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Electrolyte solution densities are used in many safety and design calculations for processes treating Hanford's high-level nuclear waste. This data is usually available in the public literature, but sometimes there are inconsistencies in the data. When these inconsistencies arise, the data user must decide which dataset should be used for their application. This study develops a method to decide between two inconsistent datasets using the Laliberte-Cooper model. The Laliberte-Cooper model can be used to estimate the density of aqueous solutions for one electrolyte from data available for set of other electrolytes that have the same cation and anion. In this study, the density of aqueous sodium citrate solutions was calculated using density data for NaOH, KOH, and potassium citrate. Those resulting density calculations were used to decide between two sodium citrate datasets in the literature that were inconsistent with each other.

I. INTRODUCTION

Tri-sodium citrate is a common organic compound in Hanford high-level nuclear waste¹. The fate and concentration of citrate in Hanford waste is important because citrate complexes metals in solution and generates hydrogen gas^{2,3}. Tracking citrate is valuable in process flowsheets because it simplifies charge balance statistical calculations⁴ and contributes to the solution density. When all of the waste components that contribute appreciably to the waste density are tracked in chemical flowsheets, it simplifies the reconciliation of the overall mass balance in the flowsheet⁵. Consequently, it is important to use the most correct density data available for sodium citrate in process flowsheets.

The densities of aqueous electrolyte solutions are inputs to many safety and process calculations throughout the nuclear industry. Most of the data comes from published journal articles or is taken from models that are parameterized by data from those journals. There is growing recognition that some of the density data in the literature is inaccurate, which can cause incorrect calculations if used unknowingly by engineers.⁶ The United States National Institute of Standards (NIST) is

partnering with a number of journals to screen physical property data and catch a higher percentage of inaccurate data before it is published.⁶ Even if the NIST and the journals are completely successful in its mission, there is a large amount of potentially inaccurate data already in the public literature.

A potential example is the density of (tri)sodium citrate in water at 25 °C (298.15 K). Fig. 1 shows the density of aqueous sodium citrate solutions as a function of citrate concentration as reported by two different studies.^{7,8} Comparing these two studies in Fig. 1 indicates that the two studies received similar results at low citrate concentrations, but there are substantial discrepancies at higher concentrations. Data users are left to decide which study is the most accurate. The present study provides data users a method they can (often) used to decide between conflicting density datasets; here using sodium citrate as an example. The method reported here could also be used in the case where there is only a single dataset available, and so there is no possibility to compare to other data.

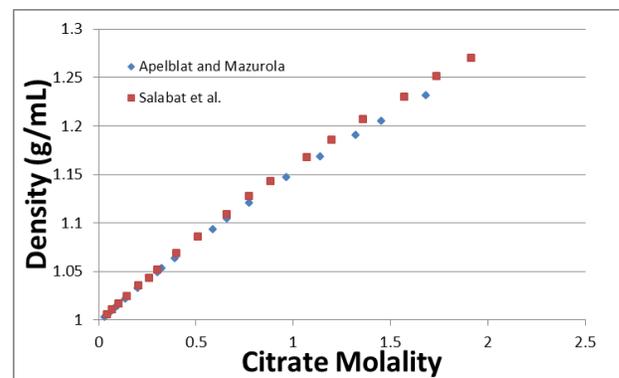


Fig. 1, Density of Sodium Citrate in Water at 25 °C, as Published by Two Different Research Groups.

II. MODEL DESCRIPTION AND DATA VALIDATION METHODOLOGY

The method of deciding between conflicting data makes use of the Laliberte-Cooper model of electrolyte solution density^{9,10} coupled with the model

parameterization method developed by Reynolds and Carter.¹¹ The Laliberte-Cooper model is⁹

$$\rho_m = \frac{1}{w_{H_2O} \bar{v}_{H_2O} + \sum_i w_i \bar{v}_{app,i}} \quad (1)$$

where ρ_m is the solution density in kg m^{-3} , w_i is the mass fraction of electrolyte i , and $\bar{v}_{app,i}$ is the electrolyte specific volume in $\text{m}^3 \text{kg}^{-1}$. The coefficient w_{H_2O} is the water mass fraction and \bar{v}_{H_2O} is the apparent specific volume of water, $\text{m}^3 \text{kg}^{-1}$. The apparent electrolyte specific volume ($\bar{v}_{app,i}$), is given by Equation 2,

$$\bar{v}_{app,i} = \frac{(1 - w_{H_2O}) + c_2 + c_3 t}{(c_0(1 - w_{H_2O}) + c_1) e^{(0.00000(T+c_4)^2)}} \quad (2)$$

where c_0 to c_4 are empirical constants. The coefficients c_0 and c_1 are in kg m^{-3} , c_2 is dimensionless, c_3 is in $^\circ\text{C}^{-1}$, c_4 is in $^\circ\text{C}$, and T is in $^\circ\text{C}$.

This equation assumes that the apparent specific volume of each electrolyte depends on the total concentration of electrolytes in solution. The specific volume of water was calculated from the correlation for the density of water as a function of temperature reported by Ref. 11.

The Laliberte-Cooper models the ions in solutions as electrolyte (cation and anion pairs) rather than as individual ions. This means that a poorly parameterized model of a mixed-electrolyte solution that has more than one cation as well as more than one anion could predict different densities depending on how cations and anions are paired together to make electrolytes. Reynolds and Carter¹² evaluated the large number of parameter sets published by Laliberte and Cooper⁹ and determined that they did not suffer from this poor conditioning.

Reynolds and Carter¹² realized that Laliberte-Cooper model coefficients could be determined without having to fit real data if coefficients were available from other electrolytes that had the same cations and anions. In their example, they were able to derive Laliberte-Cooper model c_0 through c_4 coefficients for KAl(OH)_4 from the coefficients of NaOH , NaAl(OH)_4 , and KOH . They did this by using the Laliberte-Cooper model to calculate the density of a hypothetical mixture of KOH and NaAl(OH)_4 . They then re-model the same data as a mixture of KAl(OH)_4 and NaOH instead of KOH and NaAl(OH)_4 by re-pairing the cation and anion together. The c_0 through c_4 coefficients for KAl(OH)_4 were fit to the simulated densities, using the published coefficients

for NaOH for the NaOH contribution to the densities of the mixtures following the method of Ref. 13. Here it is demonstrated that this method can be used to determine which sodium citrate dataset is more accurate.

Here, Laliberte-Cooper model coefficients are first determined for (tri)potassium citrate. The potassium citrate coefficients are then used to calculate the density of a hypothetical mixture of potassium citrate and NaOH . These cations and anions are then switched in these hypothetical mixtures, where sodium is paired with citrate and potassium is paired with hydroxide. The sodium citrate coefficients are then determined by fitting the model to the hypothetical mixture densities.

III. DETERMINATION OF LALIBERTE-COOPER MODEL COEFFICIENTS FOR POTASSIUM CITRATE

The c_0 through c_4 coefficients for the Laliberte-Cooper model were determined by fitting Equations 1 and 2 to selected experimental data reported by Sadeghi and Ziamajidi,^{14,15} using the method described by Laliberte and Cooper.⁹ Apelblat and Manzurola⁷ also report data for the density of potassium citrate solutions, but this data was not used because the potassium citrate model coefficients will be used later to evaluate their sodium citrate density data. The Solver function in a Microsoft Excel 2010 Spreadsheet was used to do the numerical optimization. The coefficients determined are shown in Table 1, and cover a temperature range between 15 and 40 $^\circ\text{C}$, as well as a potassium citrate mass fraction range of 0.0056 to 0.1867.

Fig. 2 shows an excellent fit of the Laliberte-Cooper model to select data from Sadeghi and Ziamajidi¹⁵. A similar fit was achieved for the data from Ref. 14. The R^2 for the fit of all of the data from Sadeghi and Ziamajidi^{14,15} was 0.9999. Given the excellent fit the data to the potassium citrate data, the potassium citrate c_0 through c_4 coefficients in Table 1 were used to estimate the coefficients for sodium citrate.

Table 1. Laliberte-Cooper Model Coefficients Determined in This Study.

Coefficient	Potassium Citrate	Sodium Citrate
c_0	-52.2503	-108.72
c_1	880.9498	898.78
c_2	2.282097	54.780
c_3	0.012033	0.17416
c_4	1434.305	-2277.68

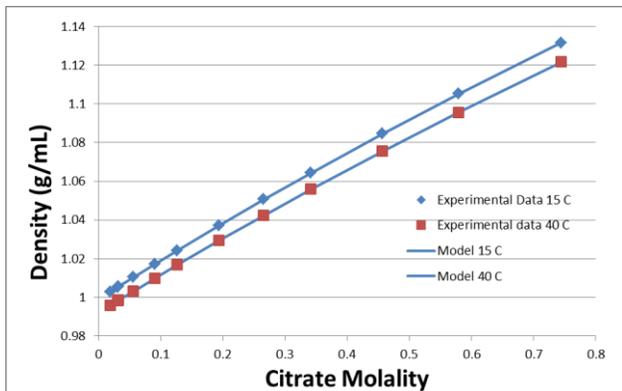


Fig. 2. Laliberte-Cooper Model Prediction of Potassium Citrate Density

IV. DETERMINING SODIUM CITRATE LALIBERTE-COOPER MODEL COEFFICIENTS FROM THE POTASSIUM CITRATE COEFFICIENTS

The coefficients for sodium citrate were determined from those of potassium citrate (Table 1) as well as NaOH and KOH (taken from Ref. 9). The NaOH and KOH coefficients reported by Laliberte and Cooper⁹ were chosen because they were used successfully previously to develop coefficients for $KAl(OH)_4$.¹² The density was calculated for a hypothetical mixture of potassium citrate and NaOH at temperatures, 15, 25, 35 and 45 °C and the electrolyte molarities in Table 2.

The molality of each cation was the same in the mixture because there are three moles of potassium per mole of potassium citrate and there are exactly three times as many moles of NaOH in each hypothetical mixture. This means that the mixture could also be modeled as a mixture of sodium citrate (three moles of Na per mole of sodium citrate) and KOH (three times as many moles of KOH as sodium citrate). The cations and anions were thus paired together in this manner to determine the Laliberte-Cooper coefficients for sodium citrate. The c_0 through c_4 parameters for sodium citrate were varied iteratively until the minimum difference between the predicted (using sodium citrate coefficients) and original densities was determined (as calculated when the solution was modeled as a mixture of potassium citrate and sodium hydroxide). These coefficients are shown in Table 1.

V. DETERMINING WHICH SODIUM CITRATE DENSITY DATASET IS CORRECT

The Laliberte-Cooper can be used to determine which of the conflicting sodium citrate datasets is correct. Using the Laliberte-Cooper model coefficients in Table 1, the aqueous solution density of sodium citrate was calculated as a function of sodium citrate concentration at 25 °C. The results are compared to the experimental data from Apelblat and Manzurola⁷ as well as Salabat et al.⁸ in Fig. 3. The model results support the conclusion that the

Apelblat and Manzurola⁷ is the preferred dataset for the density of aqueous sodium citrate solutions at 25 °C due to the excellent fit of the dataset over the entire concentration range and poor fit of the Salabat et al.⁸ data at high concentrations (Fig. 3). The author therefore suggest that the Apelblat and Manzurola⁷ dataset be used preferentially.

Table 2, Electrolyte Molalities Used in the Determination of Sodium Citrate Laliberte-Cooper Model Coefficients.

Concentrations Used for Calculating Densities		Concentrations Used for Fitting Sodium Citrate Coefficients	
Potassium Citrate Molality	NaOH Molality	Sodium Citrate Molality	KOH Molality
0.01	0.03	0.01	0.03
0.015	0.045	0.015	0.045
0.02	0.06	0.02	0.06
0.0225	0.0675	0.0225	0.0675
0.025	0.075	0.025	0.075

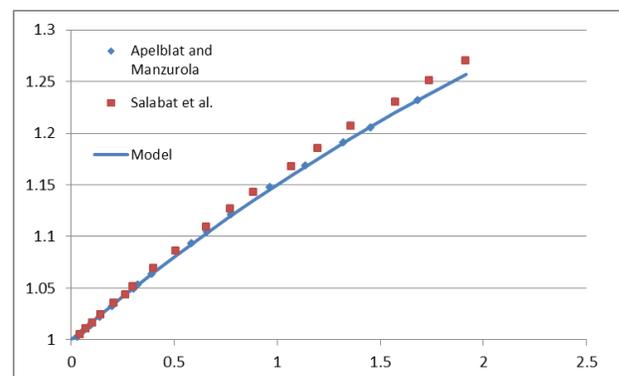


Fig. 3. Model of Sodium Citrate Density in Water at 25 °C Derived From Potassium Citrate Data

VI. CONCLUSIONS

This study developed a method to distinguish between two inconsistent aqueous electrolyte solution datasets. This method can be employed whenever Laliberte-Cooper model coefficients are available for other electrolytes that have the same cation and anions. As an example, the method was employed to decide between two inconsistent sodium citrate datasets at 25 °C. Based on the Laliberte-Cooper model coefficients for potassium citrate, the Laliberte-Cooper model indicates the data from Apelblat and Manzurola⁷ be used preferentially for aqueous sodium citrate solution density.

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