Exploring Methods of Manipulating and Optimizing the Cell Potential of Zinc-Copper Cells: Anion Effects, pH Variations, and Supplementary Electrolyte Effects

Vincent J. Cacciola

Supplementary Information

Nernst Model: This is a rudimentary equation that intends to predict cell potential at non-standard conditions and at non-ideal half-cell concentrations. This equation is derived from the Gibbs free energy model and for this study was analyzed in conjunction with activity coefficients in the reaction quotient variable to enhance its theoretical accuracy and consistency with the data. The simplified Nernst equation for the Zn/Cu reaction is shown below:

$$E = 1.10V - 0.0296\log(Q) \tag{S1}$$

Reaction quotient, Q, is defined as the ratio of aqueous products to aqueous reactants. This will be the major term that will vary and affect the cell potential throughout this study.

Activity Coefficient: Activity coefficients are a concept in physical chemistry that attempts to predict the non-ideal nature of ion interactions in a solution. A solution's activity coefficient is defined as the ratio of the "active" ion concentration to the total ion concentration. Its value can be predicted with various models that will be later discussed including the Debye Hückel and Davies models.

Debye Hückel Model: This model attempts to model the activity coefficient of a solution. Debye and Hückel derived the Debye Hückel model from an intersection of theories in relation to electrostatics, statistical mechanics, and thermodynamics. It does not have perfect accuracy, and its precision decreases at higher ionic strengths, it can be mathematically expressed as the following:

$$\log(\gamma) = \frac{-0.51 i^2 \sqrt{I}}{1 + 3.3\delta\sqrt{I}} \tag{S2}$$

This is the equation derived from the literature references in this study, however, other literature may have slightly varying constants and methodologies in calculating activity coefficients [4].

Davies Model: This model attempts to model the activity coefficient of a solution alongside the Debye Hückel model. The equation was originally published in 1938, and it was developed from mathematical analysis of experimental data rather than theoretically as the Debye Hückel model is derived. It attempts to extend the accuracy of the Debye Hückel model to higher ionic strengths, however, the research still shows that there are significant inaccuracies associated with this model at high ionic strengths, particularly when supplementary electrolytes are studied.

$$\log(\gamma) = -0.51 i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.30I\right) \tag{S3}$$

Equation S4 was the derived equation that was used to model cell potential where the zinc solution assumed to behave in accordance with the Debye Hückel Theory. This was used in the graphing Figures, 2 and 3, to determine the relationship between the collected data and the various predictive models. Both equations assume the Copper solution behaves in accordance with the Davies model since it is maintained at a relatively high molar concentration: 1.0 M. The equation is substituted with variables according to the following conventions of electrolytes: CuA^{-a} and ZnB^{-b} where [A] is the concentration of copper's anion with charge magnitude of a, and [B] is the concentration of zinc's anion with charge magnitude of b. The equation is derived from multiplying the ion concentrations by their corresponding activity coefficient; the activity coefficients are calculated either using the Debye-Huckel or Davies models where the activity coefficients are calculated by algebraic rearrangement based on Equations S2 or S3 in which 10 is raised to the value equal to log of the activity coefficient. Subsequently the expression equal to the ionic strength is substituted in for I based on Equation 5 detailed in the manuscript; the values for i and δ (2 and 0.60 nm respectively) are also then substituted based on the manuscript's introductory information.

$$E = 1.10 - 0.0296\log\left(\frac{[Zn]\cdot 10^{\frac{-2.04\sqrt{\left(2[Zn]+\frac{1}{2}b^2[B]\right)}}{1+1.98\sqrt{\left(2[Zn]+\frac{1}{2}b^2[B]\right)}}}}{[Cu]\cdot 10^{-2.04\left(\frac{\sqrt{\left(2[Cu]+\frac{1}{2}a^2[A]\right)}}{1+\sqrt{\left(2[Cu]+\frac{1}{2}a^2[A]\right)}}-0.30\left(2[Cu]+\frac{1}{2}a^2[A]\right)\right)}}\right) \tag{S4}$$

Equation S5 was the derived equation that was used to model cell potential where the zinc solution assumed to behave in accordance with the Davies Theory. This was also used in the graphing Figures, 2 and 3, to determine the relationship between the collected data and the various predictive models. The equation is also substituted with variables according to the following conventions of electrolytes: CuA^{-a} and ZnB^{-b} where [A] is the concentration of copper's anion with charge magnitude of a, and [B] is the concentration of zinc's anion with charge magnitude of b.

$$E = \ 1.10 - 0.0296\log\left(\frac{[Zn]\cdot 10^{-2.04\left(\frac{\sqrt{\left(2[Zn]+\frac{1}{2}b^2[B]\right)}}{1+\sqrt{\left(2[Zn]+\frac{1}{2}b^2[B]\right)}}-0.30\left(2[Zn]+\frac{1}{2}b^2[B]\right)\right)}}{[Cu]\cdot 10^{-2.04\left(\frac{\sqrt{\left(2[Cu]+\frac{1}{2}a^2[A]\right)}}{1+\sqrt{\left(2[Cu]+\frac{1}{2}a^2[A]\right)}}-0.30\left(2[Cu]+\frac{1}{2}a^2[A]\right)\right)}}\right) \tag{S5}$$