Models for viscosity and density
of copper electrorefining electrolytes

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Abstract: Viscosity and density of copper electrorefining electrolytes affect energy consumption and purity of cathode copper. Decreasing the viscosity and density increases the rate of falling of the anode slimes to the bottom of an electrorefining cell and increases the diffusivity and mobility of ions. Increasing the falling rate of the anode slimes decreases a risk of anode slime impurities ending up on the cathode and being entrapped into the copper deposit. This work introduces two new models for both viscosity and density of copper electrorefining electrolytes with high accuracy and one reconstructed improved model for some electrorefining data of viscosity published previously. The experimental work to build up these new models was carried out as a function of temperature (50, 60, 70 °C), copper (40, 50, 60 g/dm^3), nickel (0, 10, 20 g/dm^3) and sulfuric acid (130, 145, 160 g/dm^3) concentrations for all models, and additionally arsenic concentration (0, 15, 30, 32, 64 g/dm^3) was included in the viscosity models. Increasing concentrations of Cu, Ni, As and H$_2$SO$_4$ were found to increase the viscosity and density, whereas increasing temperature decreased both viscosity and density. The viscosity models were validated with industrial electrolyte samples from the Boliden Harjavalta Pori tankhouse. The experimental and modeling work carried out in this study resulted in improved viscosity models, having the strongest agreement with the industrial electrorefining electrolytes.

Keywords: *copper electrorefining, viscosity model, density model*

Introduction

Viscosity and density have a considerable effect on purity of cathode copper and the energy consumption (Price and Davenport, 1981; Subbaiah and Das, 1989) affecting the mass and heat transfer conditions in a copper electrorefining cell (Price and Davenport, 1980). Decreasing viscosity increases the mass transfer rate since the diffusivity and mobility of ions increase (Cifuentes and Arriagada, 2008). Thus, lowering viscosity and density increases the diffusion coefficient of cupric ion (Moats et al., 2000) as well as the falling rate of the anode slimes to the bottom of the cell (Davenport et al., 2002; Shi and Ye, 2013). Increasing the falling rate of the anode

slimes decreases movement of slimes to other directions (Davenport et al., 2002; Shi and Ye, 2013). If the anode slimes end up on a cathode, the impurities can be entrapped into a copper deposit (Davenport et al., 2002). Due to that, the viscosity and density are typically kept sufficiently low in the electrorefining process (Davenport et al., 2002). The values of density and kinematic viscosity in typical electrolytes containing 50-65 g/dm^3 Cu, 18-24 g/dm^3 Ni, 150-180 g/dm^3 H$_2$SO$_4$ are reported at 55-70 °C being 1.224-1.2939 g/cm^3 and 0.772-1.165 mm^2/s, respectively (Devochkin et al., 2015).

There are only a few studies on the viscosity and density of copper electrorefining electrolytes (Price and Davenport, 1980, 1981; Subbaiah and Das, 1989; Jarjoura et al., 2003; Devochkin et al., 2015). According to these studies, increasing concentration of the main components in the electrolyte (copper, nickel and sulfuric acid) increases both viscosity and density, while increasing temperature has an opposite effect. In addition, other impurities such as arsenic (Price and Davenport, 1981), iron (Price and Davenport, 1981; Subbaiah and Das, 1989), manganese and cobalt (Subbaiah and Das, 1989) have been suggested to increase the viscosity and density. As arsenic, a typical impurity, has been experimentally measured and modeled only by Price and Davenport (1981), there are no recent studies on the effects of arsenic on either viscosity or density of copper electrorefining electrolytes. The effect of impurities has to be taken into account due to increasing amount of impurities and lowering grade of raw materials used for copper production. The average contents of As and Bi were approximately 2- and 6-folds higher, respectively, in 2016 compared to the content in 1987 (Moats et al., 2016).

As the viscosity value has an effect on the diffusion coefficient of cupric ion ($D_{Cu(II)}$) (Moats et al., 2000), the kinematic viscosity is also a factor in equations defining $D_{Cu(II)}$. Thus, the accuracy in defining the kinematic viscosity affects the accuracy of the determined $D_{Cu(II)}$ value. The diffusion coefficient is an important factor in electrodeposition, as it determines the limiting current density which, in turn, has a strong effect on the operating current density and morphology of the deposited copper.

The objective of this work was to develop accurate mathematical models of synthetic copper electrolyte viscosity (parameters: T and concentrations of H$_2$SO$_4$, Cu(II) and Ni(II)) and density (parameters: T and concentrations of H$_2$SO$_4$, Cu(II), Ni(II) and As(III/V)). Though in industrial electrolytes arsenic is known to be present both as As(III) and As(V) (Peng et al., 2012). In the current work the ratio of As(III) vs. As(V) was not determined. However, the As parameter was investigated as a sum of content of trivalent and pentavalent ions. In addition, the objective was to study the combined effects of the variables. The developed viscosity models were also initially validated with three industrial electrorefining electrolytes.

Materials and methods

Experimental solutions in this study were prepared using $CuSO_4 \cdot 5H_2O$ (99–100%, Ph.Eur., crystallized, VWR International, LLC.), $NiSO_4 \cdot 7H_2O$ (99–100%, for analysis, crystallized, Sigma-Aldrich Co. LLC.), H_2SO_4 (95–97%, for analysis, Merck KGaA), As_2O_3 (99.5%, Alfa Aesar, Thermo Fisher Scientific GmbH), arsenic acid (containing As 322600 mg/dm^3, Cu 3400 mg/dm^3, Ni 1210 mg/dm^3, Sb 7700 mg/dm^3, Se 19.3 mg/dm^3, Te 12 mg/dm^3, Pb 16 mg/dm^3, Bi < 5 mg/dm^3, Ag < 1 mg/dm^3 and Ba < 1 mg/dm^3) and distilled water. As_2O_3 was dissolved in distilled water at 70 °C using H_2O_2 (30%, for analysis, Merck KGaA) enhancing the solubility of As, As(V) having significantly higher solubility into water compared to As(III) (Casas et al., 2003). Arsenic in arsenic acid was assumed to be present mainly as As(III) ions. In addition, three industrial electrorefining electrolytes (from Boliden Harjavalta Pori tankhouse) were used to validate the viscosity models. The concentrations of Cu, Ni, As and H_2SO_4 in the industrial samples were as follows: sample 1 contained 62.59 g/dm^3 Cu, 17.37 g/dm^3 Ni, 15.3 g/dm^3 As and 155 g/dm^3 H_2SO_4; sample 2 contained 57.07 g/dm^3 Cu, 15.57 g/dm^3 Ni, 15.3 g/dm^3 As and 138 g/dm^3 H_2SO_4; sample 3 contained 54.09 g/dm^3 Cu, 11.07 g/dm^3 Ni, 10.7 g/dm^3 As and 157 g/dm^3 H_2SO_4. These electrolytes were filtered and heated before analyses and measurements to ensure the homogeneity of the samples. The concentrations of Cu, Ni and As in the solution samples (industrial electrolytes, arsenic acid) were analyzed with ICP-OES (inductively coupled plasma optical emission spectroscopy, Perkin Elmer Optima 7100 DV, USA). Acidity was determined using the conductivity model described elsewhere (Kalliomäki et al., 2016).

Kinematic viscosities of the solutions were measured using a Ubbelohde capillary viscometer (SI Analytics GmbH) and densities using a glass tube oscillator DMA 40 Digital Density Meter (Anton Paar K. G.). The viscosity results were normalized with known viscosity values of water by subtracting the difference between the measured and theoretical water viscosities from the viscosity values. The density results were calculated from oscillation frequencies using measured oscillation frequencies and known density values of water and air for calibrating the values. The air pressure was also measured and taken into account in the theoretical air density values used. During the measurements the temperature tolerance was ±0.2 °C.

The experimental design and data analysis were carried out using modeling and design software MODDE 8 (MKS Data Analytics Solution). The experiments for kinematic viscosity and density were designed by defining factors, responses and levels of the factors (Table 1). The data were refined, and two models for viscosity and two for density were constructed. For evaluating the quality of the models, the parameters goodness of fit (R^2), goodness of prediction (Q^2), standard deviation of the response (SDY), residual standard deviation (RSD) and reproducibility values of the density models were observed. The viscosity Model A was constructed using results where arsenic acid was the source of arsenic and the Model B using the results where

the arsenic source was dissolved As_2O_3. In the density measurements arsenic was not used for the safety issues. Both of the two density models were based on the same experimental data series: the density Model $C_{streamlined}$ being a simplified version of Model C.

Since Price and Davenport (1981) developed the viscosity model using data from electrorefining and electrowinning electrolytes, one additional model was proposed using the viscosity results from their published electrorefining data. The data were refined using MODDE software and built into an improved model.

Table 1. Investigated parameters of synthetic copper electrorefining
electrolytes for viscosity and density measurements

Factor	Unit	Levels
Cu	g/dm^3	40, 50, 60
H_2SO_4	g/dm^3	130, 145, 160
Ni	g/dm^3	0, 10, 20
As *	g/dm^3	0, 32, 64 [†] or
	g/dm^3	0, 15, 30 [‡]
T	°C	50, 60, 70

* for viscosity measurements.
[†] for Model A – as from industrial As-acid
[‡] for Model B – as from dissolved As_2O_3

For evaluating the sensitivity and the accuracy of the models a sensitivity analysis was conducted. The variables were changed independently 0.5, 1, 3, 5, 10 and 15% around the point with average values of the variables and their relative effects on the viscosity and density were calculated. In addition, the sensitivity analysis was conducted for the concentration effects. Analogously, the effect of tolerances in the solution volumes and the test temperatures were investigated. These analyses were conducted utilizing the design and prediction tools of MODDE 8.

Results and discussion

Raw data

The raw data of viscosity and density measured in this study are listed in Tables 2-4. It can be observed that increase in Ni(II), Cu(II) and H_2SO_4 concentrations increases both viscosity and density. The effect of As(III/V) seems to be quite analogous to the effect of Cu(II) and Ni(II). In addition, increase in temperature was found to be the only parameter decreasing the viscosity and density. This effect is in line with the literature (Price and Davenport, 1980, 1981; Subbaiah and Das, 1989; Jarjoura et al., 2003; Devochkin et al., 2015).

Table 2. Measured viscosity values and experimental parameters
used in viscosity tests 1-63 for Model A (as originating from arsenic acid)

	Composition g/dm³			T	v			Composition g/dm³			T	v
Test	Cu	H_2SO_4	Ni	As	°C	mm²/s	Test	Cu	H_2SO_4	Ni	As	°C	mm²/s
1	40	130	0	0	50	0.82057	31	50	145	20	31.9	50	1.18120
2	60	145	0	0	50	0.94585	32	40	160	20	31.9	50	1.12377
3	50	160	0	0	50	0.90749	33	40	130	0	31.9	60	0.77098
4	50	130	10	0	50	0.94614	34	60	145	0	31.9	60	0.90070
5	40	145	10	0	50	0.89835	35	50	160	0	31.9	60	0.85589
6	60	160	10	0	50	1.04622	36	50	145	20	31.9	60	0.97920
7	60	130	20	0	50	1.09491	37	40	130	0	31.9	70	0.66594
8	50	145	20	0	50	1.03632	38	60	145	0	31.9	70	0.76619
9	40	160	20	0	50	0.99042	39	50	160	0	31.9	70	0.73646
10	40	130	0	0	60	0.69660	40	50	160	10	31.9	70	0.78241
11	60	145	0	0	60	0.80155	41	50	145	20	31.9	70	0.83583
12	50	160	0	0	60	0.76950	42	40	160	20	31.9	70	0.79545
13	50	130	10	0	60	0.79395	43	40	130	0	63.8	50	1.03644
14	40	145	10	0	60	0.75716	44	50	130	10	63.8	50	1.20936
15	60	160	10	0	60	0.87567	45	40	145	10	63.8	50	1.16640
16	60	130	20	0	60	0.92213	46	60	160	10	63.8	50	1.36887
17	50	145	20	0	60	0.87438	47	60	130	20	63.8	50	1.42169
18	40	160	20	0	60	0.83575	48	40	130	0	63.8	60	0.86405
19	40	130	0	0	70	0.60200	49	50	130	10	63.8	60	1.00246
20	60	145	0	0	70	0.68573	50	40	145	10	63.8	60	0.96683
21	50	160	0	0	70	0.66036	51	60	160	10	63.8	60	1.13154
22	50	130	10	0	70	0.68619	52	60	130	20	63.8	60	1.17774
23	40	145	10	0	70	0.65486	53	40	130	0	63.8	70	0.74091
24	60	160	10	0	70	0.75227	54	50	130	10	63.8	70	0.85498
25	60	130	20	0	70	0.78777	55	40	145	10	63.8	70	0.82040
26	50	145	20	0	70	0.74728	56	60	160	10	63.8	70	0.95612
27	40	160	20	0	70	0.71545	57	60	130	20	63.8	70	0.99342
28	40	130	0	31.9	50	0.94522	58	50	145	10	31.9	60	0.89798
29	60	145	0	31.9	50	1.06497	59	50	145	10	31.9	60	0.89768
30	50	160	0	31.9	50	1.04931	60	50	145	10	31.9	60	0.90211

T. Kalliomaki, A.T. Aji, L. Rintala, J. Aromaa, M. Lundstrom

Table 3. Measured viscosity values and experimental parameters
used in viscosity tests 1-63 for Model B (As originating from As_2O_3)

Test	Cu	H_2SO_4	Ni	As	T °C	v mm²/s	Test	Cu	H_2SO_4	Ni	As	T °C	v mm²/s
	Composition g/dm³							Composition g/dm³					
1	40	130	0	0	50	0.82057	33	40	130	0	15	60	0.70803
2	60	145	0	0	50	0.94585	34	60	145	0	15	60	0.81448
3	50	160	0	0	50	0.90749	35	50	160	0	15	60	0.78027
4	50	130	10	0	50	0.94614	36	50	145	20	15	60	0.89297
5	40	145	10	0	50	0.89835	37	40	160	20	15	60	0.85231
6	60	160	10	0	50	1.04622	38	40	130	0	15	70	0.61116
7	60	130	20	0	50	1.09491	39	60	145	0	15	70	0.69816
8	50	145	20	0	50	1.03632	40	50	160	0	15	70	0.67074
9	40	160	20	0	50	0.99042	41	50	145	20	15	70	0.76122
10	40	130	0	0	60	0.6966	42	40	160	20	15	70	0.72851
11	60	145	0	0	60	0.80155	43	40	130	0	30	50	0.86869
12	50	160	0	0	60	0.7695	44	50	130	10	30	50	0.99875
13	50	130	10	0	60	0.79395	45	40	145	10	30	50	0.94704
14	40	145	10	0	60	0.75716	46	60	160	10	30	50	1.11786
15	60	160	10	0	60	0.87567	47	60	130	20	30	50	1.17411
16	60	130	20	0	60	0.92213	48	40	130	0	30	60	0.73204
17	50	145	20	0	60	0.87438	49	50	130	10	30	60	0.83933
18	40	160	20	0	60	0.83575	50	40	145	10	30	60	0.7981
19	40	130	0	0	70	0.602	51	60	160	10	30	60	0.94704
20	60	145	0	0	70	0.68573	52	60	130	20	30	60	0.97564
21	50	160	0	0	70	0.66036	53	40	130	0	30	70	0.62781
22	50	130	10	0	70	0.68619	54	50	130	10	30	70	0.71775
23	40	145	10	0	70	0.65486	55	40	145	10	30	70	0.6852
24	60	160	10	0	70	0.75227	56	60	160	10	30	70	0.79891
25	60	130	20	0	70	0.78777	57	60	130	20	30	70	0.83208
26	50	145	20	0	70	0.74728	58	50	145	10	15	60	0.82402
27	40	160	20	0	70	0.71545	59	50	145	10	15	60	0.82132
28	40	130	0	15	50	0.84107	60	50	145	10	15	60	0.82359
29	60	145	0	15	50	0.96853	61	50	145	10	15	50	0.97737
30	50	160	0	15	50	0.92685	62	50	145	10	15	70	0.7206
31	50	145	20	15	50	1.06498	63	50	145	10	15	60	0.82552
32	40	160	20	15	50	1.01588							

Table 4. Measured density values and experimental parameters
used in density tests 1-29 for Model C and Model C$_{streamlined}$

| | Composition g/dm^3 | | | T | ρ | | Composition g/dm^3 | | | T | ρ |
Test	Cu	H$_2$SO$_4$	Ni	°C	g/cm^3	Test	Cu	H$_2$SO$_4$	Ni	°C	g/cm^3
1	40	130	0	49	1.15549	16	60	130	20	59	1.23899
2	60	145	0	49	1.20788	17	50	145	20	59	1.22499
3	50	160	0	49	1.19403	18	40	160	20	59	1.21254
4	50	130	10	49	1.20064	19	40	130	0	69	1.1427
5	40	145	10	49	1.18649	20	60	145	0	69	1.19275
6	60	160	10	49	1.23848	21	50	160	0	69	1.17969
7	60	130	20	49	1.24663	22	50	130	10	69	1.18695
8	50	145	20	49	1.23216	23	40	145	10	69	1.17337
9	40	160	20	49	1.21964	24	60	160	10	69	1.22424
10	40	130	0	59	1.14873	25	60	130	20	69	1.23237
11	60	145	0	59	1.20026	26	50	145	20	69	1.21801
12	50	160	0	59	1.18665	27	50	145	10	59	1.20242
13	50	130	10	59	1.1946	28	50	145	10	59	1.20215
14	40	145	10	59	1.17982	29	50	145	10	59	1.20201
15	60	160	10	59	1.23112						

Kinematic viscosity

The models for kinematic viscosity were constructed from the raw data measured. Model A (Table 4) was constructed from the results (Table 2) for arsenic acid as a source of arsenic in the electrolytes, while Model B (Table 4) from the results (Table 3) where arsenic originated from As$_2$O$_3$. The models were constructed to the form:

$$\log_{10}(v) = a_1 + a_2\ [Cu] + a_3\ [H_2SO_4] + a_4\ [Ni] + a_5\ [As] + a_6\ T$$
$$+ \ldots + a_n \cdot (\text{comb. effect term}) \tag{1}$$

and the calculated statistical values for Models A and B are presented in Table 4.

Significance as well as the combined effects of the parameters were investigated. However, most of the combined effect terms were shown to be insignificant according to high probability values defined with MODDE 8. The viscosity models A and B contained only one significant combined effect term being $T \cdot [As]$ for Model A and $[Cu] \cdot [Ni]$ for Model B. Both viscosity models (Model A and Model B) were shown to be valid according to high correlation coefficients and reproducibility values as well as low deviation values calculated (Table 4).

The effects of Cu(II), Ni(II), temperature and As on the kinematic viscosity are presented in Table 4 and Fig. 1. The models show that increase in Cu(II), Ni(II), As

and H_2SO_4 concentrations increased viscosity, while increasing the temperature had an opposite effect (Fig. 3). Temperature had the strongest and H_2SO_4 the weakest effect on the viscosity (Table 4).

These viscosity models were found to be generally in a good agreement with the model proposed by Price and Davenport (1981) and Devochkin et al. (2015) where the effect of As was not taken into account (Fig. 1, [As] = 0 g/dm^3). In addition, the viscosities were predicted with the model of Price and Davenport (1981) and a new Model PD constructed of the electrorefining results from Price and Davenport (1981) for comparison. Price and Davenport (1981) constructed their viscosity model using data from both electrorefining and electrowinning electrolytes. In this study, a new model, Model PD (Table 4), was built using only the electrorefining data published by Price and Davenport (1981). The constructed viscosity Model A was shown to be similar to the model from Price and Davenport (1981) (Fig. 1), while Model PD similar to Model B (Figs. 1 and 2). It seems that Models PD and B predict viscosity more accurately (Figs. 1, 2 and 4) compared to the original model published by Price and Davenport (1981). The viscosity values of Price and Davenport (1981) model gave the maximum 6.4% higher values than the predictions compared to Model PD and the maximum 5.2% higher than Model B in the investigated range.

Table 5. Coefficients, R^2, Q^2 (goodness of prediction), SDY (standard deviation of the response), RSD (residual standard deviation) and reproducibility values of the viscosity models (Model A, Model B and Model PD) built for copper electrorefining electrolyte

$\log_{10}(v)$ (mm^2/s)	Model A	Model B	Model PD
Constant	0.0799	0.09059	0.0201
[Cu]	0.00287	0.002594	0.00368
[H_2SO_4]	0.000529	0.0005569	0.000637
[Ni]	0.00335	0.001967	0.00382
[As]	0.002242	0.0007715	0.000921
[Fe]	-	-	0.0038
T	-0.00704	-0.007057	-0.00617
[Cu]·[Ni]	-	$2.741 \cdot 10^{-5}$	-
Cu·T	-	-	$-1.68 \cdot 10^{-5}$
Ni·T	-	-	$-1.34 \cdot 10^{-5}$
T·[As]	$-1.020 \cdot 10^{-5}$	-	-
R^2	0.996884	0.997296	0.999029
Q^2	0.996086	0.996686	0.998492
SDY	0.081243	0.068193	0.070912
RSD	0.004785	0.003731	0.002426
N	60	63	48
Reproducibility	0.999784	0.999819	-

Figure 3 shows the sensitivity analysis for Model B. According to the sensitivity analysis, Model B was not sensitive to changes in concentrations, however, the temperature value significantly affected the viscosity. For example, 15% decrease in temperature resulted in approximately 15% increase in the viscosity. The sensitivity analysis results also suggested that the accuracy of the Model B was good in the measured concentration ranges since fluctuation in the purity of the chemicals had only a minor effect on the viscosity. The total error in the viscosity values due to fluctuation in the purity of the chemicals and the tolerances in the measured volumes and the measuring temperatures were calculated to be maximum 1.4% if all the values of these variables were assumed as inaccurate as possible.
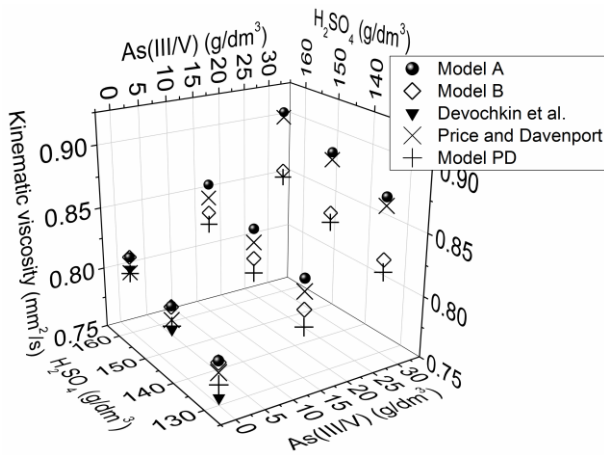
Fig. 1. Effect of H_2SO_4 and As(III/V) on kinematic viscosity of copper electrorefining electrolyte at 65 °C with [Cu(II)] = 50 g/dm^3 and [Ni(II)] = 18 g/dm^3 plotted using Models A and B from this work, and the models of Devochkin et al. (2015), Price and Davenport (1981) and Model PD
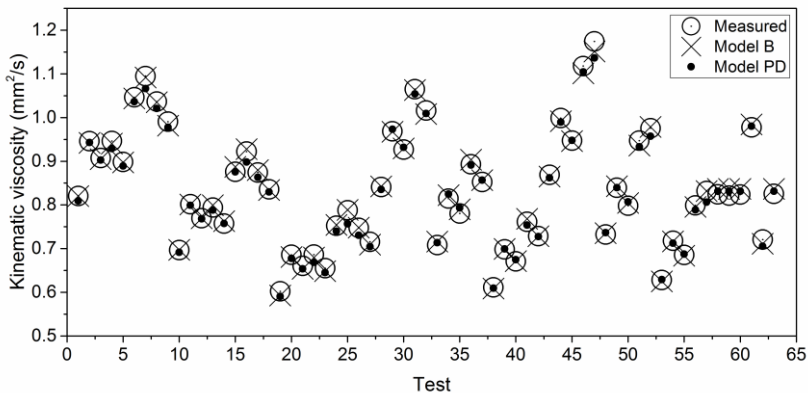
Fig. 2. Kinematic viscosities predicted with Model B and Model PD compared with equivalent measured viscosities of synthetic copper electrorefining electrolytes
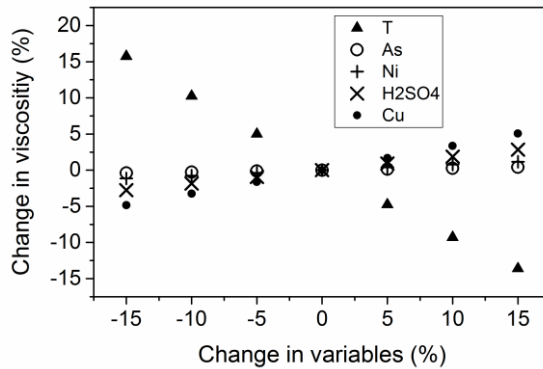
Fig. 3. Effect of changing variables on viscosity with the Model B
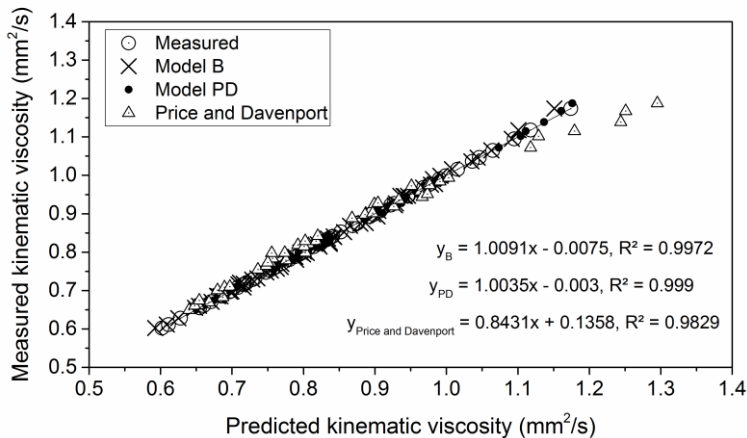
Fig. 4. Measured kinematic viscosity values of copper electrorefining electrolyte
vs. predicted values from Model B, Model PD and Price and Davenport (1981) model

Models A, B and PD were evaluated against industrial electrolyte samples 1-3. For all the samples, Models B and PD were shown to predict the viscosity most accurately. Model B was shown to predict best the viscosity value of the industrial electrolyte (sample 2) and the Model PD (samples 1 and 3) nearest to the measured values (Fig. 5). However, the difference between measured and modeled values was the highest for sample 3 (having the lowest concentration of Cu, Ni and As). The errors between measured and modeled values were the following: Model A 3.7-6.9%, model of Price and Davenport 2.3-6.5%, Model B 0.9-4.5% and Model PD 1.1-3.2%. Consequently, Model PD and Model B seemed to predict the viscosity of the industrial electrolytes with the highest accuracy. It is clear that the synthetic electrolytes are not identical to the industrial ones. The industrial copper electrolytes contain additives such as chlorides and thiourea as well as minor amounts of impurities such as Bi and Sb.

However, the initial validation taking into account the major parameters of the copper electrolyte (copper, nickel, arsenic and sulfuric acid concentrations) indicated a good prediction with Models B and Model PD. This suggests that the effect of additives and minor solution elements is small compared to the effect of parameters investigated.
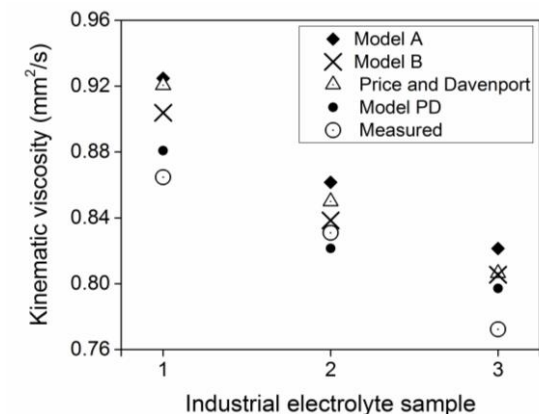

Fig. 5. Kinematic viscosity values of the industrial electrorefining electrolyte samples 1-3
measured at 65 °C vs. values modeled with the Model A, the model
of Price and Davenport (1981), the Model B and the Model PD

Density

Model C constructed for density (Table 5, presented in similar form as viscosity models in Table 4) was shown to have four significant combined effect terms in addition to single effect terms. The combined effect terms were shown to be less significant than the single terms. Therefore, also a streamlined Model $C_{streamlined}$ (Table 5) was constructed by removing the combined effects. The previously published density models did not contain any combined effect terms (Price and Davenport, 1981; Subbaiah and Das, 1989; Jarjoura et al., 2003; Devochkin et al., 2015). The density models constructed were shown to be valid according to high correlation coefficients and reproducibility values calculated (Table 5).

According to the sensitivity analysis, the density models were not sensitive to changes in either concentrations or temperature. The sensitivity results were almost identical in Model C and Model $C_{streamlined}$. For example, 15% decrease in Cu, H_2SO_4 and Ni concentrations resulted in approximately 1.4, 1.0 and 0.3% decrease in the density, respectively, and similar decrease in temperature resulted in approximately 0.5% increase in the density in Model C (Fig. 7). These results of sensitivity analysis also suggested that the accuracies of both density models (Model C and Model $C_{streamlined}$) were good in the measured range (Table 1) since fluctuation in the purity of the chemicals and the tolerances in temperatures had only a minor effect on the density predicted. The error in the density values due to fluctuation in the purity of the

chemicals and the tolerances in solution volumes and the measuring temperatures were calculated to be maximum 0.3%, if all the values of these variables were as inaccurate as possible.

Table 6. Coefficients, R^2, Q^2 (goodness of prediction), SDY (standard deviation of the response), RSD (residual standard deviation) and reproducibility values of the density models (Model C and Model C$_{streamlined}$) built for copper electrorefining electrolyte

ρ (g/cm^3)	Model C	Model C$_{streamlined}$
Constant	0.9828000	1.0346
[Cu]	0.0032690	0.0021617
[H$_2$SO$_4$]	0.0008269	0.00053377
[Ni]	0.0014520	0.002344
T	-0.0005230	-0.00070307
[Cu]·[H$_2$SO$_4$]	$-6.354 \cdot 10^{-6}$	-
[Cu]·[Ni]	$4.364 \cdot 10^{-6}$	-
[Cu]·T	$-3.461 \cdot 10^{-6}$	-
[H$_2$SO$_4$]·[Ni]	$4.37 \cdot 10^{-6}$	-
R^2	0.99989	0.999704
Q^2	0.999759	0.999537
SDY	0.026956	0.026956
RSD	0.000335	0.000501
N	29	29
Reproducibility	0.99994	0.99994
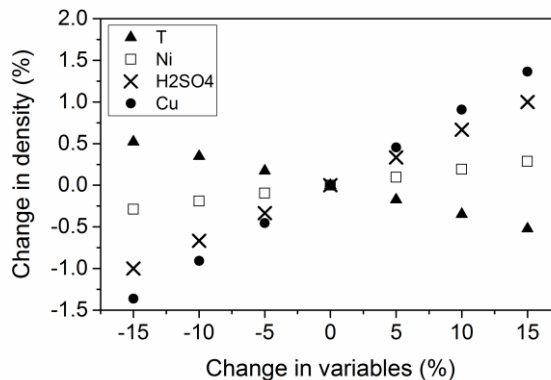
Fig. 6. Effect of changing the variables on density with Model C

The density Model C proposed in this work (Table 6) was shown to be in a good agreement with the results of Price and Davenport (1981) and Devochkin et al. (2015) (Figs. 7 and 8). The density values calculated with the models of Subbaiah and Das

(1989) (Fig. 7) as well as values measured by Jarjoura et al. (2003) were approximately 2% lower than the values calculated with other models (C, C$_{streamlined}$ and Price and Davenport, 1981). The model of Subbaiah and Das (1989) was constructed of experimental results measured mainly at 30 °C which is below the temperature range used in the electrorefining process, and can result in error at higher temperatures. The results of Jarjoura et al. (2003) may be explained by the pipetting method, used for sampling the electrolyte and weighting it as a measuring procedure, being probably less accurate than the use of pycnometer in other studies (Price and Davenport, 1980, 1981; Subbaiah and Das, 1989; Devochkin et al., 2015).
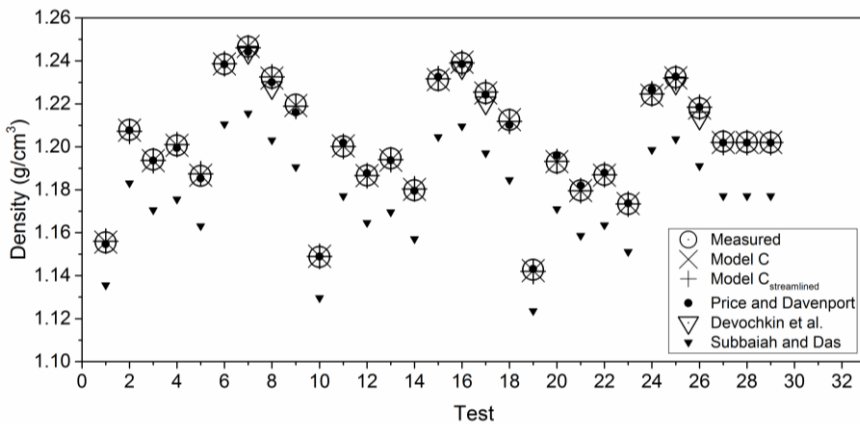
Fig. 7. Densities predicted with Model C, Model C$_{streamlined}$, and models of Price and Davenport (1981), Subbaiah and Das (1989) and Jarjoura et al. (2003) compared with densities measured

$$y_C = 1x - 9 \cdot 10^{-7}, R^2 = 0.9999$$

$$y_{C,streamlined} = 1x + 9 \cdot 10^{-6}, R^2 = 0.9997$$

$$y_{Price\ and\ Davenport} = 0.9799x + 0.0276, R^2 = 0.9921$$
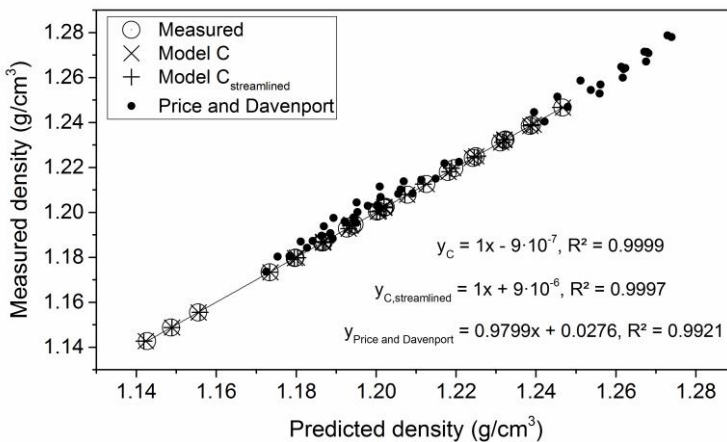
Fig. 8. Measured density values of copper electrorefining electrolyte vs. predicted values from Model B, Model PD and model of Price and Davenport (1981)

Conclusions

Viscosities and densities were measured from synthetic copper electrorefining electrolytes containing various amounts of copper (40-60 g/dm^3), nickel (0-20 g/dm^3) and sulfuric acid (130-160 g/dm^3), as well as arsenic (0-64 g/dm^3). The measurements were conducted at three different temperatures (50, 60 and 70 °C). Based on the results, two models for viscosity (Model A and B) and two for density (Model C and C$_{streamlined}$) were constructed. In addition, one improved viscosity Model PD) was built using the data based on synthetic solution measurements published earlier by Price and Davenport (1981). The models were validated by measuring viscosities of three industrial electrolyte samples of known composition.

Increase in the concentrations of Cu, Ni, As and H$_2$SO$_4$ was found to increase both viscosity and density, whereas temperature was shown to decrease both viscosity and density. This is in agreement with the literature. The effect of arsenic presence on viscosity was found to vary depending on the arsenic source (arsenic acid vs. arsenic from As$_2$O$_3$), As$_2$O$_3$ resulting in higher validity of the viscosity model (Model B). The acid content and minor impurities present in the industrial arsenic acid were shown to increase the value of viscosity measured.

Another model (Model PD) was built based on data published by Price and Davenport (1981). The earlier published model of Price and Davenport (1981) was based on combined data from electrorefining and electrowinning. However, by excluding the electrowinning data of low copper concentrations and taking into account the combined effects of the parameters, a high accuracy refined model for copper electrorefining conditions could be built also from the earlier published data. This model showed good agreement with the Model B (As$_2$O$_3$ as As source).

It was shown that the modeling work carried out in this study (Model B and Model PD) could provide the most reliable and accurate models for copper electrorefining electrolyte in the investigated composition range. Both these viscosity models showed improved accuracy compared to the model of Price and Davenport (1981). One advantage of the viscosity models constructed was that they reveal also the combined effect of parameters investigated. Furthermore, these two models also seemed to predict the viscosity of the industrial electrolytes with the highest accuracy.

The modeled density values based on the data measured in this work were in a good agreement with the earlier published models of Price and Davenport (1981) and Devochkin et al. (2015). Model C was shown to be the most accurate (R^2 and Q^2 values approaching the unity) density model built.

Acknowledgements

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