2 dm^3, Metrohm AG), circulating water bath (MGW Lauda MT/M3), Cu/$CuSO_4$ reference electrode (B 521 Ch.:1407, SI Analytics) and a Pt plate counter electrode. The potentiostat used was an Autolab 30 (Ecochemie, Nl) controlled by GPES software. The limiting current densities (j_{lim}, example in Fig. 1) measured were used to build a limiting current density model that decreased the fluctuation in j_{lim} values. Calculated j_{lim} values were then used to determine the $D_{Cu(II)}$ values using the Levich equation (1), Koutecký-Levich equation (2) and mixed-control Newman equation (3). Nonetheless, the original measured j_{lim} values were used for determining the $D_{Cu(II)}$ values of the reproduced runs and the industrial samples. The viscosity values used in the equations were calculated with a model previously published by Kalliomäki et al. (2017) (Eq. 4) and Model L_{PD} used the viscosities outlined by Price and Davenport (1981).

$$\log_{10}(v) = 0.09059 + 0.002594\,[Cu] + 0.0005569\,[H_2SO_4] + 0.001967\,[Ni] + 0.0007715\,[As] - 0.007057\,T + 2.741\cdot10^{-5}\,[Cu]\cdot[Ni] \quad (4)$$

where v = kinematic viscosity (mm^2/s), and the concentrations are in g/dm^3 and T in °C.

a



b

c

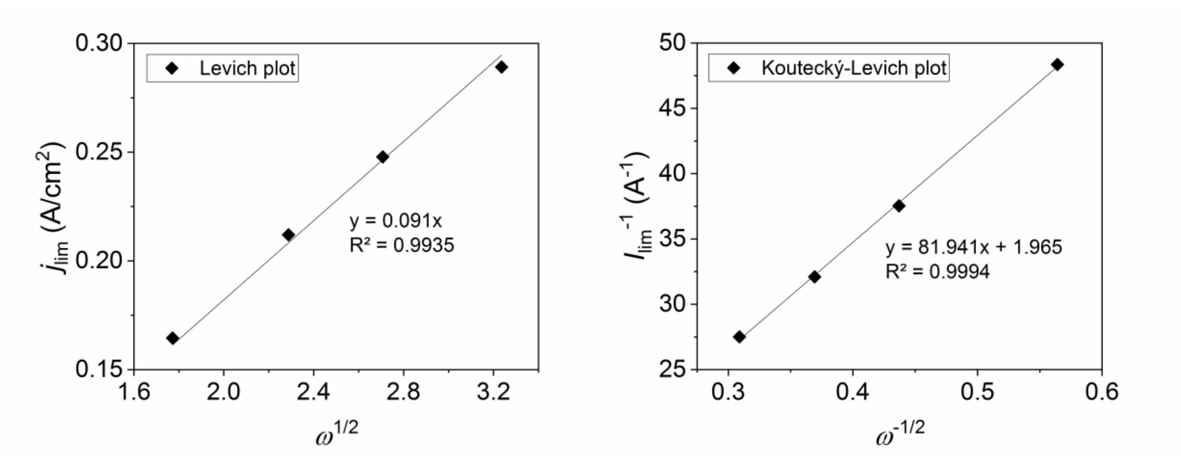


Fig. 1. Examples of (a) current density potential curves as well as (b) Levich and (c) Koutecký-Levich plots determined with original j_{lim} values. ([Cu] = 40 g/dm^3, [H_2SO_4] = 145 g/dm^3, [Ni] = 10 g/dm^3, [As] = 30 g/dm^3 and T = 60 °C)

Koutecký-Levich plots were also used to evaluate the activation-limited current (I_K) values. Furthermore, the j_{lim} plots were utilized in defining the I_K values by Tafel method (Fig. 2).

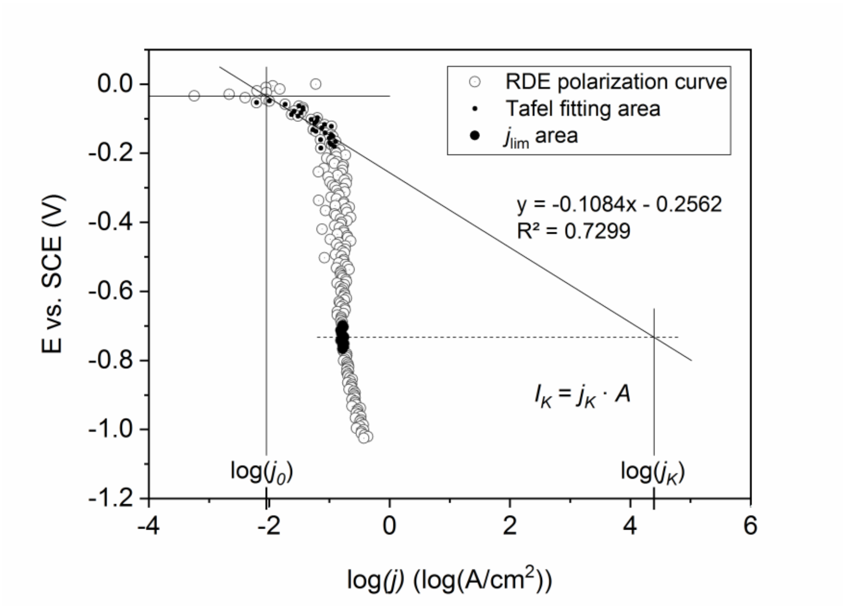


Fig. 2. Example of defining the I_K value by Tafel method.

The platinum RDE working electrode tip (diameter 4 mm) was polished prior to each experiment using silicon carbide paper (P1200 grit, Struers). After the polishing step was complete, the Pt surface was electrodeposited with copper and the uniformity of the surface was visually controlled.

Electrolytes were heated to the desired temperature (50–70 °C) and deaerated by sparging with nitrogen gas for at least 15 min to minimize the dissolved oxygen content. The same deaeration procedure was used by Hinatsu and Foulkes (1991) prior to their measurements that were performed in approximately the same volume (~0.15 dm^3) of electrolyte.

Scan rate in RDE measurements was 0.01 V/s, with a potential step 4.88 mV and rotation rates of 30, 50, 100 rpm and in 6 cases additional measurements also performed at 70 rpm. The lower limit of the rotation rates was chosen according to Eq. (5) (Bard and Faulkner, 2001) whilst the upper limit was determined experimentally such that the linear limiting current area of the current-potential curve could be defined (Fig. 1). The limiting factor for low rotation rates is the hydrodynamic boundary layer, whereas reaction rate limitations restrict high rotation rates (Bard and Faulkner, 2001). Ideally, the hydrodynamic boundary layer (δ_H) - the liquid layer rotating with the working electrode - has to be thinner than the radius of the working electrode (Eq. 5) (Bard and Faulkner, 2001).

$$r_1 > 3.6\,(v/\omega)^{1/2} = \delta_H, \qquad (5)$$

where r_1 is radius of the electrode, v is kinematic viscosity and ω is angular velocity.

The models obtained from this work were utilized to calculate the limiting current density values of the industrial solutions with Eq. (6) using two thicknesses for the diffusion boundary layer. These thicknesses were selected based on two studies where the electrodes used comprised of stationary parallel plates, similar to those used in industrial setups. The first thickness of 0.3 mm was approximated from previously published data (Leahy and Schwarz, 2011) and by neglecting any effects due to turbulent flow. The second thickness of 0.16 mm was taken from Schab and Hein (1992), where the effect of turbulent flow of copper electrorefining electrolyte is mainly induced by natural convection (Kawai and Miyazawa, 2014).

$$j_{\mathrm{lim}} = \mathrm{n} \cdot \mathrm{F} \cdot \mathrm{D}_{\mathrm{Cu(II)}} \cdot (c_0 / \delta_N) \qquad (6)$$

where j_{lim} is limiting current density, n is the number of transferred electrons in the reaction, $\mathrm{D}_{\mathrm{Cu(II)}}$ is the diffusion coefficient (cm^2/s), c_0 is the concentration of Cu(II) ions ($\mathrm{mol/cm}^3$) and δ_N is diffusion boundary layer thickness.

3. Results and discussion

The results present the j_{lim} model as well as the $\mathrm{D}_{\mathrm{Cu(II)}}$ models without (Model L, K, M, L_{PD}) and with the combined effects of variables (Model L_{ce}, K_{ce}, M_{ce}). The j_{lim} model is presented in generic form in Eq. 7. The form of $\mathrm{D}_{\mathrm{Cu(II)}}$ models are similar except that there is no angular velocity term and of these, Model L_{PD} is built utilizing the viscosity model of Price and Davenport (1981). In addition, the validation of linear models (Model L, K and M) was determined with industrial copper electrolytes (Sample 1–11).

$$j_{\mathrm{lim}} = a_1 + a_2\,[Cu] + a_3\,[H_2SO_4] + a_4\,[Ni] + a_5\,1/T + a_6\,[As] + \mathrm{a}_7\,\omega^{1/2} \ldots + a_{\mathrm{n}} \cdot (comb.\ effect\ term) \qquad (7)$$

3.1 Limiting current density model and diffusion coefficient models

The $D_{Cu(II)}$ models for copper electrorefining electrolyte were constructed from the diffusion coefficients calculated utilizing the j_{lim} model – outlined in Table 3 – and was built from the raw measured j_{lim} data. This data was refined and validated by use of R^2 (goodness of fit), Q^2 (goodness of prediction), model validity and reproducibility values, the results of which are outlined in Tables 3–5. In the $D_{Cu(II)}$ models (Model L, K, M, L_{PD}, Table 4) no combined effects of the parameters were taken into account, whereas Models L_{ce}, K_{ce}, M_{ce}, (Table 5) take into account the combined effects of the terms. Furthermore, Fig. 3 presents the measured vs. predicted plot of j_{lim} model and Fig. 4 plots of $D_{Cu(II)}$ of Model K (Koutecký-Levich, Eq. 2), M (mixed-control Newman, Eq. 3) and L (Levich, Eq. 1), respectively. Calculation of the $D_{Cu(II)}$ for Models K, M and L utilized the viscosities previously measured by Kalliomäki et al. (2017) (Eq. 4) and Model L_{PD} used the viscosities outlined by Price and Davenport (Price and Davenport, 1981).

Tables 3–5 and Figs. 3 and 4 show that all the models were valid as they displayed high correlation coefficients and reproducibility. Additionally, the model validity values were high in all cases except in the j_{lim} model, although this low model validity is likely erroneous as the R^2, Q^2 and reproducibility values were high. In the j_{lim} and $D_{Cu(II)}$ models, the concentrations are in g/dm^3 and T in K.

Table 3

j_{lim} model coefficients, R^2, Q^2, model validity and reproducibility values for Cu electrorefining electrolytes.

$\log_{10}(j_{lim})$ (A/cm^2)	j_{lim} model
Constant	-2.814E-01
[Cu]	3.146E-02
$[H_2SO_4]$	-7.999E-04
[Ni]	1.065E-04
$1/T$	-3.228E+02
[As]	-1.630E-02
$\omega^{1/2}$	1.665E-01
[Cu] · [Ni]	-5.428E-05
[Cu] · 1/T	-7.773E+00
[Ni] · [As]	3.668E-05
1/T · [As]	4.997E+00
R^2	0.969
Q^2	0.966
Model validity	0.182
N	230
Reproducibility	0.981

Table 4

Coefficients, R^2, Q^2, model validity and reproducibility values of the $D_{cu(II)}$ models (K, M, L, L_{PD}) for Cu electrorefining electrolytes (***excluding*** combined effect terms).

	Model			
$D_{Cu(II)}$ (cm^2/s)	K	M	L	L_{PD}
Constant	9.200E-05	1.004E-04	7.934E-05	7.881E-05

[Cu]	-4.237E-08	-4.700E-08	-2.163E-08	-2.272E-08
$[H_2SO_4]$	-3.160E-08	-3.440E-08	-2.763E-08	-2.901E-08
[Ni]	-6.860E-08	-7.623E-08	-6.805E-08	-6.795E-08
$1/T$	-2.345E-02	-2.572E-02	-2.034E-02	-2.006E-02
[As]	-2.365E-08	-2.602E-08	-3.096E-08	-2.770E-08
R^2	0.886	0.889	0.943	0.941
Q^2	0.859	0.8615	0.927	0.926
Model validity	0.780	0.769	0.839	0.864
N	68	68	69	68
Reproducibility	0.898	0.903	0.940	0.934

Table 5
Coefficients, R^2, Q^2, model validity and reproducibility values of the $D_{cu(II)}$ models for Cu electrorefining electrolytes (***including*** combined effect terms).

	Model		
$D_{Cu(II)}$ (cm^2/s)	K_{ce}	M_{ce}	L_{ce}
Constant	4.640E-05	5.336E-05	8.563E-05
[Cu]	1.197E-06	1.251E-06	6.784E-07
$[H_2SO_4]$	-3.414E-08	-3.715E-08	-2.098E-07
[Ni]	-6.063E-08	-6.744E-08	-4.471E-09
$1/T$	-8.151E-03	-9.941E-03	-2.247E-02
[As]	-1.023E-06	-1.117E-06	-8.491E-07
$[Cu] \cdot [Ni]$			-1.428E-09
$[Cu] \cdot 1/T$	-4.119E-04	-4.312E-04	-2.297E-04
$[H_2SO_4] \cdot 1/T$			6.002E-05
$[Ni] \cdot [As]$			1.550E-09
$1/T \cdot [As]$	3.317E-04	3.623E-04	2.670E-04
R^2	0.907	0.908	0.985
Q^2	0.877	0.879	0.978
Model validity	0.956	0.953	0.985
N	69	69	68
Reproducibility	0.850	0.855	0.968

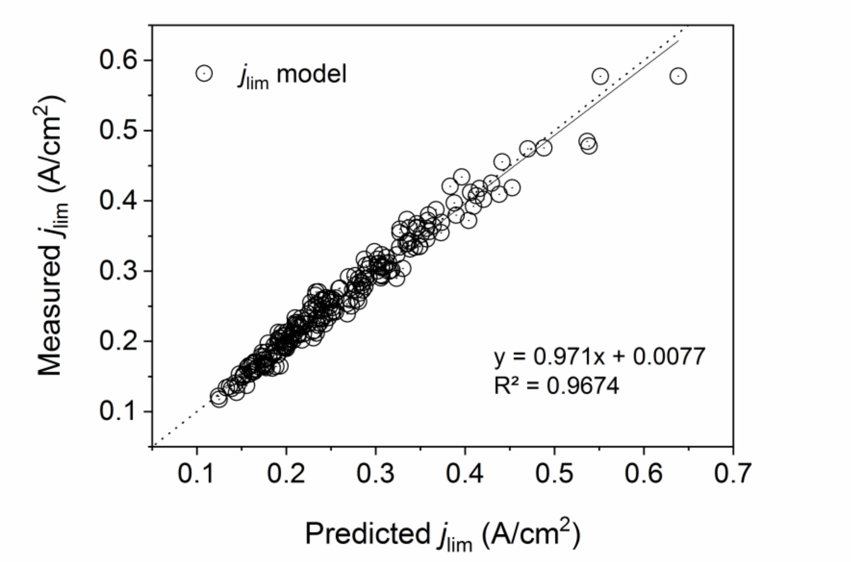


Fig. 3. Measured vs. predicted j_{lim} of copper electrorefining electrolyte. Prediction with j_{lim} model (r_1 = 2 mm).

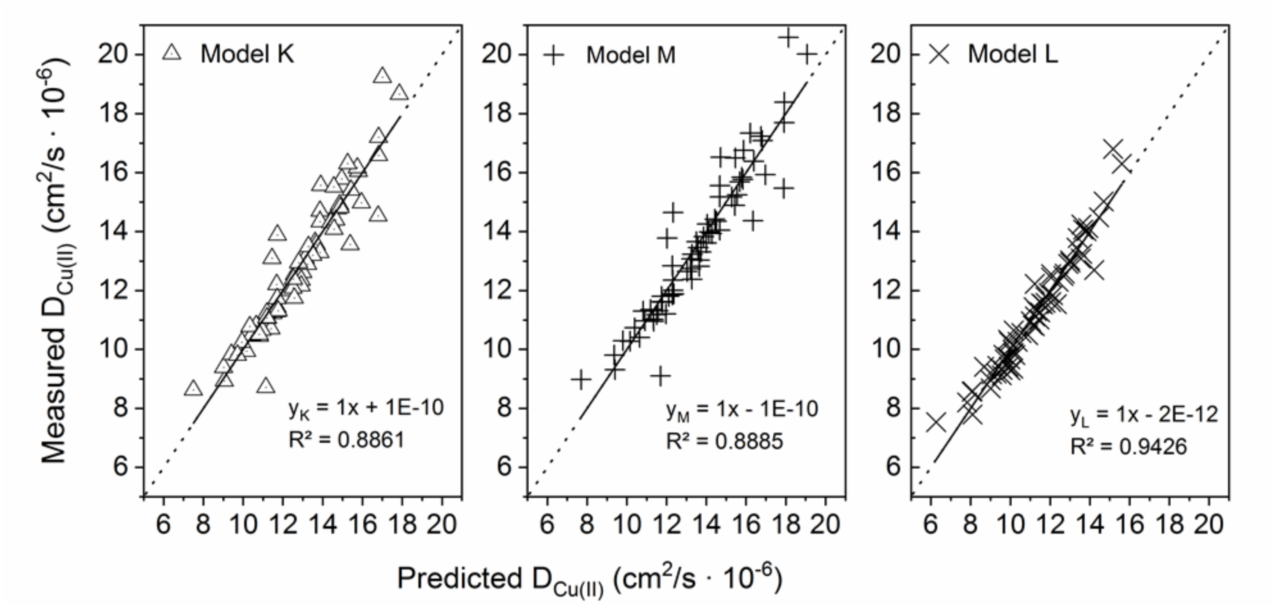


Fig. 4. Measured vs. predicted $D_{cu(II)}$ of copper electrorefining electrolyte. Prediction with Model K, M and L.

3.2 Evaluation of the diffusion coefficient models

The $D_{Cu(II)}$ equations defined in Model K, M and L consist exclusively of single factors; *T*, *[Cu]*, *[Ni]*, *[As]* and *[H_2SO_4]* (Table 4). In contrast, Models K_{ce}, M_{ce} and L_{ce} also contain the combined effect terms *[Cu]* · 1/*T* and 1/*T* · *[As]* (Table 5). Moreover, Model L_{ce} contains the terms *[Cu]* · *[Ni]*, *[H_2SO_4]* · 1/*T* and *[Ni]* · *[As]*. According to the probability values, these combined effect terms were significant; however, inclusion of these terms resulted in significant sensitivity to concentrations change for the models. Consequently, the models without the combined effect terms were deemed more suitable for further investigation.

The effects of the factors investigated can be seen from the equations constructed (Tables 4 and 5), although their impact was similar for Models K, M, L and L_{PD}. Nevertheless, the models built using different equations are plainly distinct as can be seen in Tables 4 and 5 and from the sensitivity analysis (Fig. 5). The factors of Model L and L_{PD} also showed that the impact of the viscosity value origin (Kalliomäki et al. (2017) vs. Price and Davenport (1981)) had only a minor effect on the diffusion coefficient equation constructed. These results indicate that increasing concentrations of Cu, Ni, H_2SO_4 and As decreases the diffusion coefficient value, while an increase in temperature leads to a direct increase in $D_{Cu(II)}$. Furthermore, the findings clearly establish for the first time, that the increase in As concentration leads to a decrease in $D_{Cu(II)}$.

The sensitivity analysis shown in Fig. 5 demonstrates that Models K, M and L were relatively insensitive to changes in concentration, unlike for changes in temperature, which visibly affected the sensitivity. For example, a 15% rise in temperature increased the $D_{Cu(II)}$ by 14.3–14.8% as calculated by these models, whereas a similar increase in concentration levels led to a maximum decrease in $D_{Cu(II)}$ of 6.6%. Models K_{ce}, M_{ce} and L_{ce} were found to be slightly more sensitive with the determined equivalent values for temperature being 13.7–15.0% and for concentration 7.1%, respectively. Moreover, the combined effects significantly increased the sensitivity of the models with the impact of the effect of temperature affected by As and Cu concentrations as can also be seen in Table 5. The difference in the effect of temperature on the $D_{Cu(II)}$ with changes in As was calculated to be a maximum of 9.3% and for Cu it was 6.2%.

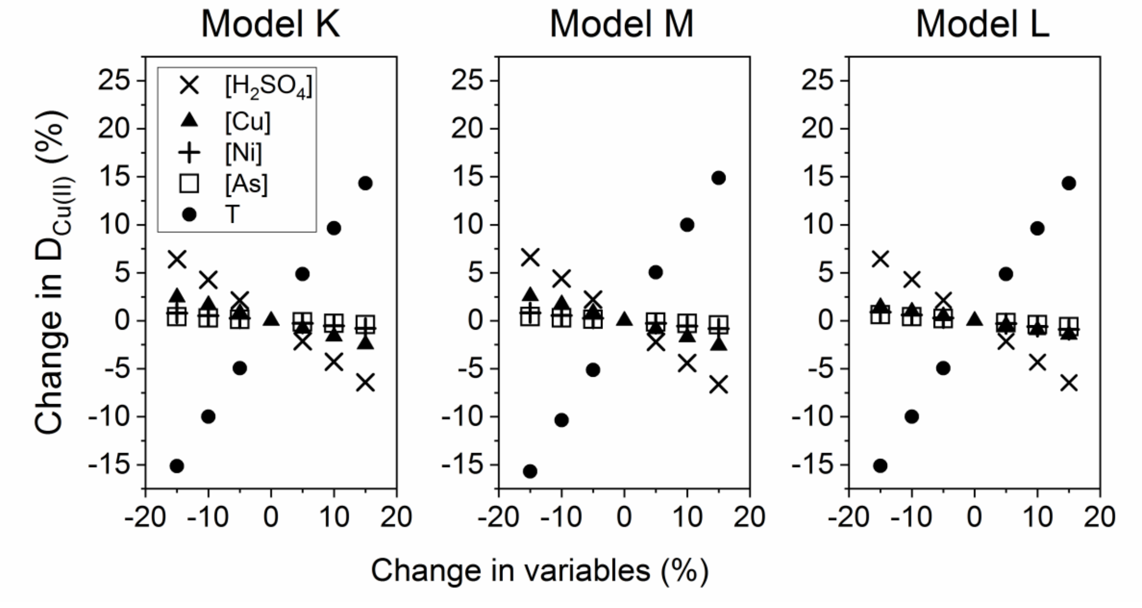


Fig. 5. Sensitivity analysis for $D_{Cu(II)}$ models K, M and L for as a function of the percentage change in variables.

Activation-limited current (I_K) values (Fig. 3) were calculated from the intercepts of Koutecký-Levich plots and were found to vary mainly between 0.15 and 3.20 A. Nevertheless, the I_K values fluctuated significantly and the effect of activation polarization was found to be smaller when the RDE polarization curves were analyzed via the Tafel method. The Tafel coefficients defined varied between -0.12 and -0.07 V and the exchange current density (j_0) values between 0.0037 and 0.020

A/cm^2. The I_K values calculated with this data varied between 189 and 703 000 A, these values that are significantly higher and have much more variation than those defined from the slopes of Koutecký-Levich plots. This discrepancy between the values may be explained however by the interference sensitivity of the RDE measuring method. Overall, these results suggest that the activation polarization has minor effect on Cu limiting current density measurements and the effect is difficult to measure.

3.3 Comparison of the diffusion coefficient results with the results of previous research

The effects of As and Ni on $D_{Cu(II)}$ found in this work and by the previous investigations of Jarjoura et al. (2003) are presented in Fig. 6, whereas the analogous effects of Cu and H_2SO_4 are presented in Fig. 7 and include a comparison with the results from Moats et al. (2000). Fig. 8 shows the temperature effects determined in this work compared with the results of Moats et al. (2000), Subbaiah and Das (1989), and Jarjoura et al. (2003). In addition, the original measured values of one sample are presented in Fig. 8. As can be seen from Figs. 6–8, there is a distinct variation between the results defined with the M, K and L Models presented here and those in the previous research. $D_{Cu(II)}$ values defined by Jarjoura et al. (2003) (Figs. 6 and 8) as well as by Subbaiah and Das (1989) (Fig. 8) are observed to be higher. The difference between the $D_{Cu(II)}$ values defined using our models and the that of Subbaiah and Das (1989) results primarily from the fact that their experiments were performed mostly at 30 °C – a temperature that is significantly lower than that used in electrorefining – consequently the model of Subbaiah and Das results in increased error levels at higher temperatures.

The $D_{Cu(II)}$ models in this work defined using the Levich equation (1) were calculated to be close to the corresponding measured data of Moats et al. (2000) (Fig. 8). Nevertheless, when the Koutecký-Levich equation (2) and mixed-control Newman equation (3) were used to define the $D_{Cu(II)}$, the values obtained were observed to be higher than those obtained using Levich equation, as previously highlighted by Quickenden and Xu (1996). This highlights the fact that the $D_{Cu(II)}$ models obtained from the limiting current density data depend primarily on the equation used to determine $D_{Cu(II)}$.

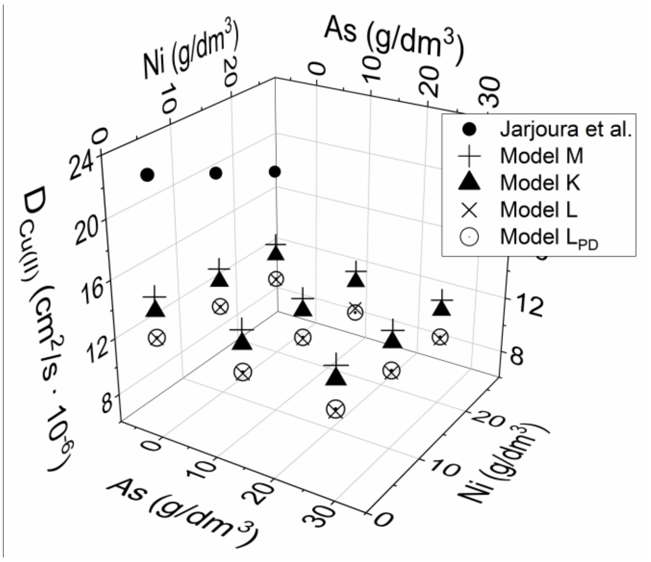


Fig. 6. Effect of As and Ni concentration on $D_{Cu(II)}$ in copper electrorefining electrolyte according to Model M, K, L and L_{PD} (this work) and Jarjoura et al. (2003) at T = 60 °C, [Cu] = 40 g/dm^3, [H_2SO_4] = 160 g/dm^3.

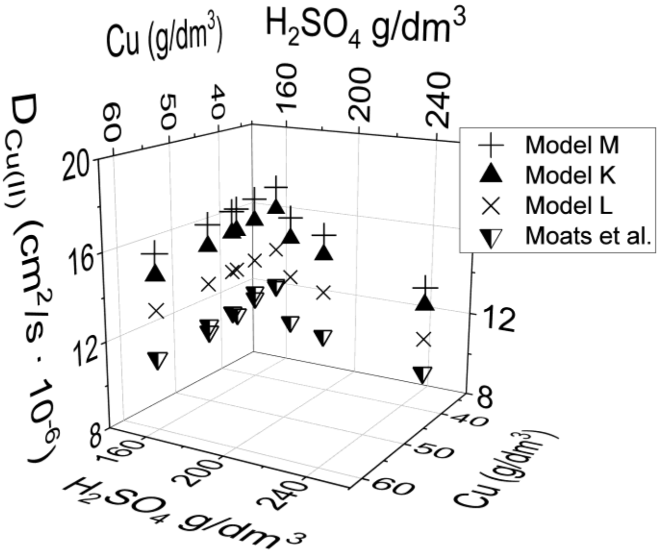


Fig. 7. Effect of sulfuric acid and copper concentration on $D_{Cu(II)}$ in copper electrorefining electrolyte at 65 °C according to Model M, K and L (this work) and Moats et al. (2000).

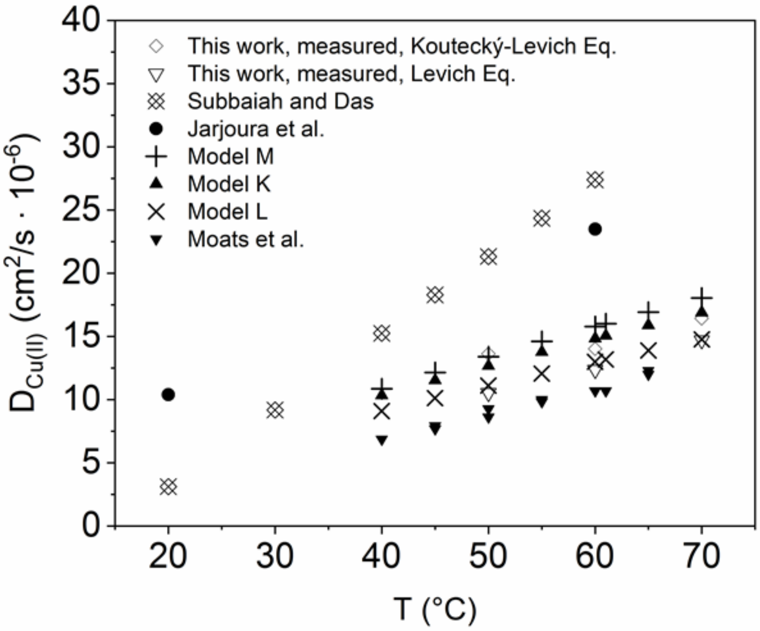


Fig. 8. Effect of temperature on $D_{Cu(II)}$ in simple copper electrorefining electrolyte ([Cu] = 40 g/dm^3, [H_2SO_4] = 160 g/dm^3) according to Models M, K and L (this work), $D_{Cu(II)}$ defined from the measured data by Koutecký-Levich equation, Levich equation as well as models by Subbaiah and Das (1989), Jarjoura et al. (2003) and Moats et al. (2000).

3.4 Validation of the limiting current density model and the diffusion coefficient models

The j_{lim} and $D_{\mathrm{Cu(II)}}$ models from this work were validated by comparing the predicted values with the measured values from 11 different industrial electrorefining electrolytes with known concentrations (Figs. 9 and 10). Initial j_{lim} values can be predicted relatively accurately with the model shown in Table 3, although the measured values were on average slightly higher than the predictions – in particular the j_{lim} values of those samples that were fresher or had been subject to shorter heating period before the measurements were higher. The reason for these observations is probably the presence of additives such as gelatin, which based on the research of Winand et al. (1984), is known to increase the j_{lim} or more specifically the diffusion limiting current density (j_L). It has been previously reported by Troch (1983) that the j_L value changed from 11.5 to 14.8 A/dm^2 when the gelatin concentration was increased by 3 mg/dm^3. In addition, gelatin is also known to hydrolyze when heated and in solutions with low pH (Winand et al., 1984). Consequently, the j_{lim} values of the equivalent electrolytes with industrial amounts of non-hydrolyzed gelatin are most probably slightly higher than the values measured in this work. The $D_{\mathrm{Cu(II)}}$ predictions with Model L were relatively close to the measured values with the maximum difference being 18.7%, whereas the predictions from Models K and M were 27.6 and 28.3% respectively when compared to the values obtained for the industrial electrolytes. It is known that addition agents like gelatin, thiourea and chloride can affect the $D_{\mathrm{Cu(II)}}$, but this usually leads to a lowering of the overall value (Araneda-Hernández et al., 2014). Based on the study of Araneda-Hernández et al. (2014), addition of 1, 10 and 100 mg/dm^3 of glue in electrolytes containing 40 g/dm^3 Cu and 200 g/dm^3 H_2SO_4 decreases $D_{\mathrm{cu(II)}}$ 19.3%, 17.2% and 17.9%, respectively. Similar additions of thiourea decrease $D_{\mathrm{cu(II)}}$ 23.4%, 13.3% and 18.4%, and chloride 0.09%, 33.3% and 34.7%, respectively. Therefore, according to the results of this work, there are likely to be inaccuracies in defining $D_{\mathrm{Cu(II)}}$ particularly using Koutecký-Levich (2) and mixed-control Newman (3) equations, although some other factors present in the industrial electrolytes may also result in an increase in the diffusion coefficient value. One explanation why the models with higher correlation values and better predictability result from use of the Levich equation (1) is that the Levich slope is forced to go through origin (Fig. 1) which stabilizes the data fluctuation although this may also decrease some effects. Koutecký-Levich (2) and mixed-control Newman (3) equations take into account all effects - including activation polarization - but these in turn, also result in other inaccuracies. Consequently, the results suggest that Model L ($D_{\mathrm{Cu(II)}}$ based on Levich equation) provided the best correlation with the industrial solutions when compared to the other constructed models (K and M) and the earlier published $D_{\mathrm{Cu(II)}}$ data.

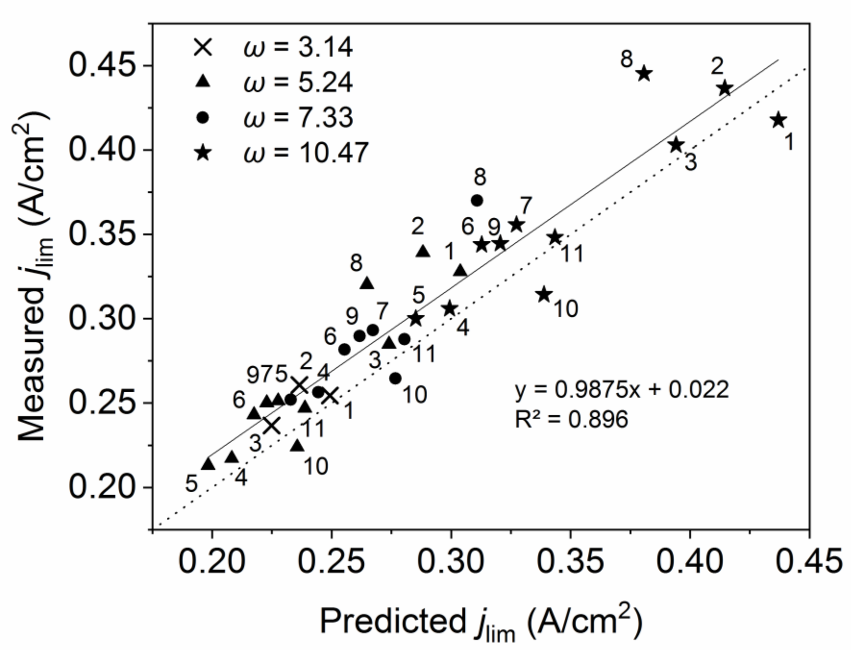


Fig. 9. Limiting current density values of industrial copper electrorefining electrolytes (Sample 1–11, Table 2) measured at 65 °C using three angular velocity (ω) rates, compared with the equivalent predicted values defined with j_{lim} model of this work (r_1 = 2 mm).

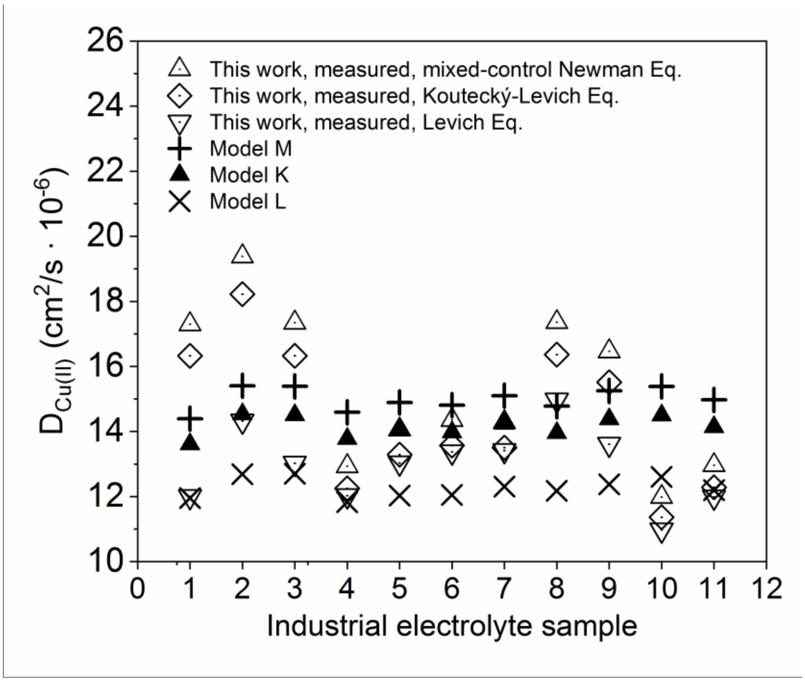


Fig. 10. $D_{Cu(II)}$ values of industrial copper electrorefining electrolytes measured at 65 °C, compared with the equivalent predicted values defined with models from this work.

3.5 Estimation of the limiting current densities under industrial conditions

Limiting current densities under the conditions used for the industrial samples were calculated using Eq. 6 with δ_{N1} = 0.3 mm (Leahy and Schwarz, 2011), δ_{N2} = 0.16 mm (Schab and Hein, 1992) and Model L. The limiting current density values calculated (Table 6) with δ_N thickness 0.3 mm were shown to be slightly less and with δ_N thickness 0.16 mm slightly more than three times the typical current density (300 A/m^2) used in industry (Hemmati et al., 2013). The most favorable operating current density can be estimated to be around 1/3 of the limiting current density. Furthermore, as can be seen in Table 6, there are two important factors that should be taken into account when optimizing j_{lim}. The first is *[Cu]*, as known based on literature (Winand, 1984) and the second the thickness of δ_N which can be affected with electrolyte flow (Bard and Faulkner, 2001). Based on the results of this work, a 37% decrease in *[Cu]* resulted in a 37% decrease in j_{lim}, and 88% increase in δ_N thickness caused 47% decrease (Table 6). Optimization of these factors would enable the industrial operations to be enhanced, however, increases in *[Cu]* should be limited as it decreases $D_{Cu(II)}$. Nonetheless, since these limiting current density definitions themselves are approximate it can be possible that industrial operations with the compositions investigated (Sample 1–11). In particular, those with higher *[Cu]* (Samples 1–3) can operate at even higher current densities without deteriorating the quality of the cathode copper deposit due to the presence of additives like gelatin, which increase the j_L. Although there was variation in the $D_{Cu(II)}$ results, the predictions for j_{lim} under industrial conditions obtained with Eq. 6 utilizing Model L (Table 6) were close to triple of the operating current densities (193–390 A/m^2) used in industry (Moats et al., 2007).

Table 6
Limiting current density values defined for industrial copper electrorefining electrolytes at 65 °C, using modeled (with Model L) $D_{Cu(II)}$ values.

Sample	j_{lim}, A/m^2 *	1/3 · j_{lim}, A/m^2 *	j_{lim}, A/m^2 **	*1/3* · j_{lim}, A/m^2 **
1	760	250	1420	470
2	730	240	1370	460
3	700	230	1300	430
4	510	170	960	320
5	480	160	900	300
6	540	180	1020	340
7	570	190	1070	360
8	670	220	1260	420
9	560	190	1050	350
10	600	200	1120	370
11	600	200	1130	380

* $\delta_N = 0.3$ mm
** $\delta_N = 0.16$ mm

4. Conclusions

The results detailed here outline for the first time the effect of arsenic on the $D_{Cu(II)}$ under copper electrorefining conditions, an increase in which decreases the $D_{Cu(II)}$. This effect on $D_{Cu(II)}$ was shown to be of approximately the same magnitude as the effect of acid and other metals species investigated with regard to coefficients of the $D_{Cu(II)}$ models (Table 4) and based on the sensitivity analysis, almost equivalent to the effect of changes in nickel concentration (Fig. 5). The effect of the other species concentrations and temperature on the $D_{Cu(II)}$ were in line with previous studies (Jarjoura et al, 2003;

Moats et al., 2000; Subbaiah and Das, 1989) *i.e.* that increasing Cu, Ni and H_2SO_4 concentrations decreased the $D_{Cu(II)}$ while increasing temperature increased $D_{Cu(II)}$.

Combined effects of parameters composition and temperature on $D_{Cu(II)}$ were investigated for the first time. Nevertheless, the combined effect terms were shown to cause excess sensitivity for the models, although the models were confirmed being valid. Consequently, the more robust models (K, M, L) without the presence of combined effect terms were favored. Of the robust models used for $D_{Cu(II)}$ prediction, Model L was determined to be the most valid as it had the highest level of validity (Table 4) and moderate sensitivity to variable changes. Furthermore, it could predict the $D_{Cu(II)}$ of the industrial copper electrorefining electrolytes with the highest accuracy when compared to both the other models constructed (Fig. 10) and previously published data. These results also confirm that activation polarization has only a minor effect on limiting current density measurements as Model L was constructed with the values calculated from the limiting current density results using the Levich equation.

Evaluation of the j_{lim} values calculated for the industrial electrolytes with Eq. 6 and using the $D_{Cu(II)}$ predictions (with Model L) clarified the significance of the effects of *[Cu]* and thickness of δ_N on j_{lim}. It was found that decreasing the *[Cu]* by 37% decreased j_{lim} 37%, and increasing δ_N thickness by 88% decreased j_{lim} 47% (Table 6). Nevertheless, it is known that the increase in the concentration of gelatin increases j_L (Troch, 1983; Winand et al., 1984). Furthermore, the effect of temperature was found to be crucial, as this increases both j_{lim} and $D_{Cu(II)}$ according to the RDE measurement results (Table 3).

Overall, it can be concluded that in order to enhance industrial Cu electrorefining deposition rates it is important to maximize both j_{lim} and $D_{Cu(II)}$ by optimizing *[Cu]*, temperature, *[H_2SO_4]* and gelatin concentration, as well as minimize δ_N by controlling electrolyte flow such that the operational current density can be as high as possible.

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