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Physicochemical Properties of $ZnSO_4-H_2SO_4-H_2O$ Electrolytes of Relevance to Zinc Electrowinning

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To facilitate the optimization of and/or design of zinc electrowinning reactors, certain properties of zinc electrolytes, which are functions of electrolyte composition and temperature, have been investigated through a literature review that has been complemented, where applicable, by theoretical calculations. A new set of Pitzer model parameters has been determined for $ZnSO_4-H_2SO_4-H_2O$ solutions from an examination of isopiestic data. Empirical correlations for zinc electrolyte conductivity, absolute viscosity, and density have also been examined. An expression for predicting the diffusion coefficient of zinc ions in acidic zinc sulfate solutions was also developed.

Introduction

Zinc metal is mainly produced by electrowinning in parallel plate electrolytic cells from aqueous solutions containing zinc sulfate (55 to 75 $g\cdot dm^{-3}$ Zn^{2+}) and sulfuric acid (125 to 175 $g\cdot dm^{-3}$ H_2SO_4) at 35 to 45 °C at current densities ranging from 400 to 650 $A\cdot m^{-2}$. These ranges of operating conditions have been determined through years of trial and error using conventional solution purification techniques. The possible application of solvent extraction[1−3] and insoluble dimensionally stable anodes,[3−8] capable of maintaining ultrapure electrolytes, raises the possibility of electrowinning zinc under solution conditions outside the conventional ranges of temperature and composition. However, predicting the performance of zinc electrowinning in nonconventional electrolytes requires estimates of certain properties of the electrolyte, such as the reversible potential for zinc deposition, electrolyte conductivity, viscosity, density, and the diffusion coefficient for zinc ions. Although this information often exists in the literature, it appears scattered and sometimes conflicts from one source to another, making it difficult to decide which data to employ in engineering calculations. This article focused on reviewing previously reported expressions for calculating the properties of zinc electrolytes and, where deemed necessary, offers new expressions for calculating those properties in order to create a single reliable source to assist in the design and optimization of zinc electrowinning reactors.

Typical Electrochemical Reactor Design Calculations

Electrowinning performance is often reported in terms of the specific electrical energy consumption, SEEC (kWh (ton of Zn)$^{-1}$), which is a function of cell voltage, U (V), and fractional current efficiency, Φ_e:

$$\text{SEEC/kWh (ton of Zn)}^{-1} = \frac{nF|U|}{3.6 M_{Zn} \Phi_e} \qquad (1)$$

where M_{Zn} (65.39 $g\cdot mol^{-1}$) is the molecular mass of zinc, n (2) is the number of electrons in the overall deposition reaction, and F (96485 C equiv^{-1}) is the Faraday's constant. Conventional zinc electrowinning consumes a large amount of electricity, ca. 3300 kWh (ton of Zn)$^{-1}$. The contributions to the SEEC of zinc electrowinning from the cell voltage and current efficiency largely depend on electrolyte composition and temperature. The cell voltage is a function of the equilibrium potentials for oxygen evolution (the conventional anode reaction) and zinc deposition, E_{H_2O} and E_{Zn}, their associated overpotentials, η_{H_2O} and η_{Zn}, and the ohmic drop through the cell as follows:

$$U = -\left(E_{H_2O} + \eta_{H_2O} - E_{Zn} - \eta_{Zn} + \frac{I}{\sigma}\left(\frac{l}{A_e}\right)\right) \qquad (2)$$

where I (A) is the current, σ ($S\cdot m^{-1}$) is the specific conductivity of the electrolyte, l (m) is the interelectrode gap, and A_e (m) is the electrode area. Although the overpotentials depend somewhat on solution composition, they are also a function of cell geometry and the production rate of zinc. Their prediction is beyond the scope of this work.

The design of new electrowinning processes or modifications to existing processes often involves scale-up of testwork performed in a laboratory-sized cell. The mass transport within the cell, expressed as the Sherwood number (Sh), is usually fit to a dimensionless group correlation of the following form:

$$Sh = aRe^{b}Gr^{c}Sc^{d} \qquad (3)$$

where a, b, c, and d are constants. Evaluation of the Reynolds number (Re), Grashof number (Gr), and Schmidt number (Sc) for a given set of experimental conditions requires estimates of certain physicochemical properties of the electrolyte, namely, absolute viscosity, η ($kg\cdot m^{-1}\cdot s^{-1}$); density, ρ ($kg\cdot m^{-3}$); and diffusion coefficient of zinc ions, $D_{Zn^{2+}}$ ($m^2\cdot s^{-1}$). A description of methods for determining the constant terms in eq 3 as well the dimensionless numbers therein appears elsewhere.[9]

Results

Activities of Species. The familiar Nernst equation relates equilibrium potentials to concentrations and electrolyte temperature, provided the relationship between concentration and activity can be modeled. In this regard, models that are extensions of the Debye−Hückel limiting law (DHLL) may be applied to $ZnSO_4-H_2SO_4-H_2O$ electrolytes. Such a model was

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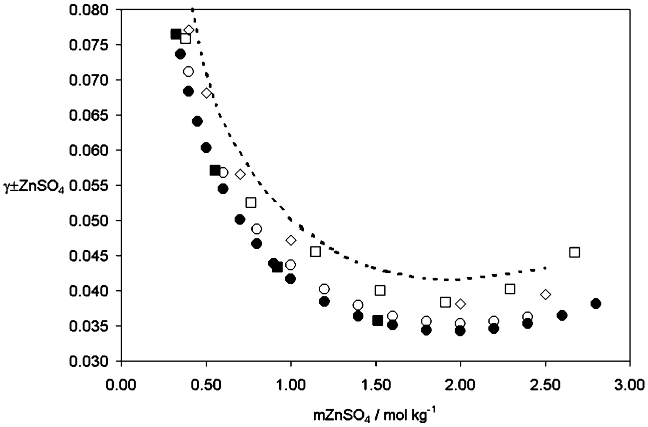

Figure 1. Mean activity coefficient of zinc sulfate at 25 °C, from - - -, ref 13; □, ref 16; ○, ref 14; ◇, ref 15; ●, ref 17; and ■, ref 18 plotted against zinc sulfate molality.

Table 1. Single Salt Pitzer Parameters for 0 to 4.3 mol·dm^{-3} ZnSO$_4$ at 25 °C

$\beta^{(0)}$ $Zn^{2+}-SO_4^{2-}$	$\beta^{(1)}$ $Zn^{2+}-SO_4^{2-}$	$\beta^{(2)}$ $Zn^{2+}-SO_4^{2-}$	C^{ϕ} $Zn^{2+}-SO_4^{2-}$	χ^2
0.189	2.870	−66.467	0.0329	0.022

developed by Filippou et al.[10] and later extended by Wang and Dreisinger.[11] In the model, activity coefficients for each species are calculated using empirical correction terms that are solely functions of ionic strength. Although predicted and measured pH values showed generally good agreement for the zinc sulfate electrolytes tested, folding all ion interactions into the single effect of ionic strength must be recognized as a potential source of error, particularly when the model is applied to strong industrial zinc electrolytes.

The Pitzer model has been widely employed to model the effects of specific ion interactions on activity coefficients for complex high ionic strength electrolytes. The physical meanings of the parameters of the Pitzer model and their determination from isopiestic data have been described elsewhere.[12] In fact, Pitzer parameters for the $ZnSO_4-H_2SO_4-H_2O$ system at 25 °C have been reported by Klocker et al.[13] from a fit of the isopiestic data of Majima et al.[14] Data for this system has also been reported by Tartar et al.[15] and Horváth and Wéber.[16]

By inspection of Figure 1, the values of mean zinc sulfate activity coefficient reported by Majima et al. closely match those recently reported by Albright et al.[17] and Malatesta and Zamboni[18] for pure zinc sulfate. However, as also indicated in Figure 1, the calculated mean activity coefficients of zinc sulfate using the Pitzer parameters reported by Klocker et al.[13] do not match the values reported by Majima et al.[14] This is unfortunate, given these parameters were purportedly derived solely from a fit of the data set of Majima et al.

Various sets of Pitzer parameters were fit to the isopiestic data of Majima et al.[14] by the procedure described in Appendix A. The uncertainty in the osmotic coefficient data of Majima et al. (σ_{obs}) was assigned as the combined variance of the differences in corresponding osmotic coefficients reported by Albright et al.[17] for $ZnSO_4$ (σ_{Zn}) and by Clegg[19] for H_2SO_4 (σ_H), which were assumed to be accurate:

$$\sigma_{obs} = \sqrt{(\sigma_{Zn})^2 + (\sigma_H)^2} = \sqrt{(0.059)^2 + (0.003)^2} = 0.059 \quad (4)$$

Pitzer parameters for the interactions between Zn^{2+} and SO_4^{2-} (Table 1) were fit using a set of 62 osmotic coefficients, $N_{obs} = 62$, reported by Albright et al.[17] for pure $ZnSO_4$, while other interactions parameters which included Zn^{2+} ions (Table 2) were subsequently fit using the set of 69 observed osmotic coefficients, $N_{obs} = 69$, of Majima et al. of $ZnSO_4-H_2SO_4-H_2O$ electrolytes. The Pitzer parameters for H_2SO_4 of Hovey et al.[20] were not modified since they are relatively well-established and have been used to generate ternary mixing parameters for the similar $M_xSO_4-H_2SO_4-H_2O$ systems.[20−23] The introduction of additional ternary mixing parameters, beyond those presented in Table 2, did not improve the fit significantly and resulted in higher χ^2 values. Although parameter sets 2 to 5 yielded similar χ^2 values, Set 3 was accepted as the best choice since their values were within typical ranges for similarly evaluated parameters.[24] In comparison, the value of χ^2 calculated using the parameter set of Klocker et al.[13] was 0.084. The distribution of residuals using parameter set 3 (see Figure 2) also appears random, which adds further confidence for accepting them for this system.

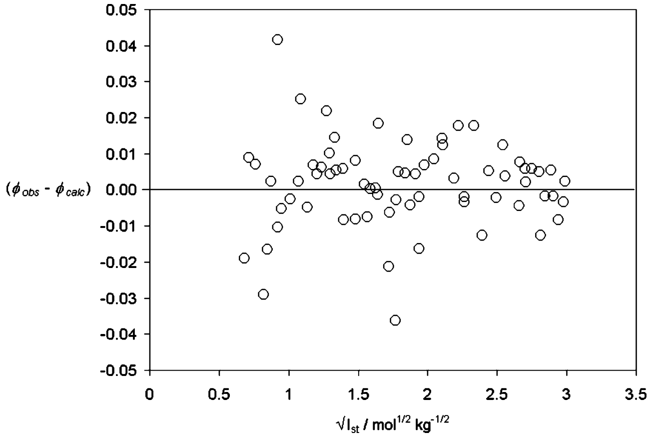

Figure 2. Deviations between measured and fitted stoichiometric osmotic coefficient for $ZnSO_4-H_2SO_4-H_2O$ (○) at 25 °C plotted against the square root of stoichiometric ionic strength. Data taken from ref 14.

Table 2. Ternary System Pitzer Parameters for 0 to 2.5 mol·dm^{-3} ZnSO$_4$ and 0 to 2.0 mol·dm^{-3} H$_2$SO$_4$ at 25 °C[a]

set	$\beta^{(0)}$ $Zn^{2+}-HSO_4^-$	$\beta^{(1)}$ $Zn^{2+}-HSO_4^-$	C^{ϕ} $Zn^{2+}-HSO_4^-$	Ψ $Zn^{2+}-HSO_4^- -SO_4^{2-}$	χ^2
1	0.568				0.205
2	0.535	1.093			0.044
3	0.439	1.811	0.0397		0.044
4	0.507	1.326		0.0242	0.045
5	0.437	1.796	0.0616	−0.0432	0.043

[a] $\sigma_{obs} = 0.059$, $N_{obs} = 69$.

Pitzer ion interaction parameters are functions of temperature. Equations for adjusting the set of Pitzer parameters for sulfuric acid have been reported by Reardon.[22] The following expressions for adjusting the $Zn^{2+}-SO_4^{2-}$ interaction parameters as a function of temperature (K) have been generated by the authors using the corresponding temperature derivatives reported by Silvester and Pitzer:[25]

$$\beta^{(0)}_{Zn^{2+}SO_4{}^{2-}} = 1.280 - 0.00366T \quad (5)$$

$$\beta^{(1)}_{Zn^{2+}SO_4{}^{2-}} = -4.077 + 0.0233T \quad (6)$$

$$\beta^{(2)}_{Zn^{2+}SO_4{}^{2-}} = 32.817 - 0.333T \quad (7)$$

$$C^{\phi}_{Zn^{2+}SO_4{}^{2-}} = -1.151 + 0.00397T \quad (8)$$

The temperature dependency of the $Zn^{2+}-HSO_4^-$ ion interaction parameters have not been estimated. However, the temperature derivatives of these terms are expected to be relatively small, and temperature changes of even 20 deg should cause little change in these parameters.[25] Thus, for engineering calculations, extrapolation of Pitzer model calculations to temperatures more relevant to industrial zinc electrowinning, ca. 35 to 45 °C, should be possible after adjustment of the Debye−Hückel term (A) and equilibrium constant for bisulfate dissociation (K), for example:

$$A \approx 0.377 + 4.684 \times 10^{-4}(T - 273.15) + 3.74 \times 10^{-6}(T - 273.15)^{2} \text{ [26]} \quad (9)$$

$$\log (K) \approx 562.69486 - 102.5154 \ln (T) - 1.117033 \times 10^{-4}\, T^{2} + 0.2477538T - 13273.75/T \text{ [19]} \quad (10)$$

Electrolyte Conductivity. There are a few empirical expressions for calculating the specific conductivity of acidic zinc sulfate electrolytes in the literature:

$$\sigma = 23.92 + 0.27[H_2SO_4](T - 308) + 19.6[H_2SO_4] - 11.1([Zn^{2+}] + [Mn^{2+}] + [Mg^{2+}] + 0.5[NH_4^{+}]) \text{ [27]} \quad (11)$$

$$\sigma = 12.3 + 18.93[H_2SO_4] - 7.78[Zn^{2+}] + 0.114(T - 273) \text{ [28]} \quad (12)$$

$$\sigma = 0.4 + 0.115(T - 273) + 0.282[H_2SO_4](T - 273) + 34.42[H_2SO_4] - 4.51[H_2SO_4]^2 + 2.86([Zn^{2+}] + [Mg^{2+}])^2 + ([Zn^{2+}] + [Mg^{2+}])(-0.114(T - 273) - 10.58[H_2SO_4] - 2.24) \text{ [29]} \quad (13)$$

$$\sigma = -10.79[Zn^{2+}] - 53.90[H_2SO_4] - 1.814[Zn^{2+}]^2 - 6.380[H_2SO_4]^2 - 1.027[Zn^{2+}][H_2SO_4] + 16.73[Zn^{2+}]^2[H_2SO_4] + 0.0585[Zn^{2+}]T + 12.46[Zn^{2+}][H_2SO_4]^2 - 6.762[Zn^{2+}]^2[H_2SO_4]^2 + 0.3345[H_2SO_4]T - 0.1341[Zn^{2+}][H_2SO_4]T \quad (14)$$

Concentrations in the above equations, as well as in subsequent equations for calculating viscosity, density, and diffusion coefficients, are not those of specific aqueous species but are rather total molar concentrations (mol·dm^{-3}), as would be obtained through chemical analysis of solution samples. The final correlation was generated by the authors by a least-squares fit of the conductivity measurements reported by Hinatsu et al.[30] and matches their data to within ±0.55 $\Omega^{-1}\cdot m^{-1}$ (see Figure 3). All the above correlations give similar results for typical industrial zinc electrolytes, ca. 1 mol·dm^{-3} $ZnSO_4$ and 1.5 mol·dm^{-3} H_2SO_4 at 308 K (38.42 ±0.75 $\Omega^{-1}\cdot m^{-1}$), but differ significantly when applied to nonconventional electrolyte compositions and temperatures. The higher order expressions reported by Tozawa et al.[29] and the authors of this work were both generated for solutions containing ca. 0 to 1.2 mol·dm^{-3} Zn^{2+}, with <2 mol·dm^{-3} H_2SO_4, at 25 to 60 °C, and either are applicable for predicting electrolyte conductivity over a wider range of electrolyte compositions and temperatures as compared to the other expressions.

It should be pointed out that during zinc electrowinning, a fraction of the electrolyte becomes entrained with evolved oxygen and hydrogen gas bubbles. These bubbles act as insulating spheres that reduce the overall conductivity of the electrolyte. Hence, the calculated electrolyte conductivity should be adjusted according to a prediction of the mean fraction of bubbles in the electrolyte, f_m.[31,32]

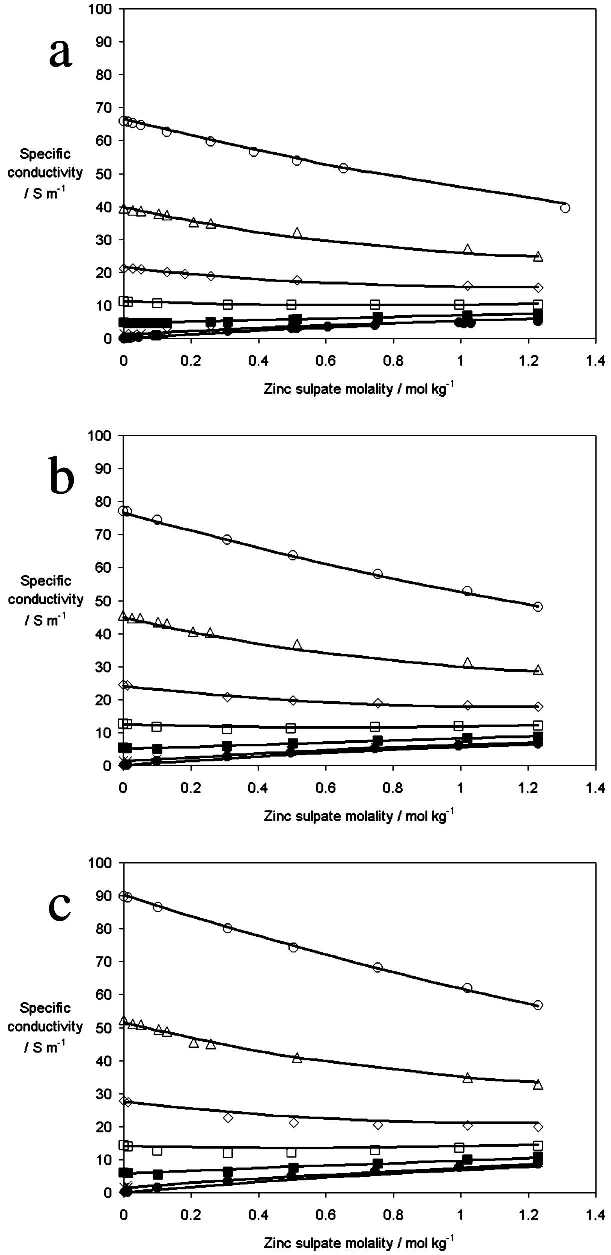

Figure 3. Specific conductivity of zinc sulfate electrolytes containing ●, 0; ×, 0.0253; ■, 0.101; □, 0.253; ◇, 0.507; △, 1.01; and ○, 2.02 mol·kg^{-1} H_2SO_4 at 25 °C (a), 40 °C (b), and 60 °C (c), and corresponding fitted curves (—) according to ref 11, plotted against zinc sulfate molality. Data taken from ref 30.

Current Efficiency. Zinc electrodeposition from acidic sulfate electrolytes is always accompanied by some degree of hydrogen evolution. The following empirical relationship, which is commonly referred to as Wark's rule,[33] predicts current efficiency in industrial zinc electrowinning based on the ratio of concentrations of zinc sulfate and sulfuric acid:

$$\frac{\Phi_e}{1 - \Phi_e} = \frac{1}{k}\frac{[ZnSO_4]}{[H_2SO_4]} \quad (15)$$

Biegler and Frazer[34] estimated k to be 0.0137 for $[ZnSO_4]/[H_2SO_4]$ ratios of between 0.3 and 2.0 using synthetic electrolytes containing no detectable impurities. The highest achievable current efficiencies occur for impurity-free electrolyte since enhanced hydrogen evolution generally occurs on co-deposited impurities.[35−38] As such, if even trace levels of impurities are

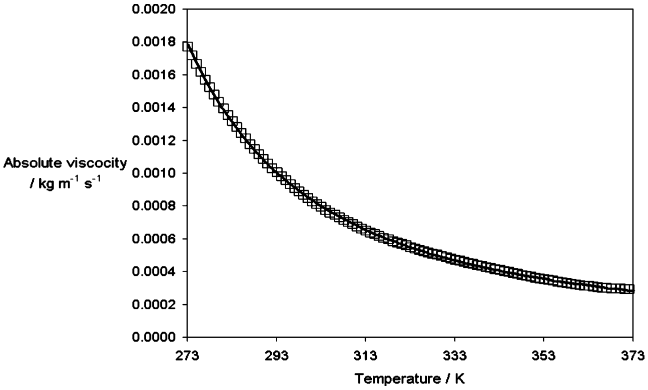

Figure 4. Absolute viscosity of pure water (□) and corresponding fitted curve (—) according to eq 15 plotted against absolute temperature. Data taken from ref 42.

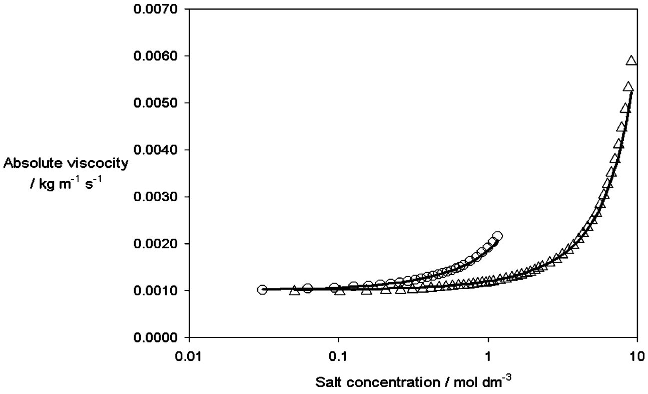

Figure 5. Absolute viscosity of aqueous zinc sulfate (○) and sulfuric acid (△) at 21 °C and corresponding fitted curves (—) according to eq 15 plotted against salt concentration. Data taken from ref 42.

present in a real zinc electrolyte, then the magnitude of k should be experimentally determined.

Electrolyte Viscosity. Though there are several instances where individual measurements of zinc electrolyte viscosity have been reported, only two expressions for calculating absolute viscosity of zinc electrolytes as a function of composition (mol·dm^{-3}) were found in the literature:

$$\eta = \{255.6 + 9.1[\mathrm{H_2SO_4}] + 1.0[\mathrm{H_2SO_4}]^2 - 4.0(T - 273) + 0.036(T - 273)^2 - 1.6([\mathrm{Zn^{2+}}] + 0.83[\mathrm{Mn^{2+}}])(T - 273)\} \times 10^{-5}\,\text{[39]} \qquad (16)$$

$$\eta = \left\{17.7 + 4.1[\mathrm{H_2SO_4}] - (1.0 + 2.5[\mathrm{H_2SO_4}])([\mathrm{Zn^{2+}}] + [\mathrm{Mg^{2+}}]) \exp\left(\frac{15\,200 + (1850 + 225[\mathrm{H_2SO_4}])([\mathrm{Zn^{2+}}] + [\mathrm{Mg^{2+}}])}{RT}\right)\right\} \times 10^{-7}\,\text{[40]} \qquad (17)$$

The viscosities calculated using the above expressions differ significantly, ca. 100 % over the typical industrial zinc electrolyte compositional range (0.84 to 1.15 mol·dm^{-3} $\mathrm{ZnSO_4}$ and 1.27 to 1.78 mol·dm^{-3} $\mathrm{H_2SO_4}$) and temperature range (35 to 45 °C). To test the validity of the above equations, a viscosity model of the type employed by Immura and Toguri[41] for nickel electrolytes (eq 18) was fit to viscosity data for pure water from 0 to 100 °C, zinc sulfate solutions at 21 °C, and sulfuric acid solutions at 21 °C:[42]

$$\eta = (0.4332344 - 4.998831 \times 10^{-3}T + 2.174276 \times 10^{-5}T^2 - 4.216447 \times 10^{-8}T^3 + 3.072309 \times 10^{-11}T^4) \exp(0.6182[\mathrm{ZnSO_4}] + 0.1801[\mathrm{H_2SO_4}]) \qquad (18)$$

The preexponential polynomial calculates the temperature-dependent viscosity of the pure solvent (Figure 4) while the exponential terms represent the modifying effect of each salt's concentration (Figure 5). Although developed independently, eq 18 fits the data of Umetsu et al. almost as well as their own expression (the standard deviation between predicted and measured absolute viscosities was 5.9 × 10^{-5} kg·m^{-1}·s^{-1} using eq 15 and 4.2 × 10^{-5} kg·m^{-1}·s^{-1} using eq 17). Thus, eq 17 is suggested for calculating the absolute viscosity of zinc electrolytes.

Electrolyte Density. Several equations for calculating zinc electrolyte density, ρ (kg·m^{-3}), as a function of electrolyte composition (mol·dm^{-3}) were found in the literature:

$$\rho = 1153.82 + 66.748[\mathrm{H_2SO_4}] + 181.436[\mathrm{Zn^{2+}}] + 158.354[\mathrm{Fe^{2+}}] + 396.312[\mathrm{Fe^{3+}}] - 0.55T\,\text{[10]} \qquad (19)$$

$$\rho = 1000 + 54.9[\mathrm{H_2SO_4}] + 142.6([\mathrm{Zn^{2+}}] + 0.93[\mathrm{Mn^{2+}}] + 0.74[\mathrm{Mg^{2+}}] + 0.41[\mathrm{NH_4^+}])\,\text{[27]} \qquad (20)$$

$$\rho = 1054 + 39[\mathrm{H_2SO_4}] + 130([\mathrm{Zn^{2+}}] + 0.83[\mathrm{Mn^{2+}}]) - 0.47(T - 273)\,\text{[39]} \qquad (21)$$

$$\rho = 1011.2 + 61.1[\mathrm{H_2SO_4}](1 - 0.08[\mathrm{M}]) + 156.8[\mathrm{M}] - (0.44 + 0.08[\mathrm{H_2SO_4}] + 0.13[\mathrm{M}])(T - 273)\,\text{[40]} \qquad (22)$$

$$[\mathrm{M}] = [\mathrm{Zn^{2+}}] + 0.83[\mathrm{Mn^{2+}}] + 0.68[\mathrm{Mg^{2+}}] + 0.32[\mathrm{Na^+}] + 0.37[K^+]$$

All the above expressions yield relatively close predictions of electrolyte density for typical zinc electrolytes, but the relationships developed by Barton and Scott[27] and Umetsu et al.[40] match almost perfectly at 308 K (the temperature at which Barton and Scott performed their density measurements). Thus, the latter relationship, which incorporates the effect of temperature, is recommended for solutions containing 1 to 2 mol·dm^{-3} $\mathrm{H_2SO_4}$ and 0 to 1.2 mol·dm^{-3} $\mathrm{ZnSO_4}$ at temperatures from 20 to 60 °C.

Zinc Ion Diffusion Coefficient. Zouari and Lapique[43] reported the following expression for the diffusion coefficient of zinc ions, $D_{\mathrm{Zn^{2+}}}$ (m^2·s^{-1}), in 0.2 mol·dm^{-3} $\mathrm{Na_2SO_4}$ supporting electrolyte, which was generated from limiting current density data at a rotating disk electrode in the concentration range of 0.01 to 0.15 mol·dm^{-3} $\mathrm{ZnSO_4}$:

$$D_{\mathrm{Zn^{2+}}} = 0.78 \times 10^{-6} \exp\left(\frac{-2186}{T}\right) \qquad (23)$$

However, the above expression is for a pH-neutral electrolyte of relatively low ionic strength and is not applicable to industrial zinc electrolytes. In this regard, there have been only a few reported estimates of zinc ion diffusion coefficients in industrial zinc electrolytes[43−45] and each for a single electrolyte composition.

The diffusion coefficient of zinc sulfate, $D_{\mathrm{ZnSO_4}}$ (m^2·s^{-1}), was measured by Awakura et al.[46] in 0 to 2.0 mol·dm^{-3} $\mathrm{ZnSO_4}$ with

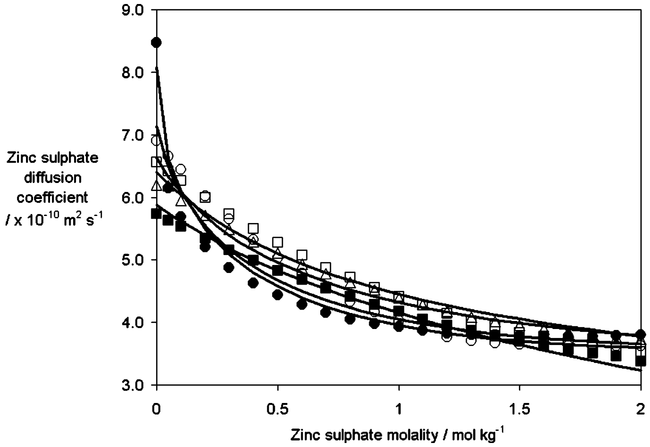

Figure 6. Diffusion coefficient of zinc sulfate in ●, 0 mol·dm^{-3} H_2SO_4; ○, 0.1 mol·dm^{-3} H_2SO_4; □, 0.5 mol·dm^{-3} H_2SO_4; △, 1.0 mol·dm^{-3} H_2SO_4; and ■, 2.0 mol·dm^{-3} H_2SO_4 at 25 °C and corresponding fitted curves (—) using eq 23 plotted against zinc sulfate molality. Data taken from ref 46.

0 to 2.0 mol·dm^{-3} H_2SO_4 at 25 °C. The zinc ion diffusion coefficient may be separated from the diffusion coefficient of zinc sulfate according to the following fundamental relationship:

$$D_{Zn^{2+}} = \frac{D_{ZnSO_4}\left[\nu_{Zn^{2+}}\frac{D_{SO_4^{2-}}}{D_{Zn^{2+}}} + \nu_{SO_4^{2-}}\right]}{\frac{D_{SO_4^{2-}}}{D_{Zn^{2+}}}(\nu_{Zn^{2+}} + \nu_{SO_4^{2-}})\left[1 + \frac{d \ln y_{\pm}ZnSO_4}{d \ln[ZnSO_4]}\right]} \qquad (24)$$

where $\nu_{Zn^{2+}}(1)$ and $\nu_{SO_4^{2-}}(1)$ are the numbers of each ion formed by complete dissociation of zinc sulfate, and $y \pm ZnSO_4$ is the stoichiometric mean molar activity coefficient of zinc sulfate. The above equation may be simplified by assuming that the activity coefficient of zinc sulfate does not change significantly with electrolyte composition (verifiable from Pitzer model calculations) and that the ratio of $D_{Zn^{2+}}$ to $D_{SO_4^{2-}}$ is close to that at infinite dilution:

$$D_{Zn^{2+}} \approx \frac{D_{ZnSO_4}}{2}\left[1 + \frac{D^{\circ}{}_{Zn^{2+}}}{D^{\circ}{}_{SO_4^{2-}}}\right] = \frac{D_{ZnSO_4}}{2}\left[1 + \frac{7.03 \times 10^{-10}\ m^2{\cdot}s^{-1}}{1.065 \times 10^{-9}\ m^2{\cdot}s^{-1}}\right] = 0.83 D_{ZnSO_4} \qquad (25)$$

The following expression for calculating D_{ZnSO_4} was generated by the authors from a least-squares fit of the data set by Awakura et al. (see Figure 6) and may be substituted into eq 25:

$$D_{ZnSO_4} = [8.083 - 7.496([ZnSO_4] + 0.296[H_2SO_4])^{0.5} + 4.105[ZnSO_4] + 3.924[H_2SO_4] - 0.739([ZnSO_4] + 1.615[H_2SO_4])^{1.5}] \times 10^{-10} \qquad (26)$$

The standard deviation of differences in the reported and calculated diffusion coefficients using this expression was ± 0.17 × 10^{-10} m^2·s^{-1}. Using eqs 25 and 26, the diffusion coefficient of zinc ions in 0.84 mol·dm^{-3} $ZnSO_4$ with 1.54 mol·dm^{-3} H_2SO_4 at 25 °C was estimated to be 3.7 × 10^{-10} m^2·s^{-1}, which is close to 3.8 × 10^{-10} m^2·s^{-1} as measured by Hosny et al.[44]

Conclusions

A new set of Pitzer model parameters for $ZnSO_4-H_2SO_4-H_2O$ electrolytes has been presented in order to improve predictions of the equilibrium potentials for electrowinning reactions. Several correlations for electrolyte conductivity have also been critically examined in order to assist in estimation of the ohmic drop component of cell voltage of a zinc electrowinning reactor. Wark's rule has been suggested as an appropriate tool for predicting current efficiency of zinc electrowinning as a function of electrolyte compositions only if the constant term were determined for specific levels of impurities and additives. Existing correlations for calculating electrolyte viscosity and density using have been compared and contrasted. Finally, a new correlation for calculation of the diffusion coefficient of zinc ions has also been presented. These aforementioned electrolyte properties are functions of electrolyte temperature and composition and were examined in order to facilitate accurate predictions of cell voltage, SEEC, as well as the transport properties of the electrolyte. Accurate predictions of such measures of electrowinning performance should assist in the optimization of conventional zinc electrowinning reactors and/or design of new zinc electrowinning reactors.

Appendix A: Procedure for Determination of Pitzer Parameters from Osmotic Data

The following description uses the basic equations and nomenclature of the Pitzer model reported by Kim and Frederick.[12,47] Fitting of the Pitzer model appears to be most commonly based on sets of isopiestic data, where a number of observations (N_{obs}) of solvent activity (a_s) (which is often water), are directly made for corresponding solute(s) molatities (m, mol·kg^{-1}). The stoichiometric molal osmotic coefficient (ϕ_{st}) is calculated for each solute molatity as follows:

$$\phi_{st} = \frac{-1000 \ln(a_s)}{\nu m M_s} \qquad (A1)$$

where ν is the number of mols of ions created by complete dissociation of a mol of solute, and M_s (g·mol^{-1}) is the molar mass of the solvent. If some knowledge exists for the actual degree of dissociation of the solute at each salt molality (e.g., from Raman data), then the observed osmotic coefficient (ϕ_{obs}) may be adjusted as follows:

$$\phi_{obs} = \frac{\nu m \phi_{st}}{\sum m_i} \qquad (A2)$$

where Σm_i is the sum of all the molalities of solvated species. Otherwise, it is conventional to assume complete dissociation (i.e., $\phi_{obs} = \phi_{st}$).

The first step in modeling the observed data is to estimate the set of adjustable parameters for specific interactions of each particular cation, M, and anion, X:

(a) $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $\beta^{(2)}_{MX}$: second virial coefficients for interactions of oppositely charged ions including ion pair formation.

(b) C^{ϕ}_{MX}: third virial coefficient describing ion triplet formation.

(c) $\theta_{MM'}$ and $\theta_{XX'}$: terms that account for interactions between like charged ions, where $M \neq M'$ and $X \neq X'$.

(d) $\psi_{MM'X}$ and $\psi_{XX'M}$: terms that account for the modifying influence of an oppositely charged ion on θ interactions.

The parameters listed in a and b should be derived from binary mixtures of the ions with parameters in c and d being added to account for the influence of additional ions in more complex solutions.

The following sequence of calculations is then followed with the ionic strength of the electrolyte being calculated first:

$$I = \frac{1}{2}\sum_i {z_i}^2 m_i \tag{A3}$$

where z_i and m_i are the charge and molality of species i.

For all specific cation−anion interactions, the third viral coefficients, C_{MX}, are calculated:

$$C_{\mathrm{MX}} = \frac{{C_{\mathrm{MX}}}^{\phi}}{2|z_{\mathrm{M}} z_{\mathrm{X}}|^{1/2}} \tag{A4}$$

where z_{M} and z_{X} are the charges of M and X, respectively.

Next, the second viral coefficients, B^{ϕ}_{MX}, is calculated:

$$B^{\phi}_{\mathrm{MX}} = \beta^{(0)}_{\mathrm{MX}} + \beta^{(1)}_{\mathrm{MX}} e^{-\alpha_1 I^{1/2}} + \beta^{(2)}_{\mathrm{MX}} e^{-\alpha_2 I^{1/2}} \tag{A5}$$

where $\alpha_1 = 2$ and $\alpha_2 = 0$ for 1−1 and 1−2 interactions or $\alpha_1 = 1.4$ and $\alpha_2 = 12$ for higher charge interactions.

For each specific cation−cation or anion−anion interaction, the higher order electrostatic mixing terms ${}^{E}\theta_{ij}$ and ${}^{E}\theta_{ij}'$ are calculated as follows:

$${}^{E}\theta_{ij} = \frac{z_i z_j}{4I}[J(x_{ij}) - 0.5J(x_{ii}) - 0.5J(x_{jj})] \tag{A6}$$

$${}^{E}\theta_{ij}' = \frac{-{}^{E}\theta_{ij}}{I} + \frac{z_i z_j}{8I^2}[x_{ij}J'(x_{ij}) - 0.5x_{ii}J'(x_{ii}) - 0.5x_{jj}J'(x_{jj})] \tag{A7}$$

where

$$x_{ij} = 6 z_i z_j A_{\phi} I^{1/2} \tag{A8}$$

The Debye−Hückel osmotic coefficient (A_{ϕ}) may be calculated from the following expression:[26]

$$A_{\phi} \approx 0.377 + 0.0004684(T - 273.15) + 0.00000374(T - 273.15)^2 \tag{A9}$$

The terms $J(x_{ij})$ and $J'(x_{ij})$ may be calculated using the following approximations:[19]

$$J(x_{ij}) \approx \frac{x_{ij}}{4 + 4.581{x_{ij}}^{-0.7237} e^{-0.012 x_{ij} 0.528}} \tag{A10}$$

$$J'(x_{ij}) \approx \frac{J(x_{ij} + dx_{ij}) - J(x_{ij})}{dx_{ij}} \tag{A11}$$

The electrostatic mixing terms, calculated in eqs A7 and A8, are used to calculate the mixed electrolyte second viral coefficients, Φ^{ϕ}_{ij}, as follows:

$$\Phi^{\phi}_{ij} = \theta_{ij} + {}^{E}\theta_{ij} + {}^{E}\theta_{ij}' \tag{A12}$$

All the above-calculated coefficients are then used to calculate the osmotic coefficient at each solute molality:

$$\phi_{\mathrm{calc}} = 1 + \frac{2}{\sum_i m_i}\left[\frac{-A_{\phi} I^{3/2}}{1 + 1.2I^{1/2}} + \sum_c \sum_a m_{\mathrm{c}} m_{\mathrm{a}}(B^{\phi}_{\mathrm{ca}} + ZC_{\mathrm{ca}}) + \sum_{c<} \sum_c m_{\mathrm{c}} m_{\mathrm{c'}}(\Phi^{\phi}_{\mathrm{cc'}} + \sum_a m_{\mathrm{a}} \psi_{\mathrm{cc'a}}) + \sum_{a<} \sum_a m_{\mathrm{a}} m_{\mathrm{a'}}(\Phi^{\phi}_{\mathrm{aa'}} + \sum_c m_{\mathrm{c}} \psi_{\mathrm{aa'c}})\right] \tag{A13}$$

where

$$Z = \sum_i m_i |z_i| \tag{A14}$$

Typically, deviations from observed and calculated osmotic coefficients are represented by the sum of the square of the errors, SSE:

$$\mathrm{SSE} = \sum_{N_{\mathrm{obc}}} (\phi_{\mathrm{calc}} - \phi_{\mathrm{obs}})^2 \tag{A15}$$

The SSE is minimized by modifying the adjustable interaction parameters and repeating the calculation process (eqsA3 through A15) until convergence. Fitting always begins with the minimum number of adjustable parameters and acceptance or rejection of an additional parameters is made from examination of the corresponding value of χ^2:

$$\chi^2 = \frac{\sum_{N_{\mathrm{obs}}} \left[\frac{\phi_{\mathrm{obs}} - \phi_{\mathrm{calc}}}{\sigma_{\mathrm{obs}}}\right]^2}{N_{\mathrm{obs}} - \nu} \tag{A16}$$

where σ_{obs} is the estimated uncertainty in the observed osmotic coefficient data and ν is the number of adjustable parameters. An additional parameter is, generally, accepted if the value of χ^2 decreases from that calculated for the previous set of parameters.

EMF data may be used to directly calculate the activity coefficient of a particular species to influence fitting or simply be calculated after the fact. The process of calculating a single ion activity coefficient begins by, first, calculating the second viral coefficients, B_{MX} and B_{MX}' as follows:

$$B_{\mathrm{MX}} = \beta^{(0)}_{\mathrm{MX}} + \beta^{(1)}_{\mathrm{MX}} f(\alpha_1 I^{1/2}) + \beta^{(2)}_{\mathrm{MX}} f(\alpha_2 I^{1/2}) \tag{A17}$$

$$B_{\mathrm{MX}}' = \frac{\beta^{(1)}_{\mathrm{MX}} f'(\alpha_1 I^{1/2})}{I} + \frac{\beta^{(2)}_{\mathrm{MX}} f'(\alpha_2 I^{1/2})}{I} \tag{A18}$$

where the functions $f(x)$ and $f'(x)$ are given as follows:

$$f(x) = \frac{2[1 - (1 + x)e^{-x}]}{x^2} \tag{A19}$$

$$f'(x) = e^{-x} - f(x) \tag{A20}$$

Next, the following mixed electrolyte second viral coefficients, ${\Phi_{ij}}^{\phi}$ and Φ_{ij}', are calculated:

$$\Phi_{ij}' = {}^{E}\theta_{ij}' \tag{A21}$$

$${\Phi_{ij}}^{\phi} = \theta_{ij} + {}^{E}\theta_{ij}' + I\,{}^{E}\theta_{ij}' \tag{A22}$$

These coefficients are used to calculate the term F:

$$F = -A_{\phi}\left[\frac{I^{1/2}}{1 + 1.2I^{1/2}} + \frac{2}{1.2}\ln(1 + 1.2I^{1/2})\right] + \sum_c \sum_a m_{\mathrm{c}} m_{\mathrm{a}} B_{\mathrm{ca}}' + \sum_{c<} \sum_{c'} m_{\mathrm{c}} m_{\mathrm{c'}} \Phi_{\mathrm{cc'}}' + \sum_{a<} \sum_{a'} m_{\mathrm{a}} m_{\mathrm{a'}} \Phi_{\mathrm{aa'}}' \tag{A23}$$

The activity coefficient of a specific cation (M) or anion (X) are then be calculated as follows:

$$\ln(\gamma_{\mathrm{M}}) = z_{\mathrm{M}}^{2}F + \sum_{a} m_{\mathrm{a}}(2B_{\mathrm{Ma}} + ZC_{\mathrm{Ma}}) + \sum_{c} m_{\mathrm{c}}(2\Phi_{\mathrm{Mc}} + \sum_{a} m_{\mathrm{a}}\psi_{\mathrm{Mca}}) + \sum_{a<}\sum_{a'} m_{\mathrm{a}}m_{\mathrm{a'}}\psi_{\mathrm{Maa'}} + z_{\mathrm{M}}\sum_{c}\sum_{a} m_{\mathrm{c}}m_{\mathrm{a}}C_{\mathrm{ca}} \quad \text{(A24)}$$

$$\ln(\gamma_{\mathrm{X}}) = z_{\mathrm{X}}^{2}F + \sum_{c} m_{\mathrm{c}}(2B_{\mathrm{cX}} + ZC_{\mathrm{cX}}) + \sum_{a} m_{\mathrm{a}}(2\Phi_{\mathrm{Xa}} + \sum_{c} m_{\mathrm{c}}\psi_{X\mathrm{ac}}) + \sum_{c<}\sum_{c'} m_{\mathrm{c}}m_{\mathrm{c'}}\psi_{\mathrm{Xcc'}} + |z_{\mathrm{X}}|\sum_{c}\sum_{a} m_{c}m_{a}C_{\mathrm{ca}} \quad \text{(A25)}$$

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