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Experimental Determination and Thermodynamic Modeling of Electrical Conductivity of SRS Waste Tank Supernate

J. A. Pike
S. H. Reboul

June 2015

SRNL-STI-2015-00243 , Revision 0

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EXECUTIVE SUMMARY

SRS High Level Waste Tank Farm personnel rely on conductivity probes for detection of incipient overflow conditions in waste tanks. Minimal information is available concerning the sensitivity that must be achieved such that that liquid detection is assured. Overly sensitive electronics results in numerous nuisance alarms for these safety-related instruments. In order to determine the minimum sensitivity required of the probe, Tank Farm Engineering personnel need adequate conductivity data to improve the existing designs. Little or no measurements of liquid waste conductivity exist; however, the liquid phase of the waste consists of inorganic electrolytes for which the conductivity may be calculated.

Savannah River Remediation (SRR) Tank Farm Facility Engineering requested SRNL to determine the conductivity of the supernate resident in SRS waste Tank 40 experimentally as well as computationally. In addition, SRNL was requested to develop a correlation, if possible, that would be generally applicable to liquid waste resident in SRS waste tanks.

A waste sample from Tank 40 was analyzed for composition and electrical conductivity as shown in Table 4-6, Table 4-7, and Table 4-9. The conductivity for undiluted Tank 40 sample was 0.087 S/cm.

The accuracy of OLI Analyzer™ was determined using available literature data. Overall, 95% of computed estimates of electrical conductivity are within ±15% of literature values for component concentrations from 0 to 15 M and temperatures from 0 to 125 °C. Though the computational results are generally in good agreement with the measured data, a small portion of literature data deviates as much as ±76%.

A simplified model was created that can be used readily to estimate electrical conductivity of waste solution in computer spreadsheets. The variability of this simplified approach deviates up to 140% from measured values. Generally, this model can be applied to estimate the conductivity within a factor of two. The comparison of the simplified model to pure component literature data suggests that the simplified model will tend to under estimate the electrical conductivity.

Comparison of the computed Tank 40 conductivity with the measured conductivity shows good agreement within the range of deviation identified based on pure component literature data.

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LIST OF ABBREVIATIONS

HLW	high level waste
MDL	minimum detection limit
MSA	mean spherical approximation
MSE	Mixed Solvent Electrolyte
RSD	relative standard deviations
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
TTQAP	Task Technical and Quality Assurance Plan
WCS	Waste Characterization System

1.0 Introduction

SRS High Level Waste Tank Farm personnel rely on conductivity probes for detection of incipient overflow conditions in waste tanks. Minimal information is available concerning the sensitivity that must be achieved such that that liquid detection is assured. Overly sensitive electronics results in numerous nuisance alarms for these safety-related instruments. In order to determine the minimum sensitivity required of the probe, Tank Farm Engineering personnel need adequate conductivity data to improve the existing designs. Few if any measurements of liquid waste conductivity exist; however, the liquid phase of the waste consists of inorganic electrolytes for which the conductivity may be calculated.

Savannah River Remediation (SRR) Tank Farm Facility Engineering requested SRNL (Emerson, 2014) to determine the surface electrical resistivity of the supernate resident in SRS waste Tank 40 experimentally as well as computationally. SRR Engineering personnel chose Tank 40 because it was the most dilute supernate at the time. The computational modeling of conductivity will allow estimation of conductivity with an estimate of the error of the prediction for other tanks and more dilution conditions.

The models and literature report conductivity, which is the inverse of resistivity. In order to provide direct comparison of experimental and computational results, this analysis was performed and reported in terms of conductivity. In addition, SRNL was requested to develop a correlation, if possible, that would be generally applicable to liquid waste resident in SRS waste tanks. Accuracy of the computational methods is to be determined relative to existing literature as well as the waste sample. SRNL issued a Task Technical and Quality Assurance Plan (TTQAP) SRNL-RP-2014-00361 (Westbrook, Pike, & Reboul, 2014) which outlined the technical plan to be used to meet programmatic objectives.

1.1 Objective

The objectives of this work are as follows:

perform Waste Tank waste characterization to determine the surface electrical conductivity of the supernate resident in the SRS waste Tank 40 with estimation of accuracy,

determine the accuracy of computationally simulated electrical conductivity data for SRS HLW waste supernate by using OLI Analyzer™, and

develop a simplified model applicable to SRS HLW waste supernate with approximation of accuracy.

1.2 Background

Ion asymmetry, fluid friction, solvent viscous effects, electrophoretic effects, degree of dissociation, and other factors influence electrical conductivity in solutions. Early theoretical models were derived from the observation that, at very low concentration, the electrical conductivity is proportional to the square root of the concentration (Onsager & Fuoss, 1932). This model was later extended by accounting for equilibrium distribution and finite size corrections. The extended conductivity model assumes that the solvent is a continuous medium and that ions are charged hard spheres. Modern computational chemistry methods based on first principles exist to calculate transport properties that account for near and far field effects; however, these methods are not practical because of the difficulty in calculating the solute-solvent interactions in a realistic way (Roger, Durand-Vidal, Bernard, & Turq, 2009).

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In 1992, Bernard et al. proposed a novel approach in which Onsager's continuity equations were combined with the MSA (mean spherical approximation) equilibrium correlation functions by means of a Green function formalism, which considers the finite ionic radii. In the Bernard model, an electrolyte solution is approximated by a system containing charged spheres with different sizes in a dielectric continuum. Electrical conductivity of an anion-cation solution is quantified as a function of concentration if the following parameters are known: (1) limiting conductivities of the anion and cation, (2) ionic diameters, (3) ionic charges and (4) dielectric constant and viscosity of the solvent as functions of temperature. This procedure is valid to calculate conductivities in solutions up to 1 molal (Bernard, Kunz, Turq, & Blum, 1992-a) (Bernard, Kunz, Turq, & Blum, 1992-b) (Durand-Vidal, Simonin, Turq, & Bernard, 1995) (Dufrêche, Bernard, Durand-Vidal, & Turq, 2005). Roger et al. extended the MSA model from binary ion solutions to several species, with good results, by using ionic radii determined from single component solution conductivity measurements (Roger, Durand-Vidal, Bernard, & Turq, 2009).

The Anderko-Lencka model extended the practical applicability of the MSA theory used in the Bernard model from moderate electrolyte concentrations (less than 1 molal) to relatively high electrolyte concentrations (30 molal) by introducing effective ionic radii, which are determined by using ionic-strength dependent cation-anion interactions. In addition, Anderko & Lencka developed a mixing rule to predict the conductivity of multicomponent systems from those of constituent binary cation-anion subsystems. The effects of complexation are taken into account through a comprehensive speciation model, OLI Systems aqueous electrolyte model at the time, coupled with a technique for predicting the limiting conductivities of complex species from those of simple ions. This model was shown to be effective for representing electrical conductivities of concentrated aqueous electrolyte solutions over wide temperature ranges (Anderko & Lencka, 1997). Wang et. al. further developed the Anderko-Lencka model for the OLI Systems MSE model. This model combines the effects from interactions involving solvent molecules and other neutral species as well as interactions between species through changes in viscosity and solvation structure. Wang et. al. regressed the conductivity data to determine effective ionic radii for ion pairs and used crystallographic radii as default values (same method as used by Bernard in the original model) when conductivity data was not available (Wang, Anderko, & Young, 2004).

For application to waste tank supernates, the MSE model is likely to be generally applicable to the entire concentration range in the waste tanks. For dilute solutions, less than 1 M total sodium, several models derived from Bernard's model will likely perform well. In the extremely dilute case, the electrical conductivity approaches infinite dilution conductivities, where the earliest models will also provide good results. The MSE model provides a singularly comprehensive model for the entire range of concentrations of the mixed electrolyte solution.

2.0 Approach

This work consists of experimental analysis as well as computational analysis. The first part of this section discusses the computational approach and methods. The second part of this section discusses the experimental methods and designs used.

2.1 Electrolyte Thermodynamic Modeling Approach

Thermodynamic modeling using OLI Analyzer™ version 9.1.2 was used to computationally simulate SRS HLW waste supernates. These simulations generate simulated electrical conductivity data, which were then compared to literature data to satisfy the objective to determine accuracy of models. In addition, simulated electrical conductivity data were generated to satisfy the objective to develop the simplified model. The following sections describe the methods used in the evaluation in more detail.

2.1.1 Determining Model Accuracy

HLW supernates contain a very large number of compounds and most elements on the periodic chart, which complicates any model for mixtures. It may be possible to calculate the electrical conductivity with high accuracy by eliminating many components with trivial contributions. The multicomponent mixing rule of the Anderko-Lencka-Wang model has the general form of

$$\chi = \sum_k \mathrm{c}_k |z_k| \lambda_k \qquad \text{Eqn. 1}$$

where

χ = the specific conductivity of the solution,
k = k^{th} ion in mixture,
c = concentration factor based on fraction of contribution to ionic strength
$|z|$ = absolute ion charge,
λ = conductivity.

The OLI MSE model calculates conductivity for each ion pair from the MSA conductivity equations and applies the mixing rule of Equation 1 to estimate the electrical conductivity of the mixture.

In order to determine accuracy of simulated HLW supernates, electrical conductivity data from literature needs to be compiled for as many of the supernate components as practical. Examination of Equation 1 suggests that trace components or very low concentrations minimally affect the mixed solution concentration although it is difficult to know in advance what concentrations are significant because the limiting conductivity can vary widely for each ion. In this evaluation, in order to minimize the compilation of data with insignificant effect on HLW conductivity, initial attention is focused on components that may exist at concentrations greater 0.01 M. This limiting concentration may be modified if components in this range are determined insignificant or discovery of significant effects at lower concentrations.

The Waste Characterization System (WCS) is used to identify the components and ranges of concentrations expected in HLW. The WCS identifies ions and metals, typical of what would be obtained the experimental results of a HLW sample. However, the likely species are not identified. OLI Analyzer™ was used previously to determine the most likely chemical form expected in solution. It also has the benefit that the identified components are in the OLI component database (Martino, Herman, Pike, & Peters, 2014). Table 2-1 shows the compilation of all the components identified in WCS for HLW supernate along with the concentration ranges where the range maximum exceeds 0.01 M. Note that the range for sodium ion concentration is 0.37 to 15.7 M. A concentration of 0.01 M represents nearly 3% of the minimum of this range. However, the components identified include any component where the maximum concentration exceeds 0.01 M, thus, minimizing the chance of not identifying components that have significant contribution to electrical conductivity. When calculating electrical conductivity using OLI Analyzer™ for HLW supernate, one should include as many of the components identified in Table 2-1 as possible in the calculation based on available data. One should also note the potential to decrease accuracy by leaving out any components without any data. Examination of the range of magnitude of conductivity for many related pure component solutions indicates that it is sufficient to know that the concentration contributes less than 1% of the total ionic strength.

Table 2-1: Identification of HLW Components and Concentration Range in WCS[†]

WCS Identifier	Most Likely Ionic Form	Concentration Range (M)		
		Average	Min	Max
Ions				
AlOH4	$Al(OH)_4^{-1}$	0.41	0.050	1.6
CO3	CO_3^{-2}	0.20	0.036	0.73
C2O4	$C_2O_4^{-2}$	0.013	0.0045	0.081
Cl	Cl^{-1}	0.0087	0.00060	0.040
F	F^{-1}	0.028	0.0020	0.097
K	K^{+1}	0.077	0.0040	0.20
NO2	NO_2^{-1}	1.1	0.086	3.2
NO3	NO_3^{-1}	1.3	0.068	5.6
OH	OH^{-1}	3.6	0.15	12.6
PO4	PO_4^{-3}	0.019	0.00090	0.075
SO4	SO_4^{-2}	0.043	0.0026	0.22
Metals and select organics[**]				
Al	$Al(OH)_4^{-1}$	0.27	0.00000034	0.85
B	$B(OH)_4^{-1}$	0.011	0.00014	0.34
Ca	Ca^{+2}	0.00068	0.000034	0.026
Cr	CrO_4^{-2}	0.0023	0.0000029	0.010
Fe	Fe^{+3}	0.00051	0.00000018	0.018
HCOO[*]	$HCOO^{-1}$	0.043	0.0063	0.23
Li	Li^{+1}	0.0077	0.00019	0.029
K[*]	K^{+1}	0.040	0.00021	0.56
Na[*]	Na^{+1}	4.9	0.37	15.7
NH4[*]	NH_4^{+1}	0.0030	0.00017	0.011
Si	SiO_3^{-2}	0.0014	0.000000014	0.025

[†] Based on WCS data on 5/13/2014.

[*] This table excluded nonsensical or highly improbable values in WCS for these components: 164 and 500 M HCOO; 759, 1071, 4.5, and 25 M K; 615 M Na; 8.16 M NH4.

[**] WCS concentration values in units of mg/L were converted to M.

Electrical conductivity data was identified and compiled from a literature survey for the following compounds: KNO_3, Na_2SO_4, Na_3PO_4, $NaNO_2$, HNO_3, $NaNO_3$, and NaOH. Electrical conductivity data was identified in literature for several acidic forms of the ionic species identified in Table 2-1. Since the HLW supernate is basic, little value is perceived with evaluating accuracy of simulating acidic compounds.

In addition to the comparison to literature data, calculated electrical conductivity is compared to the measured conductivity for the Tank 40 supernate sample.

2.1.2 Developing a Simplified Model

Equation 1 in section 2.1.1 suggests that trace components or very low concentrations minimally affect the mixed solution concentration although it is difficult to know in advance what concentrations are significant because the limiting conductivity can vary widely for each ion. A few ionic species tend to dominate the Tank Farm supernate composition, which suggests that a simple approximation may be possible based on the concentration of the primary ionic species in solution for the limited composition range of interest. If the number of significantly contributing components can be reduced to only a few major components, reasonable results may be possible from a simplified expression. After identifying the significant components based on the mixing rule presented in Equation 1, individual component electrical specific conductivity, χ, is expressed as an Arrhenius-type equation for temperature dependence:

$$\chi_k = A_k e^{-\frac{B_k}{T}}$$
$$\ln \chi_k = \ln(A_k) + (-B_k)/T \qquad \text{Eqn. 2}$$

where

χ_k = the molar electrical conductivity (S cm^2 mol^{-1}),
A_k and B_k = constants, and
k = ion pair such as NaOH.

Specific electrical conductivity is converted to molar electrical conductivity by dividing by the molar concentration:

$$\chi_k = \frac{\lambda_k}{[k] mol/L} \cdot 1000\ cm^3/L \qquad \text{Eqn. 3}$$

where

λ_k = the specific electrical conductivity (S cm^{-1}).

OLI Analyzer™ was used to generate simulated data that is regressed to obtain constants A_k and B_k from Equation 2 for each salt. The solution conductivity was then approximated by developing a simple mixing rule similar to Equation 1.

2.2 Experimental Approach

Sample #HTF-40-14-62 was received at SRNL on May 14, 2014 and placed into the Shielded Cells Facility on May 19, 2014. The total weight of the sample was measured to be 80.12 g. A portion of the sample was filtered through a 0.45 µm membrane, to remove any potential suspended insoluble solids in preparation for measurements identifying supernatant-phase conductivity, density, dissolved solids content, ion concentrations, and elemental concentrations. A portion of the sample was left unfiltered, for measurements to determine if a detectable concentration of insoluble solids was present.

The conductivity, density, and solids content measurements were performed in the Shielded Cells, on undiluted sample aliquots. In contrast, the ion and elemental measurements were performed by Analytical Development (outside of the Shielded Cells facility), on sample aliquots that had been diluted in the Shielded Cells by factors of approximately 12X. Such dilutions were performed to assure that the dose rates associated with the aliquots submitted to Analytical Development would meet the laboratory limits. In all cases, sample analyses were performed in triplicate. Mean results and the percent relative standard deviations of the means (% RSDs) are reported in this document, with results having been corrected for dilution, as applicable. Note that the % RSDs provide an indication of the precision of the analytical results, not the accuracy of the results. In general, the accuracy of the results is in the ±10% range.

Details of each of the analytical methodologies are summarized in the following sections.

2.2.1 Conductivity

Conductivity measurements were performed by using a Myron L[1] Ultrameter II™ monitoring unit. The volume of the unit's measurement cell is 5 mL, which means that sample aliquots of approximately 5 mL were utilized during all measurements. Per the instruction manual, the measurement cell was rinsed with clean water and then subsequently rinsed with three aliquots of sample material, prior to refilling the cell with sample material for each measurement.

The Ultrameter II unit performs an automatic temperature correction to 25 °C, so all measurements are assumed applicable to 25 °C. The unit was pre-calibrated at the factory, and no additional calibration was performed prior to measurements. However, measurements of reference materials were performed prior to the sample measurements, to demonstrate the adequacy of the existing calibration, and to identify the magnitude of differences between literature values (identified in the CRC Handbook), modeled values (identified by using OLI, based on the MSE databases), and measurements (taken with the Ultrameter II). Specifically, this included measurements of 10 and 20 weight percent sodium nitrate solutions, as well as two Tank 40 supernatant simulants generated for the purpose of this comparison. The first supernatant simulant contained four simple salts (sodium nitrite, sodium nitrate, sodium hydroxide, and sodium carbonate), at concentrations within the range of previously analyzed Tank 40 supernatant samples. Based on the preliminary analytical results from the Tank 40 sample, the second supernatant simulant added three more salts to the mix (sodium aluminate, sodium oxalate, and sodium sulfate), with higher sodium hydroxide and sodium nitrate concentrations, and a lower sodium carbonate concentration. Specifics of the simulant compositions are identified in Table 4-4. A conductivity measurement of a deionized water sample was also performed, to demonstrate the unit's ability to identify "low range" conductivity.

All the initial test measurements of the sodium nitrate solutions, supernatant simulants, and deionized water were performed in a typical benchtop laboratory outside of the Shielded Cells. In contrast, the measurements of the actual Tank 40 sample were performed in the Shielded Cells, due to the relatively high radioactivity content. For quality assurance purposes, sample measurements in the Shielded Cells were preceded and followed by simulant measurements, also performed in the Shielded Cells. Consistency between the prior lab bench simulant measurements and the Shielded Cell simulant measurements provided assurance that the conductivity unit was operating properly during the sample measurements in the Shielded Cells.

To provide supplemental information on the impact of dilution, additional conductivity measurements were performed on sample aliquots diluted by factors ranging from 2X to 34X (2.1X, 4.2X, 8.5X, 17X, and 34X). These sample aliquots were prepared by diluting a single supernatant sample with water by successive factors of approximately two, until a final dilution factor of approximately 34 was obtained as shown in Table 2-2. Dilution factors and densities for the successive sample aliquots were calculated based on the following assumptions: 1) the density of the undiluted supernatant solution was 1.07 g/mL; 2) the density of the dilution water was 1.00 g/mL; and 3) the total solution volume was equal to the sum of sample aliquot volume and the dilution water volume. The dilution factors were utilized to estimate the sodium concentrations of the diluted aliquots, and the results of the conductivity measurements were then plotted as a function of the sodium concentration.

---

[1] Myron L Company, 2450 Impala Drive, Carlsbad, CA 92008-7226 USA; 760-438-2021; www.myronl.com

Table 2-2: Details of the Supernatant Sample Dilutions

Dilution Number	Sample Mass[†], g	Assumed Sample Density, g/mL	Mass of Dilution Water Added, g	Total Dilution Factor	Mass Fraction of Tank 40 Soln. in each Dilution
1	10.000	1.070	9.951	2.1	0.5012
2	10.002	1.034	10.036	4.2	0.2502
3	10.038	1.017	10.022	8.5	0.1252
4	6.932	1.008	6.995	17	0.06231
5	10.058	1.004	10.182	34	0.03097

[†] Sample mass refers to the mass of solution from the previous dilution, i.e., mass of undiluted sample for dilution 1, mass of dilution solution 1 for dilution 2, and etcetera.

2.2.2 Density

Density measurements were performed by weighing aliquots of supernatant filtrate delivered from volume-calibrated pipettes, and then dividing the weights by the volumes. The filtrate aliquot volumes were approximately one milliliter, and the temperature was approximately 25 °C.

2.2.3 Solids Content

Dissolved solids content determinations were performed by driving water from the filtrate at a nominal temperature of 110 °C, with water removal being deemed complete when weights of the dried samples remained stable over heating periods of approximately eight hours. The ratio of the mass of dried solids to the mass of the original filtrate solution defines the dissolved solids content. Filtrate aliquot masses of approximately two grams were utilized in these determinations.

Insoluble solids content is a calculated value based upon the difference between the dissolved solids content (as determined for the filtrate) and the total solids content (as determined for the unfiltered sample). In order for the insoluble solids content to be measurable, the total solids content needs to exceed the dissolved solid content by a statistically significant amount. In the case of the Tank 40 sample measurements, the total solids content did not exceed the dissolved solids content, so the insoluble solids content was deemed immeasurable – in other words, below the minimum detection limit (MDL) of the method. However, an estimate of the applicable MDL was established, based upon the deviations of the corresponding dissolved solids and total solids measurements. Note that unfiltered aliquot masses of approximately one gram were utilized in the total solids determinations.

2.2.4 Ion Concentrations

A combination of analytical methods was used to identify the concentrations of primary ions. Sodium cation and aluminate anion were determined based upon the concentrations of elemental sodium and aluminum, as measured by using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Nitrite, nitrate, oxalate, and sulfate anions were measured by using Ion Chromatography. Free hydroxide anion was determined by using the base titration method. Carbonate anion was determined by analysis of Total Inorganic Carbon (TIC).

2.2.4.1 Elemental Concentrations

All elemental measurements were performed by using ICP-AES.

2.2.4.2 Charge Balance

A charge balance comparison was performed to check consistency of the measured ion concentrations. Specifically, the charge equivalence of the dominating cation (sodium) was compared to the sum of the charge equivalence of the measurable anions (nitrite, free hydroxide, nitrate, carbonate, aluminate, oxalate, and sulfate).

2.2.4.3 Dissolved Solids Projection Based Upon the Primary Constituents

A dissolved solids projection was calculated based upon the concentrations of primary constituents measured through laboratory analysis. Specifically, the measured anion concentrations were utilized to identify the expected concentrations of the corresponding sodium salts (sodium nitrite, sodium hydroxide, sodium nitrate, sodium carbonate, sodium aluminate, sodium oxalate, and sodium sulfate). The projected dissolved solids content associated with each salt was then calculated utilizing the applicable constituent concentration, constituent molecular weight, and the measured supernatant filtrate density. The total projected dissolved solids content was calculated by summing the individual dissolved solids projections.

3.0 Quality Assurance

Work completed for this report was conducted under TTQAP SRNL-RP-2014-00361 (Westbrook, Pike, & Reboul, 2014). The calculations presented in this report are performed compliant with SRS procedure E7 Conduct of Engineering, 2.31 Engineering Calculations including technical review design verification per procedure E7 2.60 by document review. The software used in these calculations is compliant with engineering calculation procedure E7 2.31 section 5.5.1 for exemption from the software quality assurance procedure 1Q 20-1. The calculations presented in this report are consistent safety class functional designation by the Design Authority.

4.0 Results and Discussion

The experimental results follow the discussion of computational results. The experimental results are then compared to the predicted results generated by thermodynamic modelling.

4.1 Electrolyte Thermodynamic Modeling Results

4.1.1 Comparison of Computational Results to Literature

A literature survey revealed a substantial quantity of electrical conductivity measurements of pure component solutions in water. Literature was identified for most of the anion components in HLW supernate, but most of the data is for the acidic form of compound. As will be shown with the most abundant anion in HLW, nitrate, the acid form, nitric acid, is much more conductive because of the hydronium ion. As such, it is not meaningful for determining the error in predicting electrical conductivity of HLW. Electrical conductivity data was identified and compiled from a literature survey for the following compounds: KNO_3, Na_2SO_4, Na_3PO_4, $NaNO_2$, HNO_3, $NaNO_3$, and NaOH.

A large part of identified data is focused on very dilute solutions which is useful in determining the limiting conductivity at infinite dilution. In addition, most of the data is measured at or near 25°C. Electrical conductivity tends to be a strong function of temperature so any lack of data over the temperature range of interest limits the ability to evaluate error completely.

The following paragraphs examine the relative fit of the model to the data. This is followed by a discussion and estimation of model error to measured data. In all the figures, the data markers represent the actual reported results in the literature. The lines on the graph represent the thermodynamic simulation of the same conditions as measured in the data.

4.1.1.1 KNO_3

Figure 4-1 shows the data available for KNO_3 solutions from (Lobo, 1989). The reference is a compendium of 14 different original sources for KNO_3 solution data. The model predicts the electrical conductivity well for the entire range of concentrations and temperature.

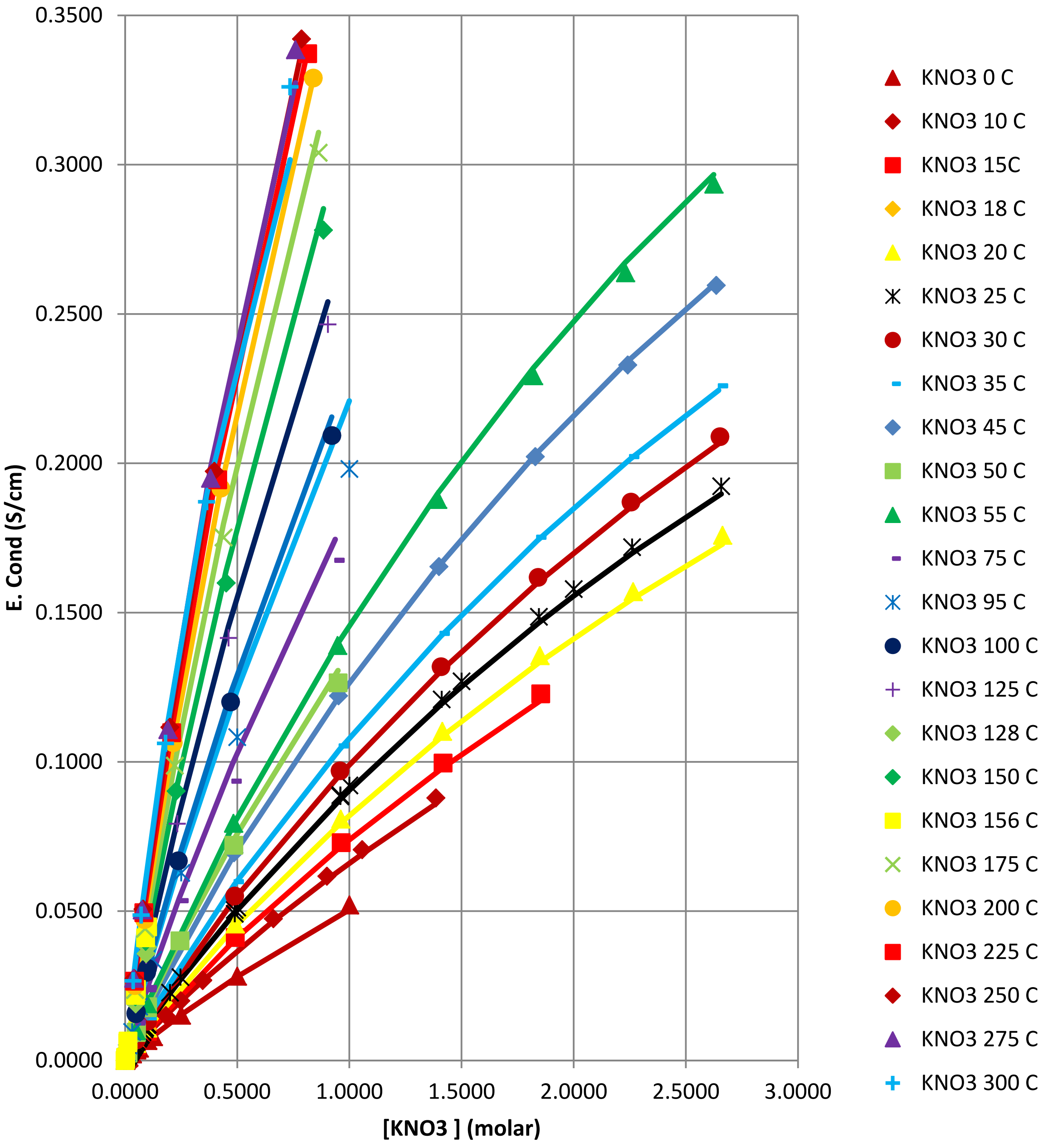

Figure 4-1: Electrical Conductivity of KNO_3 Solution
Note that the lines plot equivalent simulated solution results at each temperature.

4.1.1.2 Na_2SO_4

Figure 4-2 shows the data available for Na_2SO_4 solutions from (Lobo, 1989). The reference is a compendium of eight different original sources for Na_2SO_4 solution data. The model predicts the electrical conductivity well for the entire range of concentrations and temperature.

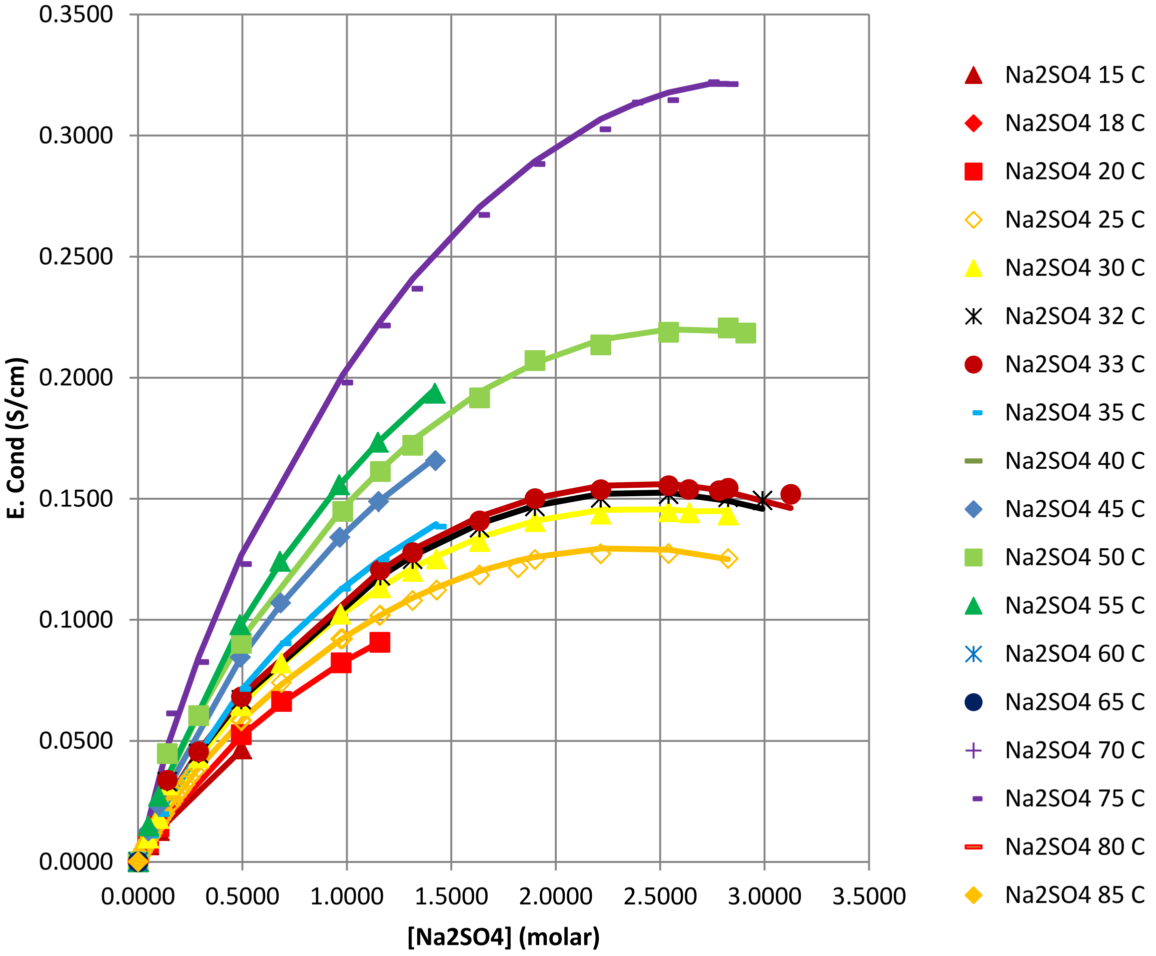

Figure 4-2: Electrical Conductivity of Na_2SO_4 Solution
Note that the lines plot equivalent simulated solution results at each temperature.

4.1.1.3 Na_3PO_4

Figure 4-3 shows the data available for Na_3PO_4 solutions from (Lobo, 1989). The reference contains only one original source for Na_3PO_4 solution data. The model predicts the electrical conductivity well for these dilute solutions.

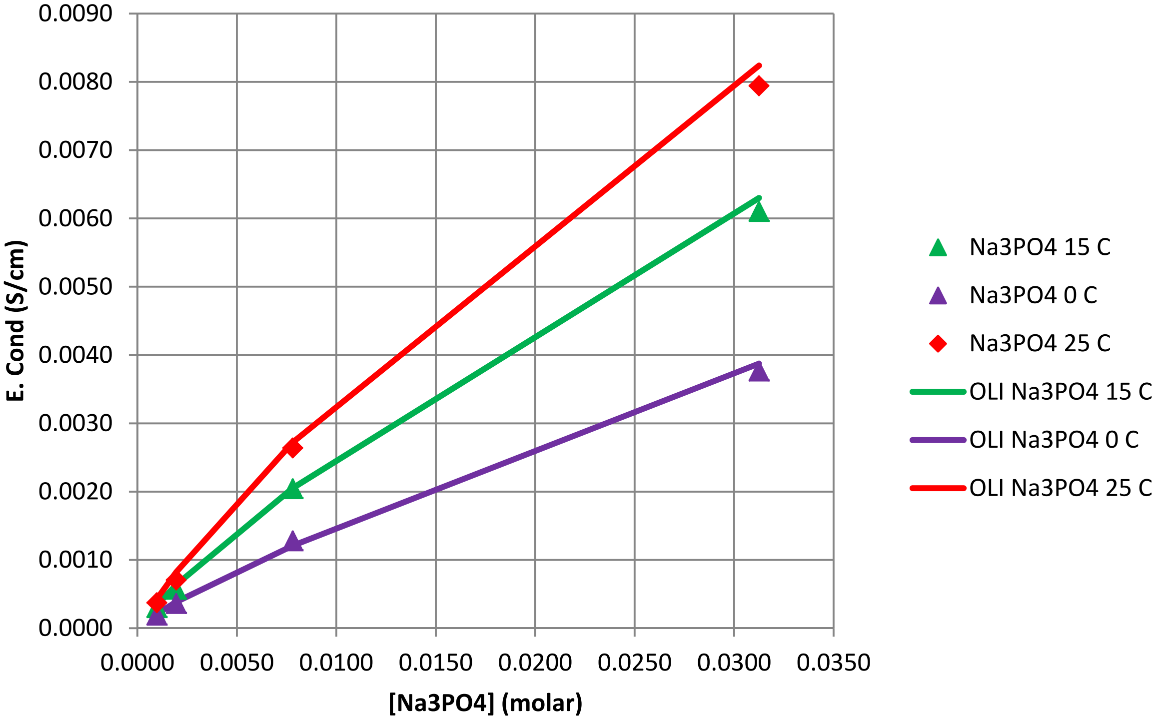

Figure 4-3: Electrical Conductivity of Na_3PO_4 Solution

4.1.1.4 $NaNO_2$

Figure 4-4 shows the data available for $NaNO_2$ solutions from (Lobo, 1989). The reference is a compendium of two different original sources for $NaNO_2$ solution data. The model predicts the electrical conductivity better at dilute concentrations and indicates a consistent bias to overestimate the conductivity at higher concentrations.

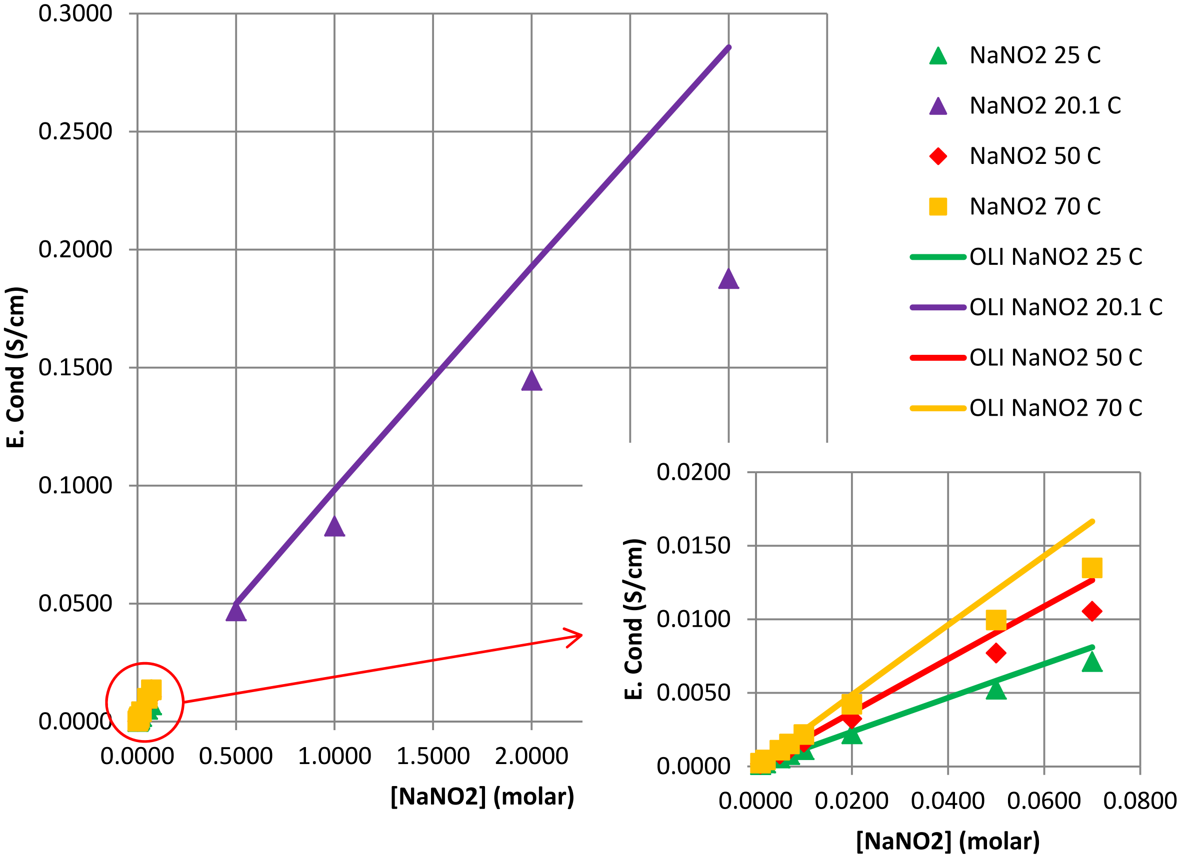

Figure 4-4: Electrical Conductivity of $NaNO_2$ Solution

4.1.1.5 $NaNO_3$

Figure 4-5 shows the data available for $NaNO_3$ solutions from (Lobo, 1989). The reference is a compendium of 14 different original sources for $NaNO_3$ solution data. The model predicts the electrical conductivity well for the entire range of concentrations and temperature.

The most abundant component in HLW supernate is $NaNO_3$ although NaOH dominates concentrated supernate. As such, it may be useful to evaluate the accuracy of the model to fit data for the conjugate acid, HNO_3, particularly because there is extensive data from 13 different original sources for the acid form. Figure 4-6 shows the data available for HNO_3. The electrical conductivity of an HNO_3 solution is about four times higher than equivalent concentrations of $NaNO_3$. This is likely due to the significantly higher mobility of hydronium ion versus the sodium ion in solution. Since the hydronium ion dominates the effect of the nitrate ion, including data for HNO_3 in the evaluation of prediction error would not be representative of nitrate ion. By extension, no other conjugate acid is included for the same reason, even if there is no data available for the basic form.

Figure 4-6 also shows the typical expectation of electrical conductivity peaking at medium concentrated solutions around 5 to 6 M and then reducing somewhat less rapidly with increasing concentration as it increased on the dilute side of the peak. The peak occurs primarily because the salt does not completely dissociate in solution at these higher concentrations. In addition, the ion mobility reduces due to viscosity increases. NaOH dominates very concentrated supernates such that one expects the NaOH content rather than $NaNO_3$ content will dominantly influence the electrical conductivity.

The model predictions are accurate for the entire HNO_3 concentration range except at very low temperatures. At 0°C or less, the model results exhibit a systematic deviation from data above 10 M HNO_3. The deviation is likely due to shifts in thermodynamically favored components in the calculated compositions. Because the waste tanks are controlled such that supernate will never reach 0°C or exceed boiling temperatures, further investigation of this deviation was not pursued. The literature data for the determination of model accuracy is parsed to include data from 0°C to 125°C. All data is similarly parsed to less than 15 M as the highest single component concentration indicated in Table 2-1 is 12.6 M for NaOH. This parsing of data inherently limits the application of the estimated error to the range of 0 – 15 M component concentrations and between 0 and 125°C, which should represent any condition encountered in HLW supernate.

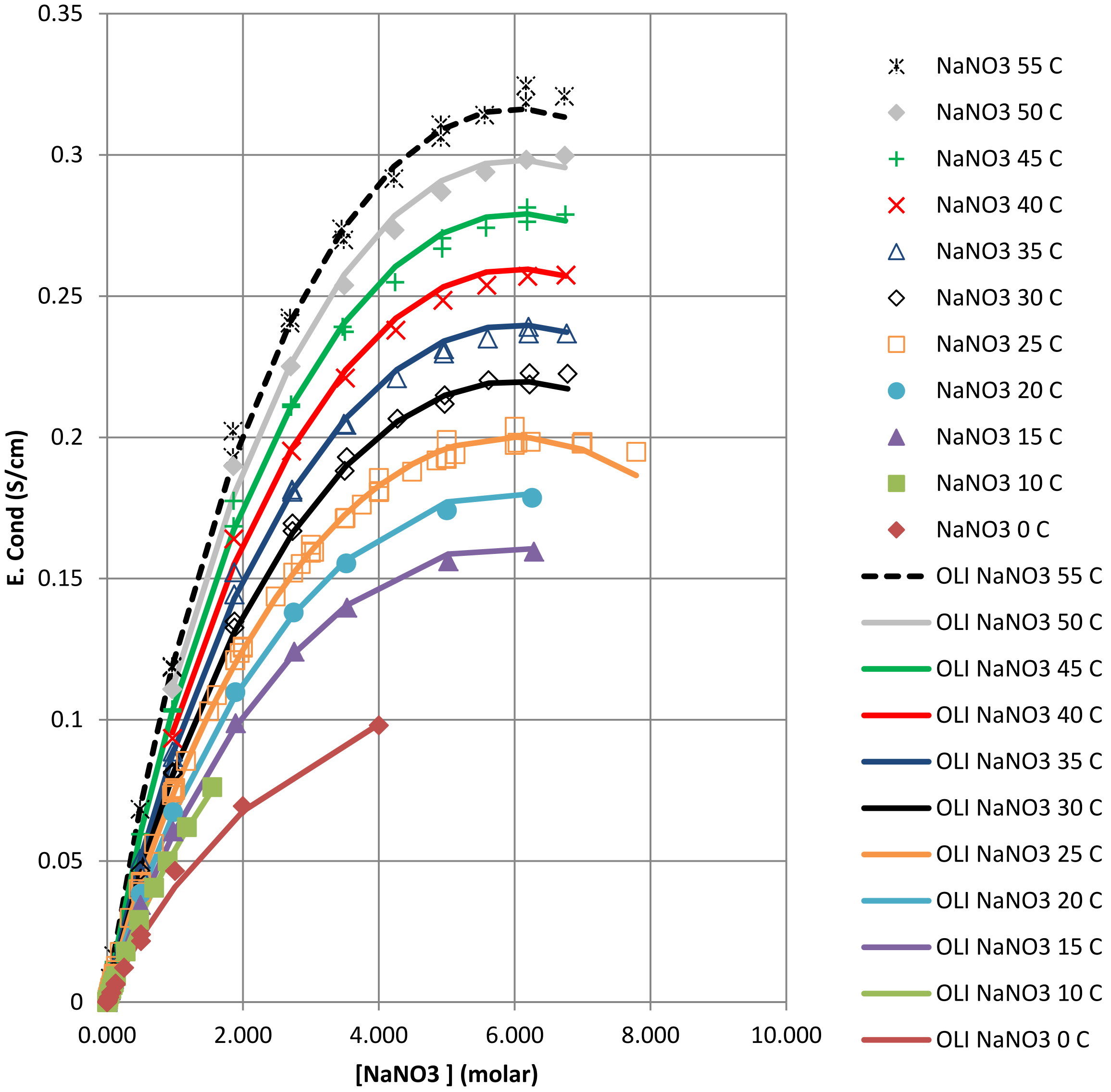

Figure 4-5: Electrical Conductivity of $NaNO_3$ Solution

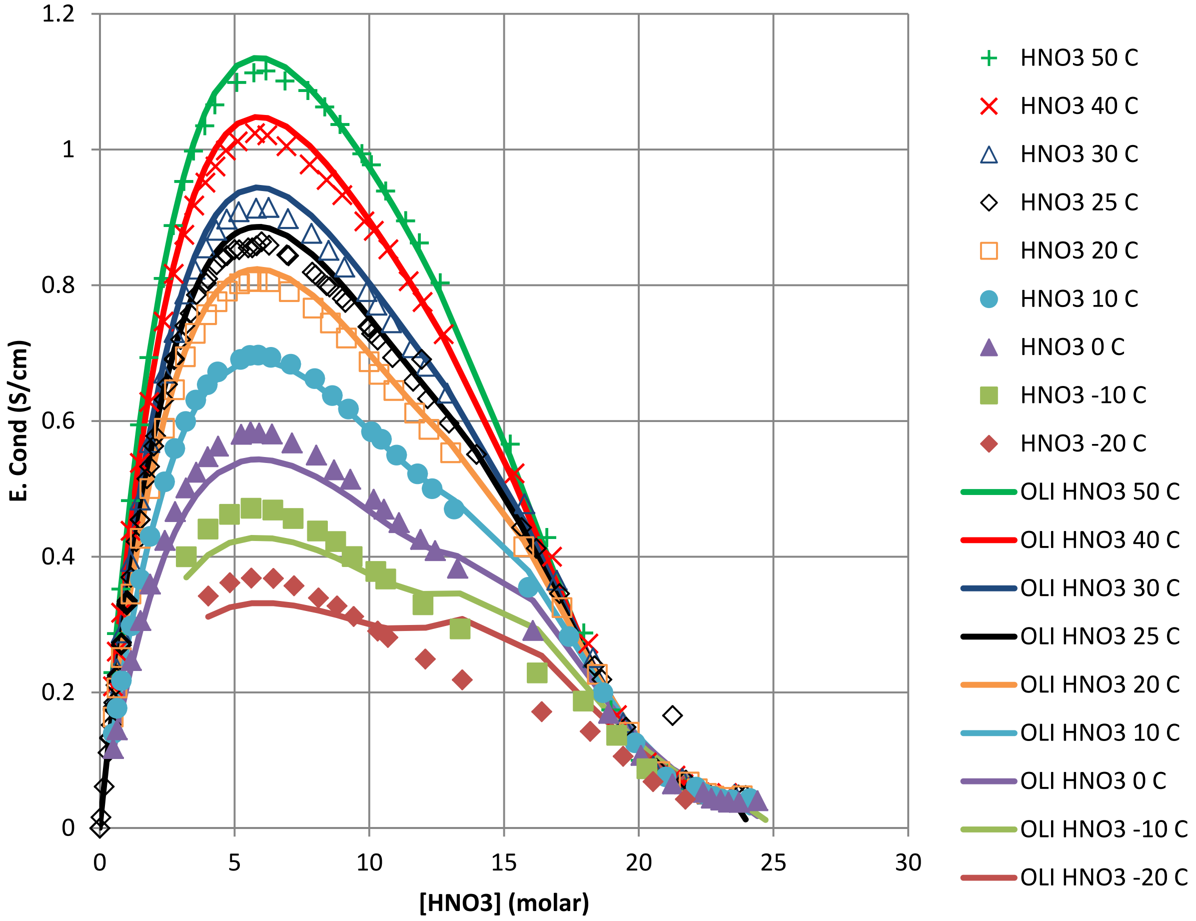

Figure 4-6: Electrical Conductivity of HNO_3 Solution

4.1.1.6 NaOH

Figure 4-7 shows the data available for NaOH solutions from (Lobo, 1989). The reference is a compendium of nine different original sources for NaOH solution data. The model predicts the electrical conductivity well for the entire range of concentrations and temperature. Careful review of the data in (Lobo, 1989) revealed that the original source data was transcribed with an error for the most dilute solutions. The original source, (Maksimova & Yushkevich, 1963), reported the conductivity data an order of magnitude lower than was reported in (Lobo, 1989). The data from the original source was used in this analysis.

Figure 4-8 expands the low concentration range data in order to see details. One can see that the model fits the data sources at low concentrations reasonably well at low concentrations as well as high concentration.

The most abundant component in HLW concentrated supernate is NaOH. As such, it is useful to evaluate the accuracy of the model to fit concentrated solution data. One may also note again that the electrical conductivity peaks around the 5 to 8 M concentration range for solutions less than 120°C as shown in Figure 4-9.

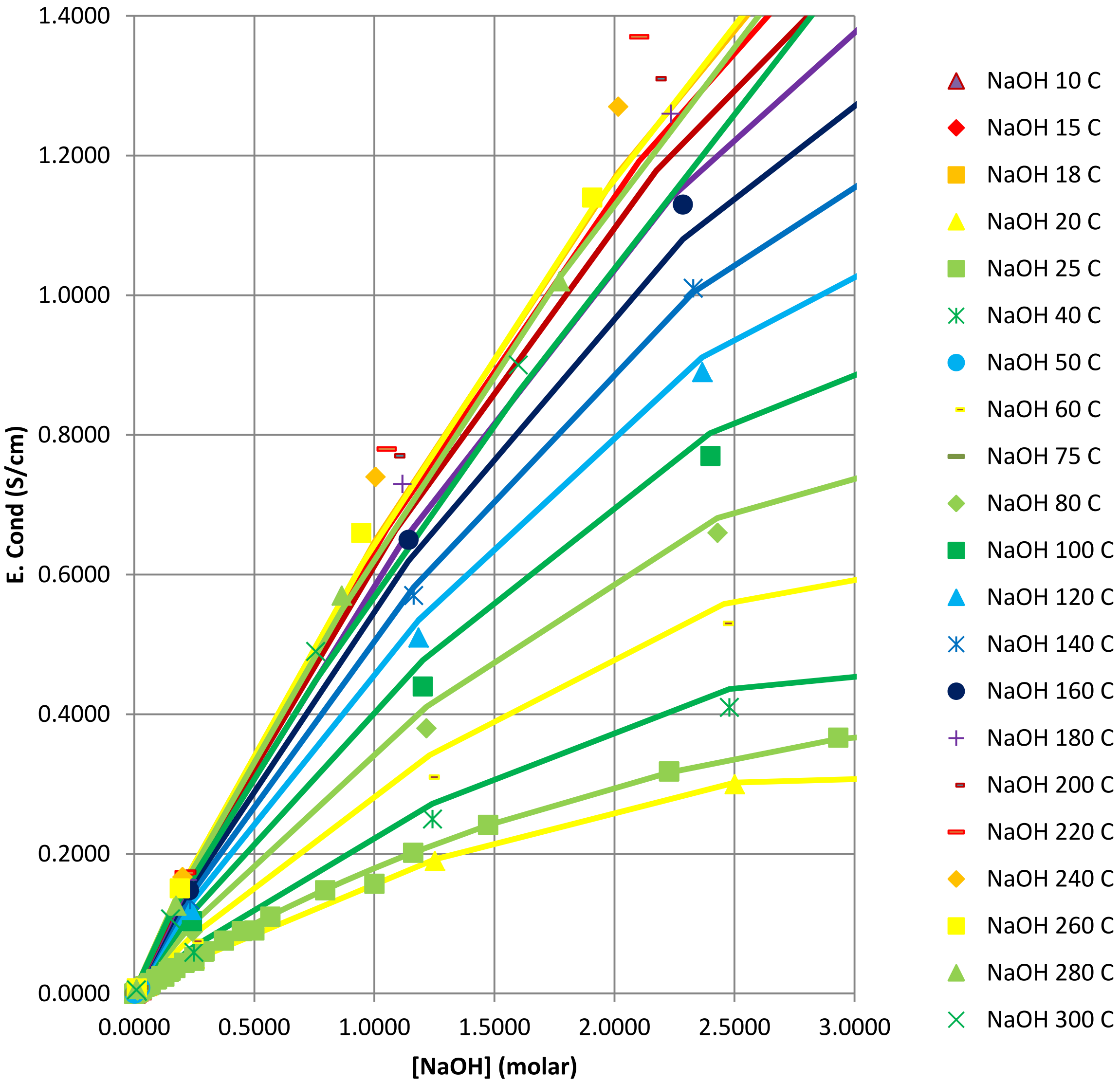

Figure 4-7: Electrical Conductivity of 0 to 3 M NaOH Solution
Note that the lines plot equivalent simulated solution results at each temperature.

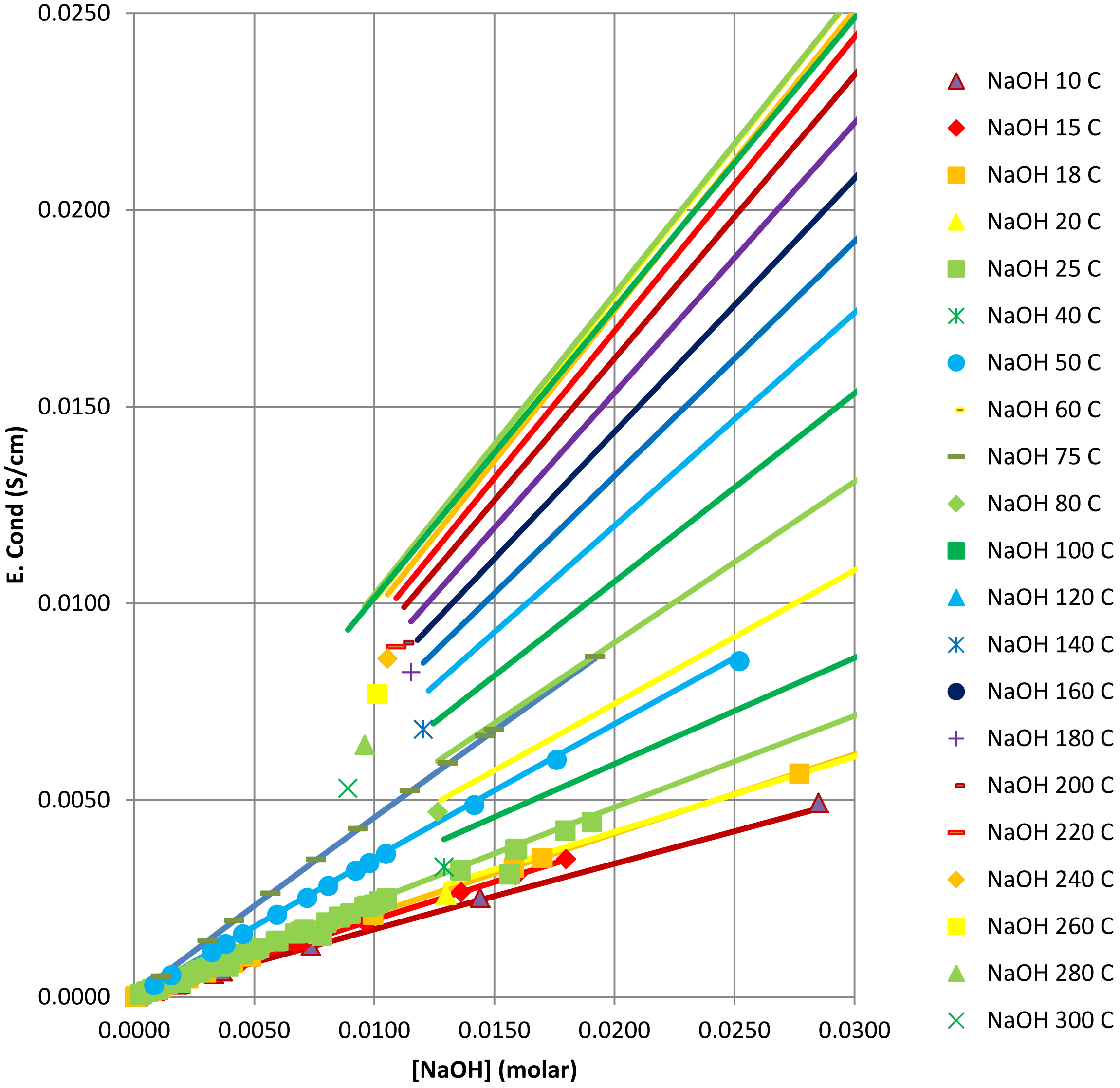

Figure 4-8: Electrical Conductivity of 0 to 0.03 M NaOH Solution
Note that the lines plot equivalent simulated solution results at each temperature.

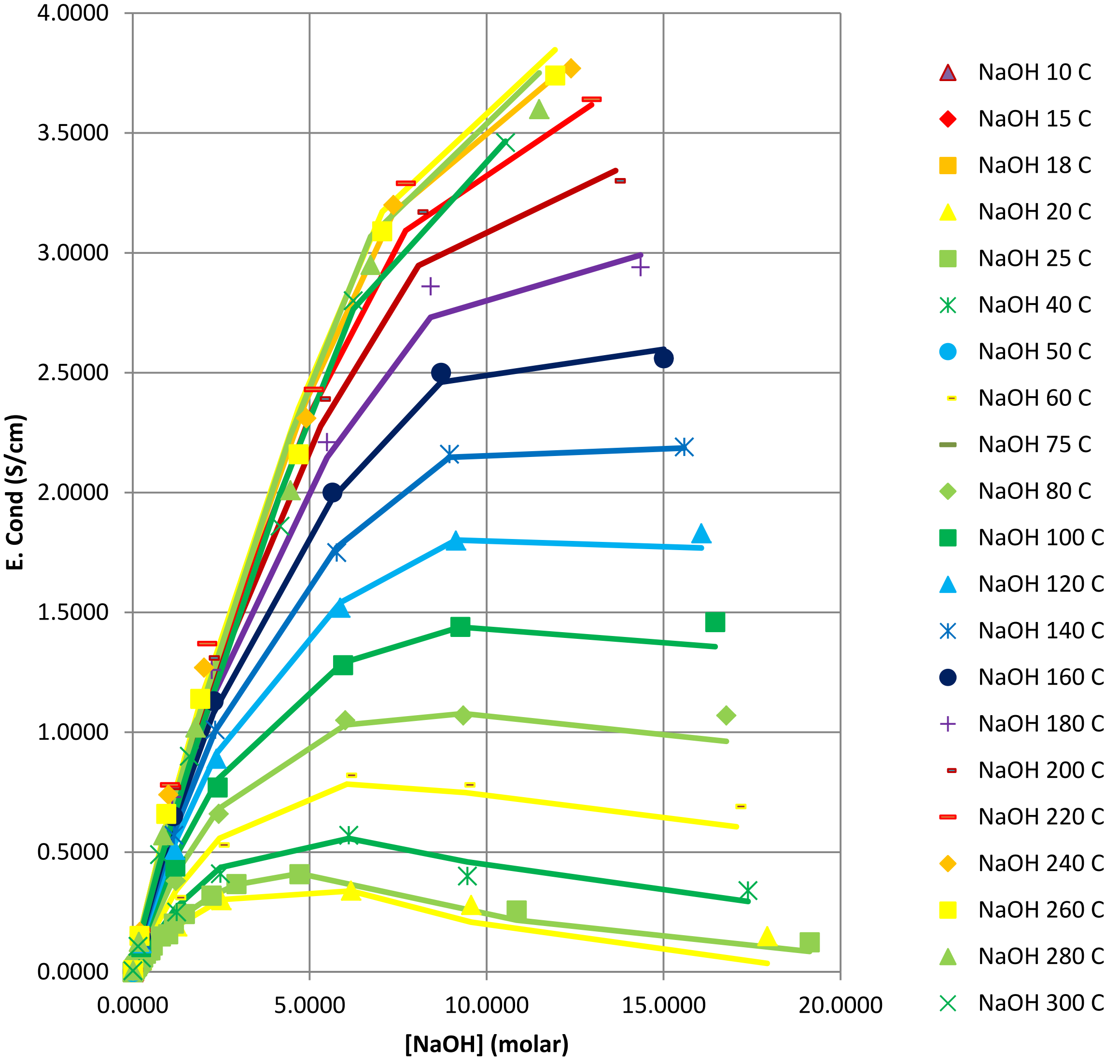

Figure 4-9: Electrical Conductivity of 0 to 20 M NaOH Solution
Note that the lines plot equivalent simulated solution results at each temperature.

4.1.1.7 Estimation of Error

Error is estimated based on the relative deviation of OLI simulated data from literature data for all the components combined. Overall, the OLI simulation data matches literature data well, as indicated in Figure 4-10. Examination of the individual components as discussed earlier reveals some source-specific deviations that may be systemic error. Such error may be resolved and removed with careful investigation of each source of data. For this estimate, all the data was included without any additional considerations in order to estimate the overall deviation. The deviation was calculated as the difference of the OLI simulated values from the measured data. The magnitude of the average deviation from literature values is 2.9%. The standard deviation of the average deviation from literature values is 6.2%. This indicates that >95% of all computed values fall with the range of ±(2.9+12)% or ±15% of 1297 literature values.

Examination of the spread in deviation indicates that a small number of points vary by substantially greater deviations. This subset of deviations was not investigated to determine cause. Though very low probability, the magnitude of an estimated conductivity can range up to ±76% as indicated by the following:

Average deviation	2.9%
Standard deviation	6.2%
Min	-76%
1st quartile	-0.70%
median	0.0050
3rd quartile	2.2%
Max	76%

Overall, 95% of computed estimates of conductivity are within ±15% of literature values. All computed estimates of conductivity are within ±76% of literature values.

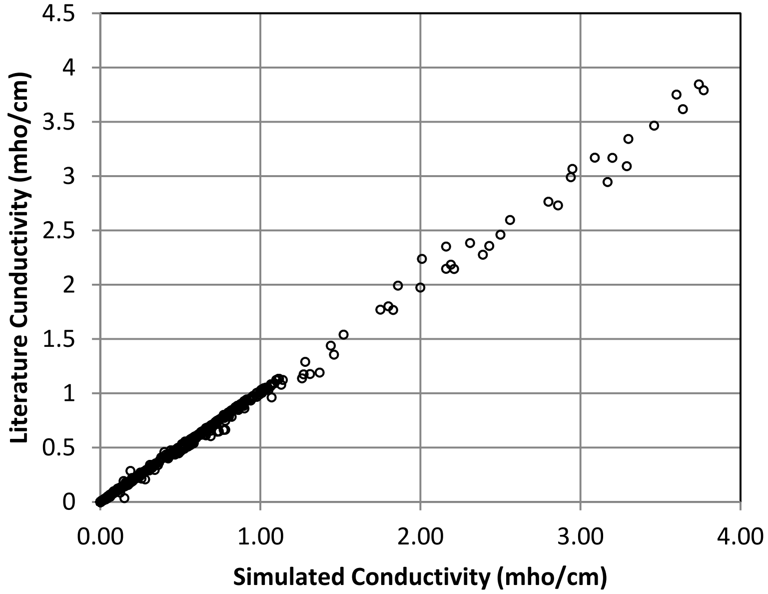

Figure 4-10: Scatter Diagram of OLI Simulation Results versus Literature Data

The largest relative deviations occur at low electrical conductivities. As such, the larger relative deviations are not evident in Figure 4-10. This can be seen more readily in Figure 4-11. In addition, conductivity predicted in OLI simulations appears to be systemically biased high for conductivities less than 0.02 S/cm. The effect is substantially more significant for conductivities less than 0.002 S/cm. Regardless, the estimate of prediction error is ±15% for the entire range.

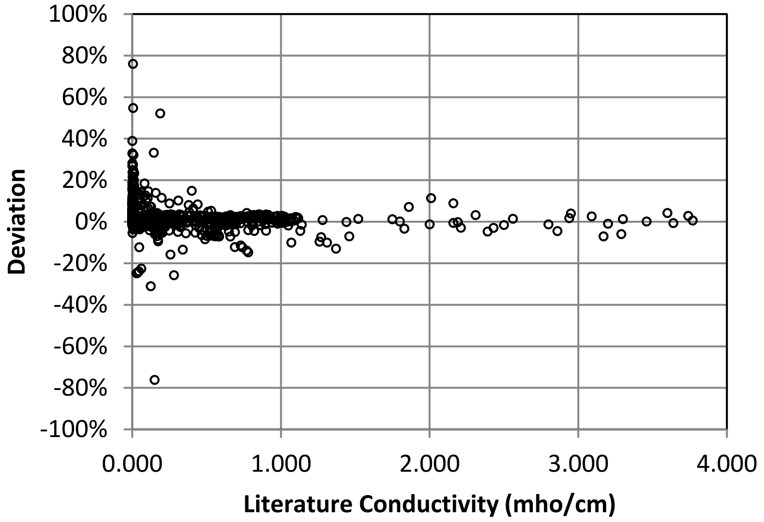

Figure 4-11: Relative Deviation of OLI Simulation Results from Literature Data

4.2 Simplified Correlation for SRS HLW Supernate

By examination of the mixing rule for calculating electrical conductivity of a mixed component electrolyte as presented in Equation 1, one can see that the contribution to the mixture by any one component is influenced by simple multiplication of three factors: concentration, ion charge, and pure component electrical conductivity. Equation 1 applies to individual ion contributions to the total solution; however, with a single dominant cation, an equivalent simpler component-mixing rule may be developed. As such, the peak electrical conductivities are calculated for the components identified earlier as most dominant in HLW and shown in Table 2-1. As discussed in section 4.1.1, electrical conductivity typically increases with increasing concentration to a peak value and then decreases continuously until the concentration is so high, it is no longer an electrolyte solution. Electrical conductivities are calculated using OLI Analyzer™ for each component identified in Table 2-1 and peak values at 25°C are presented in Table 4-1. Table 4-1 also shows a relative importance factor used to determine which components will likely be the most important contributors to the electrical conductivity. This factor is the result of multiplying the concentration, ion charge, and electrical conductivity at the maximum value of the electrical conductivity for the range of each component. The components highlighted in red are identified as the most significant contributors to electrical conductivity and include the sodium salts of NO_2^{-1}, NO_3^{-1}, OH^{-1}, $Al(OH)_4^{-1}$, and CO_3^{-2}.

Table 4-1: Maximum Calculated Electrical Conductivities for Dominant HLW Components

Most Likely Ionic Form	Assumed Compound	Max. Conc. (M)	At 25°C			Relative Importantance [x] · Z · E.C.
			Approx. Peak Conc. (M)	Calculated Peak E. Cond (S/cm)	Calculated E. Cond @ Max Conc. (S/cm)	
Ions						
$Al(OH)_4^{-1}$	**$NaAl(OH)_4$**	1.6	*	*	0.10	0.17
CO_3^{-2}	**Na_2CO_3**	0.73	*	*	0.15	0.21
$C_2O_4^{-2}$	$Na2C_2O_4$	0.081	*	*	0.018	0.0029
Cl^{-1}	NaCl	0.04	5.8	0.25	0.0045	0.00018
F^{-1}	NaF	0.097	7.1	0.13	0.0085	0.00083
K^{+1}	KNO_3	0.2	6.0	0.27	0.022	0.0045
NO_2^{-1}	**$NaNO_2$**	3.2	*	*	0.34	1.1
NO_3^{-1}	**$NaNO_3$**	5.6	6.0	0.20	0.20	1.1
OH^{-1}	**NaOH**	12.6	4.8	0.41	-	5.2
PO_4^{-3}	Na_3PO_4	0.075	0.6	0.11	0.018	0.0040
SO_4^{-2}	Na_2SO_4	0.22	2.3	0.13	0.031	0.0137
Metals and select organics**						
$Al(OH)_4^{-1}$	$NaAl(OH)_4$	0.85	*	*	0.056	0.047
$B(OH)_4^{-1}$	$NaB(OH)_4^{**}$	0.34	3.2	0.031	0.019	0.0065
Ca^{+2}	$Ca(NO_3)_2$	0.026	2.0	0.12	0.0051	0.00026
CrO_4^{-2}	Na_2CrO_4	0.01	*	*	0.022	0.00045
Fe^{+3}	$Fe(NO_3)_3$	0.018	1.3	0.13	0.0073	0.00040
$HCOO^{-1}$	NaHCOO	0.23	*	*	0.023	0.0052
Li^{+1}	$LiNO_3$	0.029	*	*	0.0031	0.000088
K^{+1}	KNO_3	0.56	6.0	0.27	0.056	0.031
Na^{+1}	**$NaNO_3$**	15.7	6.0	0.20	-	3.1
NH_4^{+1}	NH_4NO_3	0.011	8.0	0.40	0.0015	0.000016
SiO_3^{-2}	Na_2SiO_3	0.025	*	*	0.0068	0.00034

* Model response is linear; calculated electrical conductivity does not have a peak.

** Calculated electrical conductivity for $NaB(OH)_4$ solutions has dual peaks; value for higher peak is shown.

The components highlighted in bold **red** are identified as the most significant contributors to electrical conductivity

Assuming sodium salts (sodium is the dominant cation) for the dominate anionic species are NO_2^{-1}, NO_3^{-1}, OH^{-1}, $Al(OH)_4^{-1}$, and CO_3^{-2}, the following simplified mixing rule is applied:

$$\chi = \sum_k f_k \chi_k \qquad \text{Eqn. 4}$$

where f is the molar fraction of the solutes. The complete algebraic equation for estimating electrical conductivity is

$$\chi = f_{NaNO2} A_{NO2} e^{\frac{-B_{NO2}}{T}} + f_{NaNO3} A_{NO3} e^{\frac{-B_{NO3}}{T}} + f_{NaOH} A_{OH} e^{\frac{-B_{OH}}{T}} + f_{NaAl(OH)4} A_{Al(OH)4} e^{\frac{-B_{Al(OH)4}}{T}} + f_{Na2CO3} A_{CO3} e^{\frac{-B_{CO3}}{T}} \qquad \text{Eqn. 5}$$

Specific conductivity is then calculated by using Equation 6.

$$\lambda = \chi \cdot \frac{\Sigma[k]}{1000\ cm^3/L} \qquad \text{Eqn. 6}$$

Table 4-2 shows constants A and B from Equation 2 for each sodium salt that was obtained by regressing simulated data. Simulated solutions ranged from near zero to the maximum concentrations shown in Table 4-1. The temperature ranged from 0 to 125°C for each simulated solution concentration.

Table 4-2: Parameters for Simplified Electrical Conductivity Model

Component	A	B
$NaAl(OH)_4$	19,437	1705.0
Na_2CO_3	79,066	1781.6
$NaNO_2$	22,176	1595.3
$NaNO_3$	4,127.2	1300.1
NaOH	68,416	2133.8

The simplified model fails to capture the complex nature of electrical conductivity. In some cases, the simplified model matches OLI calculations very well and in other cases, the simplified model and OLI calculations do not match so well. Two examples, $NaAl(OH)_4$ and NaOH, are provided in Figure 4-12 and Figure 4-13. The lines in the figures are simplified model values; the points are OLI simulation calculated values. The electrical conductivity for $NaAl(OH)_4$ solution difference ranges up to 16%, whereas, the difference in conductivity for NaOH solution ranges up to 1000%, although this is particularly acute above 8 M and at low temperatures. Below 8 M, the difference ranges up to 65%. The $NaNO_3$ solutions differ up to 170% and the remainder fall within 20%. Based on the simplified mixing rule, this method to estimate electrical conductivity will perform poorly for high hydroxide supernates.

Electrical conductivities for several multicomponent solutions were calculated via both the simplified model and the OLI simulation model as shown in Table 4-3. The difference for the multicomponent solutions ranges from 20% to 360%, the higher deviations occurring with higher NaOH concentrations. These results indicate that the simplified model will provide reasonable estimates of electrical conductivity HLW supernates less than 8 M total sodium and can be calculated easily. This estimate can still be used for order of magnitude estimates for the most concentrated supernates.

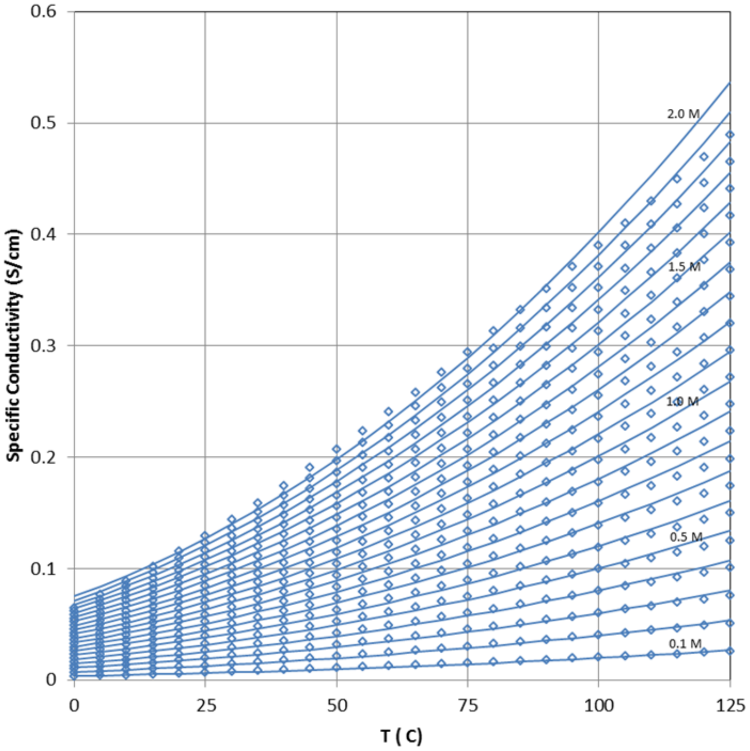

Figure 4-12: Electrical Conductivity of 0.1 to 2 M $NaAl(OH)_4$ Solution: Simplified Model Versus OLI Simulation

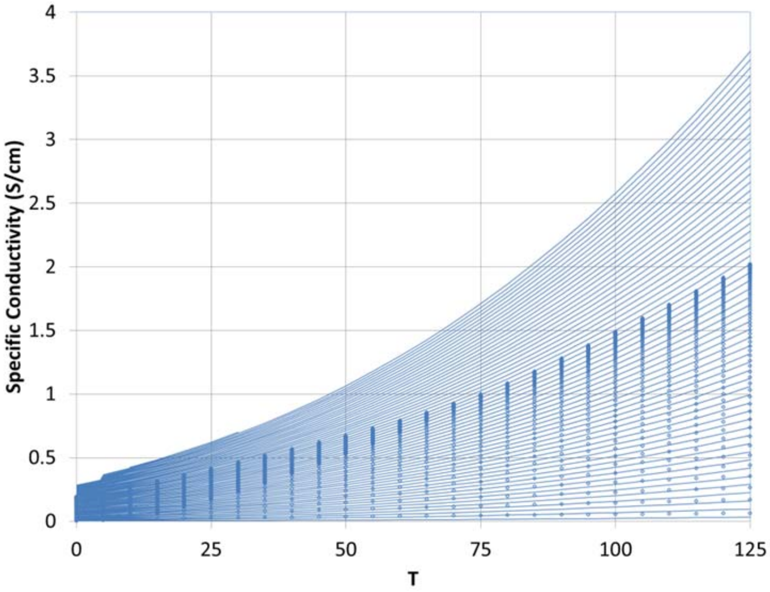

Figure 4-13: Electrical Conductivity of 0.1 to 12.6 M NaOH Solution: Simplified Model Versus OLI Simulation

Table 4-3: Comparison of Simplified Model to OLI Simulation Model for Multicomponent Solutions

Test Case	Concentration (M)					25 °C				75 °C				125 °C			
						Simplified model		OLI model	Diff. %	Simplified model		OLI model	Diff. %	Simplified model		OLI model	Diff. %
	$NaNO_2$	$NaNO_3$	NaOH	$NaAl(OH)_4$	Na_2CO_3	Molar Cond. S cm^2/mol	Specific Cond. S/cm	Specific Cond. S/cm		Molar Cond. S cm^2/mol	Specific Cond. S/cm	Specific Cond. S/cm		Molar Cond. S cm^2/mol	Specific Cond. S/cm	Specific Cond. S/cm	
Max.	3.2	5.6	12.6	1.6	0.73	65	1.5	*		157	3.7	*		308	7.3	*	
Hi Al	1.1	1.3	3.6	1.6	0.20	66	0.52	0.40	30%	159	1.2	1.02	18%	309	2.4	1.7	41%
Hi CO3	1.1	1.3	3.6	0.40	0.73	77	0.55	0.39	41%	184	1.3	1.01	29%	360	2.6	1.7	53%
Hi NO2	3.2	1.3	3.6	0.40	0.20	76	0.66	0.47	40%	177	1.5	1.2	25%	338	2.9	2.0	45%
Hi NO3	1.1	5.6	3.6	0.40	0.20	61	0.67	0.27	148%	137	1.5	0.7	114%	254	2.8	1.2	133%
Hi OH	1.1	1.3	12.6	0.40	0.20	59	0.92	0.20	360%	154	2.4	1.00	140%	319	5.0	2.0	150%
Average	1.1	1.3	3.6	0.40	0.20	67	0.44	0.38	16%	161	1.1	0.93	18%	317	2.1	1.5	40%
Hi OH-2	1.1	1.3	8.0	0.40	0.20	61	0.67	0.27	145%	156	1.7	1.02	67%	319	3.5	1.9	84%
Low	0.086	0.068	0.15	0.050	0.036	79	0.031	0.057	-46%	186	0.073	0.11	-34%	357	0.14	0.17	-18%

* A solution at the maximum concentrations is not possible and OLI simulation does not converge to a solution for this mixture.

4.3 Experimental Results

Conductivity measurements on a limited number of reference solutions are compared with literature values and modeled values in Table 4-4. For the 10 wt% sodium nitrate solution, the measured value (0.084-0.086 S/cm) was 2-4% higher than the literature value, and 4-6% lower than the OLI MSE value. Similarly, for the 20 wt% sodium nitrate solution, the measured value (0.142-0.143 S/cm) was 6-7% higher than the literature value, and ~5% lower than the OLI MSE value. Overall, these deviations were considered modest, given the typical fluctuations of analytical measurements.

In contrast, for the first Tank 40 supernatant simulant, the measured value (0.100-0.101 S/cm) was about 30% lower than the OLI MSE value. For the second Tank 40 supernatant simulant, the measured value (0.086-0.087 S/cm) was 13-14% lower than the OLI MSE value. The reason for the much larger difference between the measured value and the OLI MSE value for the first Tank 40 simulant is not completely clear. However, it demonstrates the potential for uncertainty of conductivity expectations as a function of composition, particularly in cases where multiple sources of dissolved solids are present.

The low relative conductivity measured for the deionized water (1.7E-6 S/cm) provides an indication of the values that can be expected when negligible dissolved solids are present.

Table 4-4: Comparison of Conductivity Measurements, Lit Values, & Modeled Values

Matrix	Salt Concentration	Conductivity, S/cm		
		Measured Value*	Lit Value**	OLI MSE*
Deionized water	Purity unknown	1.7E-06	NA	NA
Single salt	10 wt % $NaNO_3$	0.084-0.086	0.0826	0.0895
Single salt	20 wt % $NaNO_3$	0.142-0.143	0.134	0.150
Tank 40 simulant #1	0.30 M $NaNO_2$	0.100-0.101	NA	0.146
	0.10 M $NaNO_3$			
	0.30 M $NaOH$			
	0.30 M Na_2CO_3			
Tank 40 simulant #2	0.30 M $NaNO_2$	0.085-0.087	NA	0.109
	0.19 M $NaOH$			
	0.13 M $NaNO_3$			
	0.10 M Na_2CO_3			
	0.051 M Na_2AlO_2			
	0.021 M $Na_2C_2O_4$			
	0.016 M Na_2SO_4			

NA = not applicable
* Measurement/OLI model temperature ≈ 25 °C
** Temperature of referenced literature measurements is 20 °C (Haynes, 2014)

Conductivity, density, and dissolved solids results for the undiluted Tank 40 supernatant filtrate are given in Table 4-5, based upon the laboratory measurements. As shown in the table, the mean values are 0.087 S/cm for conductivity, 1.07 g/mL for density, and 5.8 wt% dissolved solids, with RSDs ranging from 0.2 to 3.4 %. Although not identified in the table, the concentration of insoluble solids in the unfiltered sample was below the MDL. Given that the dissolved solids measurements varied by about 0.2 wt%, the MDL for insoluble solids was estimated to be 0.2 wt%, which indicates that the sample was free of any significant insoluble solids.

Table 4-5: Measured Conductivity, Density, and Dissolved Solids Content

Measurement	Result	% RSD
Conductivity, S/cm	0.087	0.2
Density, g/mL	1.07	3.6
Dissolved solids, wt%	5.8	3.4

Conductivity for each dilution is shown in Table 4-6. The impact of dilution on the Tank 40 supernatant conductivity is illustrated in Figure 4-14, where conductivity is plotted as a function of the sodium concentration. As shown in the figure, dilution of the supernatant by a factor of ten (from one molar sodium to one-tenth molar sodium) reduces the conductivity by a factor of approximately eight (from 0.087 S/cm to ~0.011 S/cm).

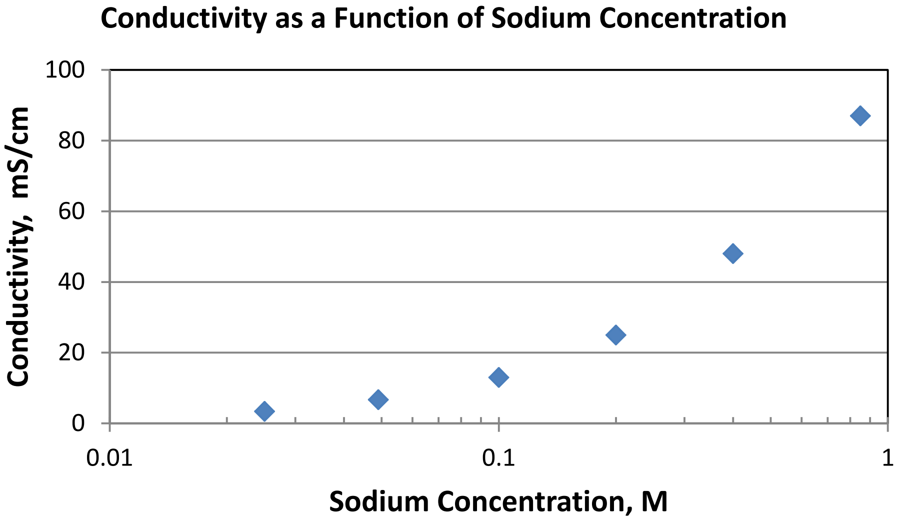

Figure 4-14: Impact of Dilution on Tank 40 Supernatant Conductivity

Table 4-6: Measured Conductivity for Each Dilution of Tank 40 Supernatant

Sample Identification	Dilution Factor	Measured Conductivity, S/cm
Undiluted Supernatant	None	0.087
Dilution #1	2.1	0.048
Dilution #2	4.2	0.025
Dilution #3	8.5	0.013
Dilution #4	17	0.0067
Dilution #5	34	0.0034

Mean concentrations of the primary ions in the Tank 40 supernatant filtrate are given in Table 4-7, along with the corresponding % RSDs and equivalence concentrations provided to assess charge balance. As shown in the table, sodium is the only dominant cation, with a concentration of approximately one molar. The most dominant anion is nitrite, with a concentration of 0.30 M, followed by free hydroxide, nitrate, and carbonate at concentrations of 0.19, 0.13, and 0.10 molar, respectively. The other detectable anions are present at smaller concentrations – 0.051 molar aluminate, 0.021 molar oxalate, and 0.016 molar sulfate. RSDs ranged from 0.3 to ten percent, which is consistent with expectations for normal analytical determinations.

A comparison of the total cationic and anionic equivalence concentrations indicates that the data are appropriately consistent with respect to charge balance. Specifically, the total cation equivalency concentration is 1.01 eg/L and the total anion equivalency concentration is 0.95 eg/L, indicating a difference of approximately 10%. Given that 10% is the typically expected analytical uncertainty, a 10% difference between the equivalency concentrations is considered reasonable, and consistent with expectations for good quality data.

Table 4-7: Primary Ion Concentrations and Charge Balance

Ion	Molarity	% RSD	Corresponding eq/L	
			Cationic	Anionic
Na^+	1.01	10	1.01	N/A
NO_2^-	0.30	1.0	N/A	0.30
Free OH^-	0.19	1.8	N/A	0.19
NO_3^-	0.13	2.9	N/A	0.13
CO_3^{2-}	0.10	0.3	N/A	0.20
$Al(OH)_4^-$	0.051	10	N/A	0.051
$C_2O_4^{2-}$	0.021	1.0	N/A	0.042
SO_4^{2-}	0.016	0.7	N/A	0.032
			Σ = 1.01	Σ = 0.95

A breakdown of the primary expected dissolved constituents is given in Table 4-8, along with the projected solids content that each constituent contributes. This distribution is based upon the anion concentrations identified in Table 4-7. As shown in the table, the concentration of all dissolved solids is projected to be 5.7 weight percent, which is agrees extremely well with the measured value of 5.8 weight percent. This is another indicator giving confidence that the data are sound and make sense.

Table 4-8: Projected Dissolved Solids Content Based Upon Primary Constituents

Constituent	Molarity	MW, g	wt%
$NaNO_2$	0.30	69	1.9
NaOH	0.19	40	0.7
$NaNO_3$	0.13	85	1.0
Na_2CO_3	0.10	106	1.0
$NaAl(OH)_4$	0.051	118	0.6
$Na_2C_2O_4$	0.021	134	0.3
Na_2SO_4	0.016	142	0.2
			Σ = 5.7

Concentrations of the elemental constituents in the Tank 40 supernatant filtrate are given in Table 4-9, along with the corresponding RSDs. As shown in the table, nine of the constituents are detectable and twenty-five of the constituents are non-detectable. Of the nine detectable constituents, only three are present at concentrations above 500 mg/L – sodium at 2.3E+04 mg/L, aluminum at 1.4E+03 mg/L, and sulfur at 5.6E+02 – and the other detectable constituents are present at concentrations ranging from about

6 to 110 mg/L. All of the RSDs for the detectable constituents were in the 10-16% range. All RSDs were considered to be in normal range.

Table 4-9: Concentrations of Elemental Constituents in Tank 40 Supernatant

Element	Concentration (mg/L)	% RSD
Ag	<3.3E-01	N/A
Al	1.4E+03	10
B	5.9E+00	10
Ba	<3.4E-01	N/A
Be	<1.2E-01	N/A
Ca	5.8E+00	10
Cd	<3.4E-01	N/A
Ce	<1.4E+00	N/A
Co	<5.1E-01	N/A
Cr	3.7E+01	10
Cu	<6.7E-01	N/A
Fe	<5.5E-01	N/A
Gd	<4.7E-01	N/A
K	1.0E+02	14
La	<3.4E-01	N/A
Li	<6.9E-01	N/A
Mg	<2.4E-01	N/A
Mn	<2.4E-01	N/A
Mo	8.3E+00	16
Na	2.3E+04	10
Ni	<6.5E-01	N/A
P	<4.4E+00	N/A
Pb	<2.4E+00	N/A
S	5.6E+02	15
Sb	<3.1E+00	N/A
Si	2.5E+01	11
Sn	<2.8E+00	N/A
Sr	<1.2E-01	N/A
Th	<2.3E+00	N/A
Ti	<3.4E-01	N/A
U	<1.1E+01	N/A
V	<3.4E-01	N/A
Zn	<6.7E-01	N/A
Zr	<2.9E-01	N/A

4.4 Comparison of Computational Results to Tank 40 Supernate

Comparison of OLI computational results and conductivity measurements obtained from literature and described in Section 4.1.1.7 show that the OLI computational results predict conductivity within ±4.1% although there are some points of deviation as much as 76%.

Table 4-10 shows the relative difference between computed conductivity and the measured conductivity for successive dilutions of Tank 40 sample material. In this comparison, the equivalent sodium concentration is used as determined by data reconciliation of the Tank 40 sample composition analysis in the computational results. The sodium ion is allowed to change during reconciliation to achieve a charge balance. The successive dilutions are then calculated using the reported mass of water added to the original Tank 40 sample as identified in Table 2-2. The sodium concentration that is reported in Table 4-10 is the calculated concentration for each dilution and implicitly accounts for density changes. The measured sodium concentrations are based on the dilution factors as shown in Table 4-6, but use the equivalent sodium concentration after charge balance reconciliation as shown in Table 4-7 rather than the measured sodium concentration so that comparison of measured and computed conductivity is on the same basis. The equivalent sodium concentration is 5.5% lower than measured which is within experimental variation of the sodium measurement. One may choose to select a different method for charge balance such as changing the dominant anion, but the relative change to the sodium concentration is within the error to detect the difference.

Table 4-10: Comparison of OLI Simulation Results to Tank 40 Sample Measurements

Simulated		Measured			% Deviation from Measured
Na Conc. (M)	Conductivity (S/cm)	Na Conc. (M)	Conductivity (S/cm)	Difference	
0.94	0.106	0.95	0.087	0.019	22.4%
0.46	0.056	0.45	0.048	0.0077	16.1%
0.18	0.023	0.23	0.025	-0.0017	-6.8%
0.091	0.012	0.112	0.013	-0.0010	-7.7%
0.045	0.0061	0.056	0.0067	-0.00058	-8.6%
0.022	0.0031	0.028	0.0034	-0.00029	-8.6%

Table 4-11 contains a comparison of measured electrical conductivity to calculated conductivity via the simplified model. When applying the simplified model, the relative concentrations of the five components in the simplified model should be increased such that the total sodium content of the approximated composition matched the total sodium content measured. If total sodium is not measured, the total sodium can be estimated from all the components measured verses the subset of components used in the simplified model.

Figure 4-15 shows the deviation of the OLI simulated results and the simplified model to measured data. The simulated conductivity deviates -9 to +22% from measured conductivity. The simplified model deviation is similar, -24 to +1% from the measured data. The interesting aspect is that the simplified model results were closer to measured values at higher concentrations while the reverse holds for the OLI simulation results. This result would be misleading if applying the models to other wastes without considering the broad range of waste compositions. This observation only holds for this particular composition and will change for other compositions, as could be inferred from the discussions in Sections 4.1 and 4.2.

Table 4-11: Comparison of OLI Simulation Results to Tank 40 Sample Measurements at 25 °C

Dilution	Concentration (M)						Conductivity (S/cm)			
	Total Na	$NaNO_2$	$NaNO_3$	NaOH	$NaAl(OH)_4$	Na_2CO_3	Simplified Model	Measured	Difference	% Deviation from Measured
0	0.95	0.30	0.13	0.19	0.052	0.10	0.088	0.087	-0.001	+1%
1	0.45	0.14	0.062	0.090	0.025	0.048	0.042	0.048	-0.006	-12%
2	0.23	0.071	0.031	0.045	0.012	0.024	0.021	0.025	-0.0040	-16%
3	0.11	0.035	0.015	0.022	0.0061	0.012	0.0104	0.013	-0.0026	-20%
4	0.056	0.018	0.008	0.011	0.0031	0.0059	0.0052	0.0067	-0.0015	-22%
5	0.028	0.0088	0.0038	0.0056	0.0015	0.0029	0.0026	0.0034	-0.0008	-24%

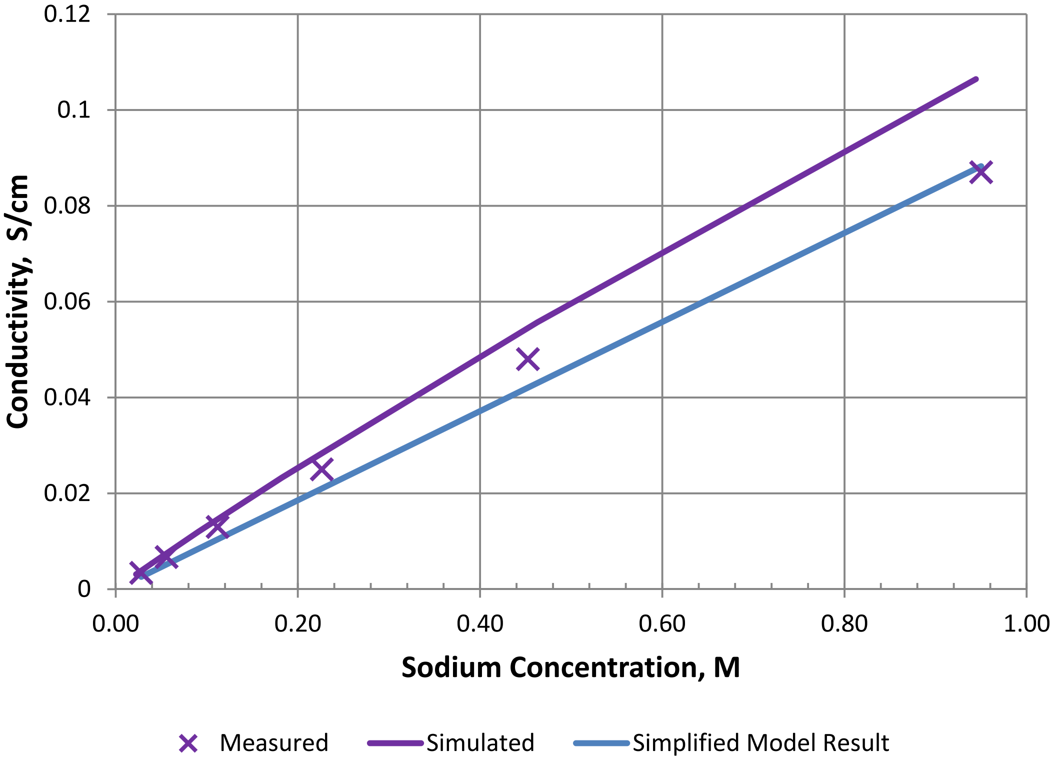

Figure 4-15: Comparison of Tank 40 Sample Conductivity Measurements to Computed Conductivity

5.0 Conclusions

Minimal conductivity data for mixed component solutions was available for model verification. Pure component solution data were compiled from literature for several waste components. Overall, 95% of computed estimates of electrical conductivity are within ±15% of literature values for component concentrations from 0 to 15 M and temperatures from 0 to 125 °C. Though the computational results are generally in good agreement with the measured data, a small portion of literature data deviates as much as ±76%.

A simplified model was created that can be used readily to estimate electrical conductivity of waste solution in computer spreadsheets. The variability of this simplified approach ranges up to 140% from measured values. Generally, this model can be applied to estimate the conductivity within a factor of two. The comparison of the simplified model to pure component literature data suggests that the simplified model will tend to under estimate the electrical conductivity.

A waste sample from Tank 40 was analyzed for composition and electrical conductivity as shown in Table 4-6, Table 4-7, and Table 4-9. The conductivity for undiluted Tank 40 sample was 0.087 S/cm. Simulated Tank 40 conductivity results from OLI Systems software as well as the simplified model agree with the measured data within the estimated error for each model.

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