Densities, Electrical Conductivities and Viscosities of $CuSO_4/H_2SO_4$ Solutions in the Range of Modern Electrorefining and Electrowinning Electrolytes

DEREK C. PRICE AND WILLIAM G. DAVENPORT

Densities, electrical conductivities and viscosities of $CuSO_4$-H_2SO_4-H_2O solutions are reported for electrorefining electrolytes over the ranges:

Temperature	50 to 70°C
Copper concentration	40 to 55 g · dm^{-3}
H_2SO_4 concentration	160 to 220 g · dm^{-3}

and for electrowinning electrolytes over the ranges:

Temperature	20 to 70°C
Copper concentration	10 to 60 g · dm^{-3}
H_2SO_4 concentration	10 to 170 g · dm^{-3}

Empirical and semiempirical equations describing the measured properties are presented.

COPPER sulfate/sulfuric acid solutions form the basis of electrolytes which are used to produce approximately 9 million tonnes of metallic copper per year, 95 pct by electrorefining and 5 pct by electrowinning. A literature survey indicated a lack of consistent density, electrical conductivity, and viscosity data for these electrolytes, a void which is filled in part by the results of the present investigation.

Density, electrical conductivity, and viscosity all have considerable economic importance, conductivity because of its impact on electrical energy consumption and density and viscosity because of their influences on mass and heat transfer. Density and viscosity also influence the carry over of impure particulates into the final copper cathode product.

EXPERIMENTAL

The experiments were carried out over the composition and temperature ranges:

Electrorefining range:

Temperature	50 to 70°C
Copper concentraion	40 to 55 g · dm^{-3}
Free H_2SO_4 concentration	160 to 220 g · dm^{-3}

Electrowinning range:

Temperature	20 to 70°C
Copper concentration	10 to 60 g · dm^{-3}
Free H_2SO_4 concentration	10 to 170 g · dm^{-3}

all concentrations being expressed in grams per dm^3 of solution at 20°C. Free sulfuric acid is defined as the amount of H_2SO_4 added to the solution or the acid equivalent to the $SO_4^=$ ions remaining after all copper is removed as $CuSO_4$.

The experimental solutions used throughout the work were prepared from analytical reagent grade $CuSO_4 \cdot 5H_2O$ and H_2SO_4 (Fisher Scientific) and doubly distilled water. The $CuSO_4 \cdot 5H_2O$ and the H_2SO_4 were analyzed chemically prior to making up the experimental solutions.

Densities were measured by means of standard 25 and 50 ml pycnometers (Fisher Scientific) with at least three measurements being taken for each reported value. The measurements gave specific gravities which were then converted to absolute densities from published[1] water density values. Electrical conductivities were measured with a Tacussel (Lyon, France) conductivity meter type CD 6NG (4000 Hz) in conjunction with a type CM 04 G/R high conductivity cell. The cell was calibrated with a standard N solution of KCl in doubly distilled, nitrogen degassed water. KCl conductivity values for the calibration were taken from the data of Jones and Prendergast[2] as represented and extrapolated by the equation:

$$k = 0.065430 + 1.73972 \times 10^{-3}t + 4.49641 \times 10^{-6}t^2 \qquad [1]$$

where k = conductivity of an N KCl solution, siemen cm^{-1} and t = temperature, °C. Conductivities calculated by this equation are expected to be within $\pm 10^{-6}$ siemen · cm^{-1} near 20°C and better than $\pm 10^{-4}$ siemen · cm^{-1} at 70°C.

Viscosities were determined by means of a Brookfield Syncro-Lectric viscometer, Model LVF (Cooksville, Ontario) with an adapter for low viscosity measurements. The viscometer was calibrated with $CuSO_4/H_2O$ solutions whose viscosities had been determined with a standard Cannon-Fenske routine viscometer (Fisher Scientific).

The results of the measurements are reported in Tables I to III and illustrated in Figs. 1 to 5. The precisions of the tabulated values are estimated to be: density ± 0.0002 g · dm^{-3}; conductivity ± 1/2 pct of the measured value; viscosity ± 0.01 centipoise.

DEREK C. PRICE and WILLIAM G. DAVENPORT are Research Associate and Professor of Metallurgy, Department of Mining and Metallurgical Engineering, McGill University, Montreal, Quebec, Canada H3A 2A7.

Manuscript submitted May 2, 1979.

ISSN 0360-2141/80/0311-0159$00.75/0

RESULTS AND DISCUSSION

1. Density

Although originally intended as a complement to the work on viscosity and electrical conductivity, the density results also fill in previously unexplored regions of electrolyte composition and temperature. Previously, much of the data on the system had been based upon the 1916 results of Holler and Peffer[3] at 25 and 40°C, with more recent contributions by Eisenberg, Tobias, and Wilke[4,5] and Claessens.[6,7] The densities of saturated solutions had also been widely examined.[8–10]

Holler and Peffer were the first to propose that density is a function of the concentration summation $[CuSO_4 \cdot 5H_2O + H_2SO_4]$ rather than of the concentrations of the individual components. This is confirmed for electrorefining electrolytes by the present results, ±2 pct (Fig. 1).

Also noticeable from the present results (Table I) is the extremely small influence of temperature on density, less than 0.0006 $g \cdot dm^{-3}$ per °C. This permits density results to be described accurately by the empirical equation:

$$d \pm 0.005\ g \cdot dm^{-3} = 1.01856 + 0.00238\,[Cu] + 0.00054\,[H_2SO_4] - 0.00059t\ {}^\circ C \qquad [2]$$

where [Cu] and $[H_2SO_4]$ are concentrations of Cu and H_2SO_4, $g \cdot dm^{-3}$ at 20°C. Results calculated by this equation agree very well with the results of Holler and Peffer[3] and Eisenberg *et al.*[4] The values are somewhat higher than those reported by Claessens.[6,7]

2. Electrical Conductivity

The results of the electrical conductivity measurements are reported in Table II and interpreted in Figs. 2 and 3. As Figs. 2 and 3 demonstrate, the strongest influence on electrical conductivity is H_2SO_4 concentration, due to the effect of hydrogen ions in the solution. This is confirmed by the earlier results of Richardson and Taylor,[11] Kern and Chang,[12] Skowronski and Rienoso[13] and several other limited studies.[14–16] The extensive results of the recent study by Claessens *et al*[6,7] confirm this trend qualitatively, but quantitatively their conductivity values are in disagreement with those from the present and other previous work, especially at higher temperatures.

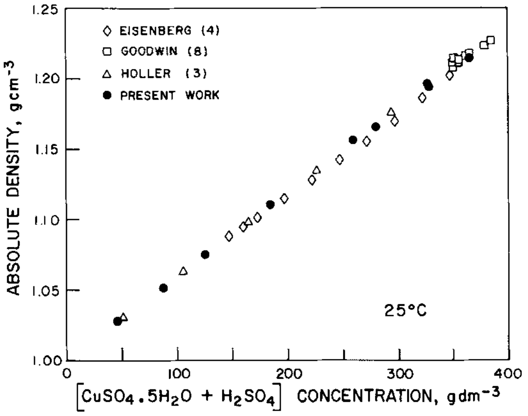

Fig. 1—Absolute densities of $CuSO_4$-H_2SO_4 solutions as a function of combined $[CuSO_4 \cdot 5H_2O + H_2SO_4]$ concentration (25°C).

Table I. Absolute Densities of $CuSO_4$-H_2SO_4 Solutions

Concentration, $g \cdot dm^{-3}$, 20°C		Absolute Density, $g \cdot cm^{-3}$		
			Electrowinning Range	
Cu	H_2SO_4	20°C	30°C	40°C
10	9.56	1.0295	1.0265	1.0226
10	47.80	1.0536	1.0496	1.0452
10	86.04	1.0768	1.0727	1.0677
35	47.80	1.1130	1.1087	1.1036
35	143.40	1.1691	1.1639	1.1573
35	191.20	1.1974	1.1911	1.1844
60	23.90	1.1581	1.1537	1.1488
60	95.60	1.1989	1.1932	1.1869
60	167.30	–	1.2325	1.2274
		50°C	60°C	70°C
25	14.34	1.0565	1.0508	1.0453
25	42.02	1.0699	1.0637	1.0581
25	71.70	1.0885	1.0824	1.0765
40	4.78	1.0870	1.0813	1.0753
40	28.68	1.0992	1.0937	1.0872
40	52.58	1.1121	1.1064	1.0999
55	9.56	1.1301	1.1244	1.1180
55	33.46	1.1423	1.1358	1.1294
55	57.36	1.1547	1.1487	1.1421
			Electrorefining Range	
		50°C	60°C	70°C
40	163.40	1.1742	1.1683	1.1617
40	182.60	1.1841	1.1784	1.1725
40	201.80	1.1955	1.1893	1.1836
40	221.00	1.2054	1.1996	1.1938
45	163.40	1.1844	1.1781	1.1718
45	182.60	1.1948	1.1886	1.1831
45	201.80	1.2054	1.1996	1.1952
45	221.00	1.2164	1.2097	1.2034
50	163.40	1.1954	1.1881	1.1827
50	182.60	1.2051	1.2000	1.1911
50	201.80	1.2161	1.2100	1.2036
50	221.00	1.2253	1.2204	1.2140
55	163.40	1.2056	1.2014	1.1974
55	182.60	1.2162	1.2119	1.2065
55	201.80	1.2273	1.2218	1.2162
55	221.00	1.2379	1.2329	1.2263

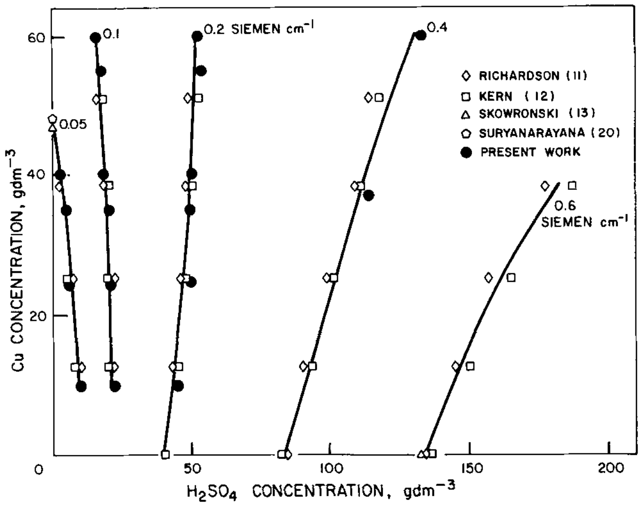

Fig. 2—Isoconductivity lines for the $CuSO_4$-H_2SO_4 system as a function of copper and sulfuric acid concentration (40°C). The points on each isoconductivity line have been interpolated from measured conductivity values (previous work and Table II).

Table II. Specific Conductivities of $CuSO_4$-H_2SO_4 Solutions

Concentration, $g \cdot dm^{-3}$, 20°C			Specific Conductivity, Millisiemen · cm^{-1}				
			Electrowinning Range				
Cu	H_2SO_4	20°C	30°C	40°C	50°C	60°C	70°C
0	23.9	103.2	114.6	124.1	134.0	144.7	153.9
0	38.24	158.0	177.2	190.0	205.2	222.5	236.3
10	9.56	44.1	48.6	51.5	54.6	58.3	59.1
10	47.80	182.0	201.2	214.8	228.3	242.8	254.8
10	86.84	304.9	335.8	363.4	384.2	411.9	433.3
35	47.80	165.8	182.5	195.0			
35	143.4	389.5	436.4	479.5			
35	191.2	461.4	521.8	574.7			
60	23.9	96.2	110.0	119.6			
60	95.6	257.4	289.5	314.6			
60	167.3	372.2	421.2	465.5			
25	14.34	65.5	73.2	78.3	83.6	87.0	90.6
25	43.02	157.8	172.5	182.2	192.1	202.9	212.3
25	71.70	241.1	266.7	284.4	307.0	324.0	341.8
40	4.78	43.7	51.5	58.1	65.3	71.3	76.6
40	28.68	108.4	120.5	131.2	140.4	147.0	153.3
40	52.58	176.2	195.4	207.8	223.4	234.0	243.3
55	9.56	62.3	72.5	81.3	93.9	99.0	107.1
55	33.46	119.4	135.7	147.4	158.3	170.4	177.6
55	57.36	178.5	198.9	213.6	230.6	242.4	254.3
				Electrorefining Range			
40	163.40				616	655	687
40	182.60				666	698	749
40	201.80				703	748	805
40	221.00				747	803	854
45	163.40				597	630	669
45	182.60				641	692	730
45	201.80				691	741	780
45	221.00				728	779	830
50	163.40				585	624	650
50	182.60				635	667	706
50	201.80				672	717	761
50	221.00				703	760	805
55	163.40				569	606	638
55	182.60				613	661	693
55	201.80				653	698	737
55	221.00				699	741	786

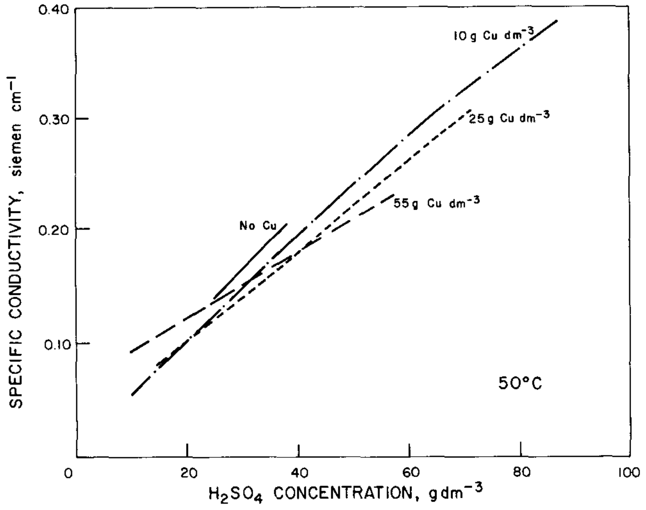

Fig. 3—Specific conductivities of $CuSO_4$-H_2SO_4 solutions at 50°C. The effect of Cu concentration on the slopes is noticeable.

The effects of copper concentration on conductivity are illustrated in Fig. 2, which plots isoconductivity lines as a function of [Cu] and [H_2SO_4], and in Fig. 3, which plots conductivities at constant copper concentrations as a function of [H_2SO_4]. It can be seen that:

a) below about 20 g $\cdot dm^{-3}$ H_2SO_4 an increasing copper concentration (constant [H_2SO_4]) increases conductivity;

b) above 40 g $\cdot dm^{-3}$ H_2SO_4 the opposite occurs. The H_2SO_4 concentration at which the effect of Cu reverses is sensitive to temperature but the effect is always noticeable (Table II).

Expression of electrical conductivity in equation form as a function of temperature and Cu and H_2SO_4 concentrations is made difficult by the complicated effect of copper. However, over the electrorefining range, the equation:

$$k = 0.134 - 0.00356\,[\mathrm{Cu}] + 0.00249\,[H_2SO_4] + 0.00426\,t^\circ\mathrm{C} \qquad [3]$$

represents the measured conductivity values (siemen $\cdot$ cm^{-1}) ± 2 pct.

Conductivites under electrowinning conditions are best interpolated directly from the experimental data in Table II.

Minimum power consumption during electrolysis is obtained at maximum electrical conductivity. From this point of view it is clear that electrorefining (H_2SO_4 concentration 160 to 220 g $\cdot dm^{-3}$) should be carried out with as low a copper concentration as possible, as should electrowinning from solvent extraction electrolytes (H_2SO_4 concentrations 130 to 150 g $\cdot dm^{-3}$).

3. Viscosity

The principal previous work on viscosities of $CuSO_4$-H_2SO_4 solutions is that of Eisenberg[4] at 10 to 30°C and Claessens[6] at 25 and 50°C. Investigations of dilute solutions have also been carried out.[17,18]

The results of the present work are presented in Table III and Figs. 4 and 5. As Fig. 4 shows, the 25°C results of the present work are in good agreement with the data obtained by Claessens. They do, however,

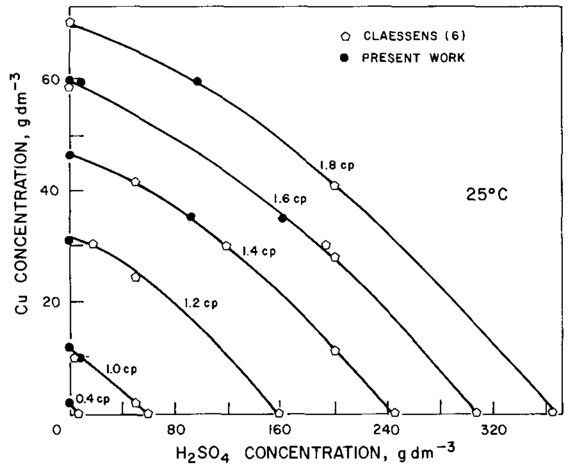

Fig. 4—Isoviscosity lines for the $CuSO_4$-H_2SO_4 system, 25°C. The points on each isoviscosity line have been interpolated from measured viscosity values.

Table III. Absolute Viscosities of $CuSO_4$-H_2SO_4 Solutions

Concentration, $g \cdot dm^{-3}$, 20°C		Absolute Viscosity, Centipoise		
		Electrowinning Range		
Cu	H_2SO_4	20°C	30°C	40°C
10	9.56	1.13	0.879	0.699
10	47.80	1.17	0.922	0.720
10	86.04	1.26	0.967	0.749
35	47.80	1.50	1.16	0.926
35	143.40	1.76	1.33	1.09
35	191.20	1.91	1.48	1.20
60	23.90	1.84	1.41	1.14
60	95.60	2.03	1.56	1.26
60	167.30	2.30	1.69	1.42
		50°C	60°C	70°C
25	14.34	0.715	0.560	0.486
25	42.02	0.759	0.607	0.518
25	71.70	0.778	0.654	0.563
40	4.78	0.820	0.678	0.563
40	28.68	0.835	0.690	0.583
40	52.58	0.855	0.711	0.627
55	9.56	0.917	0.795	0.664
55	33.46	0.935	0.813	0.701
55	57.36	0.951	0.841	0.743
		Electrorefining Range		
		50°C	60°C	70°C
40	163.40	1.03	0.891	0.768
40	182.60	1.06	0.915	0.784
40	201.80	1.10	0.946	0.811
40	221.00	1.16	0.972	0.837
45	163.40	1.07	0.925	0.784
45	182.60	1.12	0.946	0.811
45	201.80	1.17	0.988	0.850
45	221.00	1.20	1.00	0.872
50	163.40	1.10	0.946	0.811
50	182.60	1.15	0.972	0.837
50	201.80	1.20	1.00	0.872
50	221.00	1.24	1.03	0.896
55	163.40	1.19	1.00	0.850
55	182.60	1.20	1.02	0.889
55	201.80	1.25	1.04	0.923
55	221.00	1.29	1.08	0.948

tend to be somewhat higher than Claessens' results at 50°C. Eisenberg *et al*'s viscosity data have not been compared with the present results because the viscosity data of their two investigations are not consistent.[4,5]

Figure 4 demonstrates clearly that viscosity is affected by both Cu and H_2SO_4 concentrations. It is also affected significantly by temperature. For this reason it has been difficult to represent all 102 viscosity values by a simple equation. However, the empirical equation:

$$\eta = 10^{-6}(1592 + 0.0108[H_2SO_4]^2 + 2.373[H_2SO_4] + 29.93[Cu] + 76.48[Cu]^{1/2})\exp\frac{1890}{T(K)} \quad [4]$$

represents all the data $\pm 10^{-1}$ centipoise and the 50 to 70°C data $\pm 0.4 \times 10^{-1}$ centipoise.

Asmus[17] suggested that the viscosities of complex ionic solutions may be expressed in terms of the ional concentration

$$\Gamma = \Sigma C_i Z_i^2 \quad [5]$$

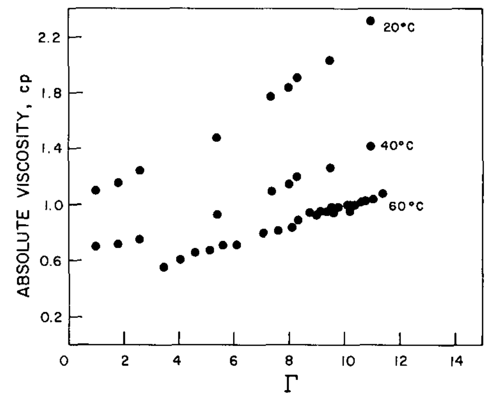

Fig. 5—Absolute viscosities of $CuSO_4$-H_2SO_4 solutions as a function of Γ, the ional concentration.

where C_i is the concentration of ion i in gram ions $\cdot dm^{-3}$ and Z_i is the valence of ion i. As Claessens[6] has pointed out, the importance of this concept is that it might be applicable to industrial electrolytes which contain significant concentrations of impurity ions, *e.g.* nickel, arsenic, and iron.

In the case of copper sulfate-sulfuric acid solutions, H_2SO_4 is assumed to dissociate into H^+ and HSO_4^- ions.[7] For these two ions, the sum of the ion concentrations is:

$$C = 2 \times \frac{[H_2SO_4]}{MW_{H_2SO_4}} \quad [6]$$

and $Z = 1$. Similarly $CuSO_4$ dissociates into Cu^{++} and $SO_4^=$ so that $Z = 2$ and,

$$C = 2 \times \frac{[CuSO_4 \cdot 5H_2O]}{MW_{CuSO_4 \cdot 5H_2O}} = 2 \times \frac{[Cu]}{MW_{Cu}} \quad [7]$$

Thus for $CuSO_4$-H_2SO_4 solutions:

$$\Gamma = 2 \times \frac{[H_2SO_4]}{98.08} \times (1)^2 + 2 \times \frac{[Cu]}{63.54} \times (2)^2 \quad [8]$$

Viscosity is plotted as a function of this variable in Fig. 5, showing a good correlation at all temperatures, while the equation:

$$\eta = 10^{-6}\,(1834 + 2.609\Gamma^{1/2} + 256.9\Gamma - 44.56\Gamma^2) \times \exp\frac{1890}{T(K)} \quad [9]$$

describes the experimental viscosities ± 0.1 centipoise. Kocharev[19] reports similar success with this type of equation for representing nickel in $CuSO_4$-H_2SO_4 electrolytes. Further data are, however, required to test it adequately for that purpose.

In practical terms, the experimental data clearly show that viscosity is minimized by high temperature and by low concentrations of sulfuric acid and copper.

CONCLUSIONS

1. Densities, electrical conductivities and viscosities of $CuSO_4$-H_2SO_4 solutions in the electrorefining and electrowinning ranges of composition and temperature have been measured. The measurements extend considerably the range of available data.

2. The density and conductivity results are in agreement with previously measured values. The viscosity results agree with previous work at 25°C but tend to be somewhat higher at 50°C.

3. In general, electrorefining and electrowinning should be carried out under conditions of high electrical conductivity and low viscosity. These are both promoted by high temperatures and low copper concentrations.

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