

Water Activity Data Assessment to be used in Hanford Waste Solubility Calculations

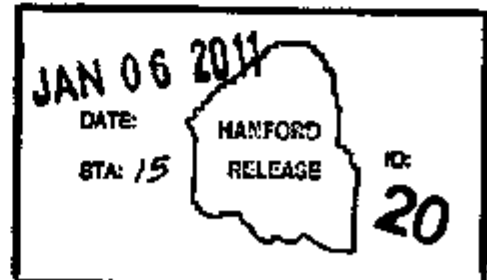
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U.S. Department of Energy Contract DE-AC27-08RV14800

EDT/ECN: DRF UC: N/A
Cost Center: 2GB00 Charge Code:
B&R Code: N/A Total Pages: 25 *Jan 16*

Key Words: Water activity, molality, ionic strength, solubility, Hanford crystal phases, isopiestic, vapor pressure, osmotic coefficient

Abstract: The purpose of this report is to present and assess water activity versus ionic strength for six solutes: sodium nitrate, sodium nitrite, sodium chloride, sodium carbonate, sodium sulfate, and potassium nitrate. Water activity is given versus molality (e.g., ionic strength) and temperature. Water activity is used to estimate Hanford crystal hydrate solubility present in the waste.


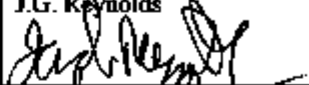
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J. D. Nardal *01/06/11*
Release Approval Date

Release Stamp

Approved For Public Release

Tank Operations Contractor (TOC)		(1) Document Number:	Page 1
RECORD OF REVISION		RPP-RPT-47795	
(2) Title:			
Water Activity Data Assessment to be used in Hanford Waste Solubility Calculations			
Change Control Record			
(3) Revision	(4) Description of Change – Replace, Add, and Delete Pages	Authorized for Release	
		(5) Resp. Engr. (print/sign/date)	(6) Resp. Mgr. (print/sign/date)
1 RS	A computer error occurred in converting the MSWord file into a PDF file. The equations that were not included because of this are now incorporated.	R.S. Disselkamp 	J.G. Reynolds 

Water Activity Data Assessment to be used in Hanford Waste Solubility Calculations

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WTP Support - Washington River Protection Systems, LLC

Richland, WA 99352

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EXTENDED ABSTRACT

Complex equilibria exist between the aqueous phase and solid phases in Hanford waste. Because these solutions contain components at high concentration, it is necessary to accurately obtain parameterizations of water activity for retrieval, transfer, and for the vitrification plant at relevant temperatures and concentrations where storage, processing, and treatment are to be performed. This information can be used to accurately predict solid hydrates known to exist in Hanford waste. The solutes considered here, and those being some of the binary solute constituents in largest concentration, include NaNO_3 , NaNO_2 , NaCl , Na_2CO_3 , Na_2SO_4 , and KNO_3 . Experimental data from the literature have been compiled and an assessment of the accuracy of this data, from which water activity data is to be extracted via unit conversions, is performed. Water activity is calculated from the experimental data, it is not directly reported in most cases. Attempts were made to use, as a first priority, experimental data that had not been smoothed, averaged, or calculated from a model of water activity. To accomplish this task, it was necessary to obtain original journal sources presenting multiple datasets of experimental data. In these cases of data assimilation, data from multiple sources under identical conditions was compared to assess their quality, when possible.

KEY WORDS

Water activity, molality, ionic strength, solubility, Hanford crystal phases, isopiestic, vapor pressure, osmotic coefficient.

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LIST OF TERMS

Abbreviations and Acronyms

BBI	Best-Basis Inventory
ECN	Engineering Change Notice
TWINS	Tank Waste Inventory Network System

Units

Celsius	°C
Kelvin	K
kilopascals	kPa
millibar	mb
molal	m

Definitions

Osmotic coefficient	ϕ
Solution water vapor pressure	P
Pure water vapor pressure	P_o
Water activity	a_w

1 INTRODUCTION

In this report, an assessment of single solute experimental water activity data is presented for a limited number of compounds. The components considered here are sodium and potassium salts that represent the components present in significant concentration in Hanford waste. Accurate parameterizations of water activity are needed to estimate many solid hydrate phases present, under equilibrium, in Hanford waste storage, processing, and treatment conditions. The fitting of functions of water activity data are not performed here, but will be the focus of a future report.

The thermodynamic property of water activity can be obtained from a variety of sources. In essence, unit conversions are required to express/convert equivalent data types into water activity. Data types include osmotic coefficients, water vapor pressure measurements, isopiestic salt concentrations using unknown and reference solutions, and electrochemical cell potential measurements. For water vapor measurements above salt solutions, the pure water vapor pressure at the same solution temperature must be known. In all but osmotic coefficient measurements, temperature must be known to compute water activity. The investigation of water activity for single solutes as a function of concentration and temperature (preferred range of 25-100 °C) was implemented using a three step procedure as given below.

1. Obtain literature sources [journal articles or textbooks] listing experimental data from which water activity can be derived.
2. Perform unit conversions from raw data to obtain water activity versus molal, and consequently ionic strength, for each solute.
3. Perform assessment of water activity data. In particular, the distribution of error (i.e., random and/or systematic errors) for each solute was examined. Our discussion here will focus primarily on the origin of systematic, and to a lesser extent random, errors associated with experimental measurements.

The water activity data obtained here will be fit to a model in a future report and used to estimate compound solubility for solutes whose solubility is intermediate between nearly freely soluble (e.g., large solubility) and insoluble under waste storage and processing conditions [RPP-PLAN-46002, Wash and Leach Factor Work Plan report]. Solubility modeling of components in Hanford waste is important because mixing waste types, caustic additions, evaporator campaigns, tank transfers and retrievals, and staging of waste to be sent to the waste treatment complex all rely upon knowing the partitioning of waste among solid and aqueous (e.g., dissolved) forms.

2 LITERATURE SOURCES OF WATER ACTIVITY

An extensive literature review identified experimental literature data, from which water activity can be computed, for single solutes applicable to tank waste storage and treatment conditions of high concentration and 25 °C to elevated temperature. For example, concentrations of anions up to 8 molal and sodium to 14 molal are preferred (RPP-PLAN-46002), within the temperature range of 25-100 °C. In addition, we restricted efforts here to examine components known to be in large concentration from the Best Basis Inventory (BBI) (TWINS; 2010). Table 1 presents the literature data sources (see reference section for full citations) of the 6 binary components we examine here. The abbreviated literature citations presented in Table 1 correspond to their full citations, given according to solute type, in the Reference section. In a latter revision of this report data for additional electrolytes (e.g., solutes) will be presented.

Table 1. Single solute literature citations and concentration/temperature ranges of journal article(s) [see references for full citation].					
Solute	Literature Citation	Dataset Designation	Data Type [see footnote for explanation]	Concentration Range (molal)	Temperature Range (K)
NaNO ₃	Galleguillos, Salavera, Vargas, Coronas, 2010 Apelblat, Korin, 1998 Voight, 1990 Bossman, 1993 Pearce, 1937 Kangro, Groeneveld, 1962	NaNO ₃ -B	E(O)	0.001-52	273-492
		NaNO ₃ -E	E(VP)		
		NaNO ₃ -H	E(VP)		
		NaNO ₃ -K	E(VP)		
		NaNO ₃ -I	E(VP)		
		NaNO ₃ -J	E(VP)		
		NaNO ₃ -G	E(VP)		
NaNO ₂	Galleguillos, Salavera, Vargas, Coronas, 2010 Ray, Ogg, 1956 Chekhouva, Protsenko, 1967	NaNO ₂ -A	E(VP)	0.1-12.3	298-353
		NaNO ₂ -D	E(O)		
		NaNO ₂ -E	E(VP)		
NaCl	Apelblat, Korin, 1998 Gibbard Jr., Scatchard, Rousseau, Creek, 1974 Hubert, Gabes, Bourdet, Schuffenecker, 1995 Olynyk, Gordon, 1943	NaCl-A	E(VP)	1.0-6.2	278-373
		NaCl-D	E(O)		
		NaCl-C	E(VP)		
		NaCl-E	E(VP)		
Na ₂ CO ₃	Vanderzee, 1982 Appleblat, Manzurola, 2003 Robinson, Macaskill, 1979 Taylor, 1955	Na ₂ CO ₃ -A,B	E(FP)	0.0001-4.56	273-368
		Na ₂ CO ₃ -C	E(O)		
		Na ₂ CO ₃ -D,F	E(O)		
		Na ₂ CO ₃ -G	E(VP)		

Table 1. Single solute literature citations and concentration/temperature ranges of journal article(s) [see references for full citation].

Solute	Literature Citation	Dataset Designation	Data Type [see footnote for explanation]	Concentration Range (molal)	Temperature Range (K)
Na ₂ SO ₄	Rard, Clegg, Palmer, 2000	Na ₂ SO ₄ -I	E(I)	0.05-4.0	273-398
	Rard, Miller, 1981	Na ₂ SO ₄ -H	E(I)		
	Robinson, Wilson, Stokes, 1941	Na ₂ SO ₄ -C	E(VP)		
	Leopold, Johnston, 1927	Na ₂ SO ₄ -D	E(VP)		
	Guendouzi, Mounir, Dinane, 2003	Na ₂ SO ₄ -A	E(O)		
	Gibson, Adams, 1933	Na ₂ SO ₄ -E	E(VP)		
	Humphries, Kohrt, Patterson, 1968	Na ₂ SO ₄ -M	E(O)		
	Moore, Humphries, Patterson, 1972	Na ₂ SO ₄ -N	E(I)		
	Hellams, Patterson, Prentice, Taylor, 1965	Na ₂ SO ₄ -L	E(O)		
	Patterson, Gilpatrick, Soldano, 1960	Na ₂ SO ₄ -G	E(O)		
	Soldano, Patterson, 1962	Na ₂ SO ₄ -J	E(O)		
KNO ₃	Guendouzi, Mounir, Dinane, 2003	KNO ₃ -B	E(VP)	0.115-5.68	270-393
	Shpigal, Mishchenko, 1967	KNO ₃ -C	E(VP)		
	Robinson, 1935	KNO ₃ -D	E(VP)		
	Kangro, Groeneveld, 1962	KNO ₃ -E	E(VP)		

DATA TYPE COLUMN. E-Experimental Data Type: (O)-osmotic coefficient; (VP)-vapor pressure; (I)-Isopiestic.

In the cited literature, water activity as a function of concentration and temperature is either given directly as water activity, as osmotic coefficient, or as water vapor pressure above the salt solution. All three of these data types are alternative, and equivalent, ways of expressing water activity. Many measurements are required, preferably from multiple data sources to ensure independent determinations free from systematic errors, for each solute in order to fit a model of the water activity datasets. The latter will be performed in a separate follow-on report.

3 OBTAINING WATER ACTIVITY FROM DATA – DATA REDUCTION

As mentioned in the introduction, numerous methods exist to obtain water activity. These include osmotic coefficients, water vapor pressure measurements, isopiestic salt concentrations using unknown and reference solutions, and electrochemical cell potential measurements. The transformation of each of these quantities into water activity data was performed as described below.

3.1 OSMOTIC COEFFICIENT DATA

One of the more common ways of expressing water activity is via osmotic coefficient. The relationship between osmotic coefficient, ϕ , and water activity, a_w , is given in Eqn.(1) below (Zemaitis et al., 1986).

$$a_w = \exp \left[-\phi v m \left(\frac{18.0153}{1000} \right) \right] \quad (1)$$

In Eqn.(1) v is the number of dissociated solute anionic or cationic moles per 1 mole of complete solute formula unit (e.g., for Na_2CO_3 $v=3$), and m is the molality of the solute species (e.g., for Na_2CO_3). It is preferred to have data of osmotic coefficient versus a range of temperature and concentration in order to extract water activities over Hanford-relevant conditions.

3.2 WATER VAPOR PRESSURE MEASUREMENTS

It is a straightforward process to convert measured water vapor pressures above salt solutions, at known temperature, into water activities. The pertinent equation used is (Zemaitis et al., 1986):

$$a_w = \frac{P}{P_o} \quad (2)$$

Where P is the water vapor pressure for the salt solution (mb) and P_o is the pure water vapor pressure (at the same temperature) in mb. The Murray equation has been employed to compute the pure water vapor pressure as a function of temperature. The functional form of this equation was originally proposed by Goff and Gratch (1946). The Murray equation computes water vapor pressure in equilibrium with pure water and is given in the equation below (Murray, 1967):

$$\log(e_{sw}) = -7.90298 \times \left(\frac{T_s}{T} - 1 \right) + 5.02808 \times \log \left(\frac{T_s}{T} \right) - 1.3816 \times 10^{-7} \times \left[10^{11.344 \times \left(1 - \frac{T}{T_s} \right)} - 1 \right] + 8.1328 \times 10^{-3} \times \left[10^{3.49149 \times \left(\frac{T_s}{T} - 1 \right)} - 1 \right] + \log(e_{ws}) \quad (3)$$

Where T is temperature (K), $T_s = 373.16\text{K}$, and $e_{ws} = 1013.246$ for water vapor pressure in mbar. [Note that the subscripts on the “e” terms are different.]

The pressure (mbar) for pure water is then given by Eqn.(4) below.

$$P_o = 10^{\log(e_{sw})} \quad (4)$$

The units of Eqn(4) are mbar pressure units for correct inclusion into Eqn(2).

3.3 ISOPIESTIC SOLUTE CONCENTRATIONS

A third type of method for water activity measurement can be made is from isopiestic solutions. In these measurements, a semi-permeable membrane is used to enable water transport separates two salt compartments and a common water vapor pressure measurement is made simultaneously for both compartments. Our approach is to compute water activity using the Aseyev equation for the known (i.e. reference) salt solution concentration and by equivalence set this equal to the identical water activity of the different salt concentration for the species of interest. Thus isopiestic measurements are datasets containing two salt concentrations at a given temperature, at equilibrium with the same water vapor pressure.

Water activities were computed for reference isopiestic solutions using the Aseyev equation (Aseyev, 1999). The pertinent equations are as follows:

$$a_w = \sum_{i=1}^k m_i P_i^* \quad (5)$$

Where

$$P_i^* = W_{0i} + W_{1i}t_i + W_{2i}m_i + W_{3i}t_i^2 + W_{4i}t_i m_i + W_{5i}t_i^2 m_i \quad (6)$$

And

t_i is temperature in Celsius

m_i is concentration in molality

W_i values are known solute-specific parameters (Aseyev, 1999).

The W parameters in Eqn(6) are known for typical reference solutes such as NaCl and KCl, among others (Aseyev, 1999).

3.4 ELECTROMOTIVE FORCE (EMF) MEASUREMENTS

Electromotive Force measurements used the Nernst equation relating cell potential to solute activity. The general form of the equation, which varies somewhat according to standard state of each unique system, can be written as:

$$\Delta E = \frac{RT}{nF} \ln(K) \quad (7)$$

where

$$K = \frac{a}{a_{reference}} \quad (8)$$

Here ΔE is the measured cell potential (V), T is temperature (K), R and F are the ideal gas law and Faraday constants, respectively, and n is the number of electrons involved in the reduction-oxidation reaction. In addition, the “ a ” parameter is the activity constant term of the solution (that contains a_w), and “ $a_{reference}$ ” are related to the standard, or known, reference cell concentrations. Typically $a_{reference}$ is known and a_w is computed from given solutions concentrations and Eqns(7) and (8). Although none of the data presented here involved EMF measurements, future use may be made of this data type.

4 ASSESSMENT OF FIDELITY OF WATER ACTIVITY DATA

In this section an assessment of water activity either derived or directly measured using literature data for each solute is performed. This is accomplished through a discussion of water activity plotted against solution ionic strength. It is not necessary that any specific functional form describe such plots, however agreement of all separate datasets is necessary. The dataset outliers are discussed and identified. Another type of “suspect” data that could be encountered was that which exhibited an unusually large random error deviation about the trend-curve average of the datasets.

4.1 DISCUSSION OF DATASET AGREEMENT FOR EACH SOLUTE

The purpose of this section of the report is to evaluate the self-consistency of the water activity data. There is, in this section, data from more than one study for each electrolyte. In those cases, it is desirable to see how the two or more datasets compare to determine if the data is self-consistent. When the datasets are not self-consistent, particularly if one is an outlier compared to many datasets, it is an indication that there might be a problem with the data. It may or may not be possible to identify the cause, but it is desirable to know if there is problematic data within a set. Hence, when there are several datasets that agree with each other and one dataset that does not agree we have chosen to exclude the inconsistent dataset from future modeling work.

Experimental measurements of water activity are less common at temperatures above 298 K, so an inter-comparison between datasets is not always possible. We have opted to cite all studies for these elevated temperatures [see Table 1] and include them in our reference list. Therefore, this section only discusses data inter-comparison where more than one dataset exists at a given temperature. This often restricts our discussion here to 298 K where more datasets exist. In a future report, discussing the modeling of water activity, further evaluation of the suitability of these datasets will be made.

4.1.1 NaNO₃

For NaNO₃, there are five datasets that have two or more data points at 298.15 K. The water activity in these datasets is plotted as a function of ionic strength in Figure 1. As can be seen from this plot, the overwhelming majority of the data are reasonably self-consistent with each other. The exception is the data by Galleguillos et al. (2010), which does not appear to be consistent with the other data.

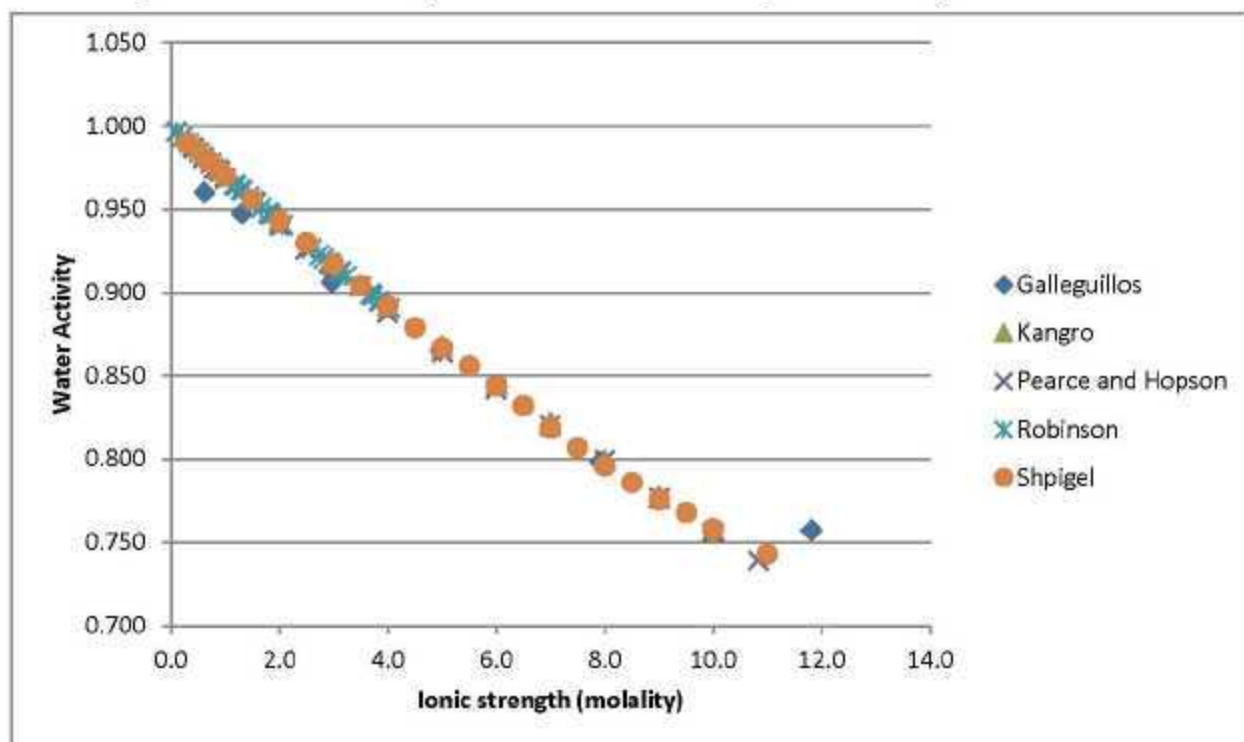
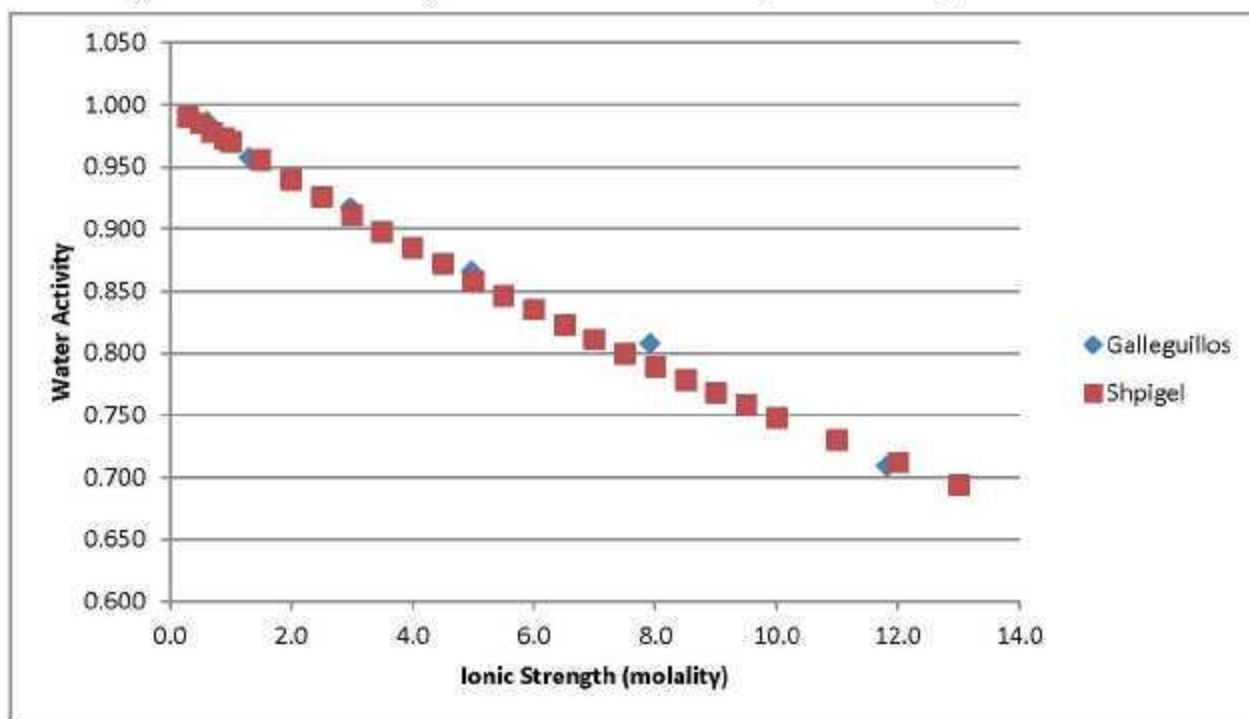
Figure 1 Water Activity as a Function of NaNO₃ Ionic Strength at 298.15 K.

Figure 2 compares the data at 323.15 K reported by Shpigel et al. (1967) and Galleguillos et al. (2010). As can be seen from this figure, there is good agreement between these two studies, but there is more scatter in the Galleguillos dataset. There were also inconsistencies (though not large) between the Galleguillos data and all other datasets at 298.15 K. However, the Galleguillos dataset was included because the inconsistencies were not too large and because this dataset covers a large temperature and concentration range that is not covered by most other datasets. The Shpigel dataset, because it resulted from smoothing, will not be considered further for use, but serves as a good comparison tool to the other datasets because of its completeness.

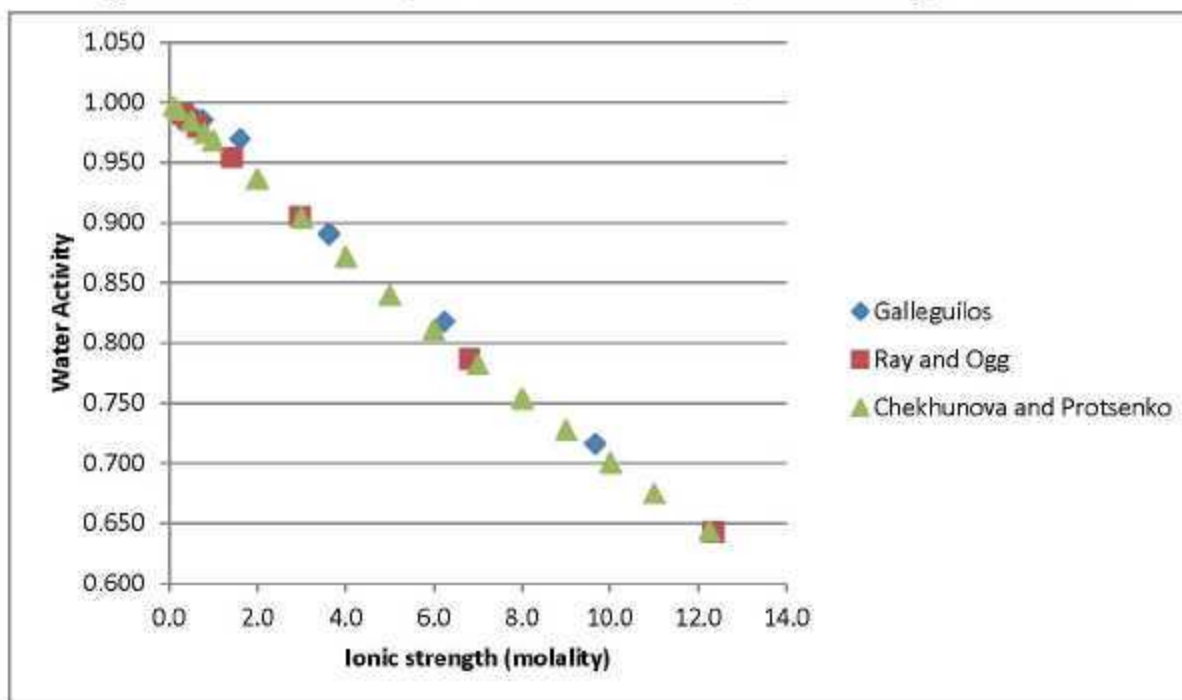
Figure 2. Water Activity as a Function of NaNO₃ Ionic Strength at 323.15 K.

Most datasets held temperature constant and varied the ionic strength. Apelblat and Korin (1998) changed both temperature and concentration in their study, which could explain the inconsistencies between their 298 K data and other datasets [data not shown]. In addition, their single 323 K data point does not agree with other data at that temperature. Their dataset was collected at saturation with respect to NaNO₃, so there might have been an error in either the water activity measurement or measurement of the saturated solution concentration. The Apelblat and Korin (1998) data was not used in the present study, despite the inconsistencies being small.

The dataset of Voight et al. (1990) only has data at 373.45 K and it is the only dataset at this temperature. Thus, this data set was assumed to be acceptable in the absence of any contrary data.

4.1.2 NaNO₂

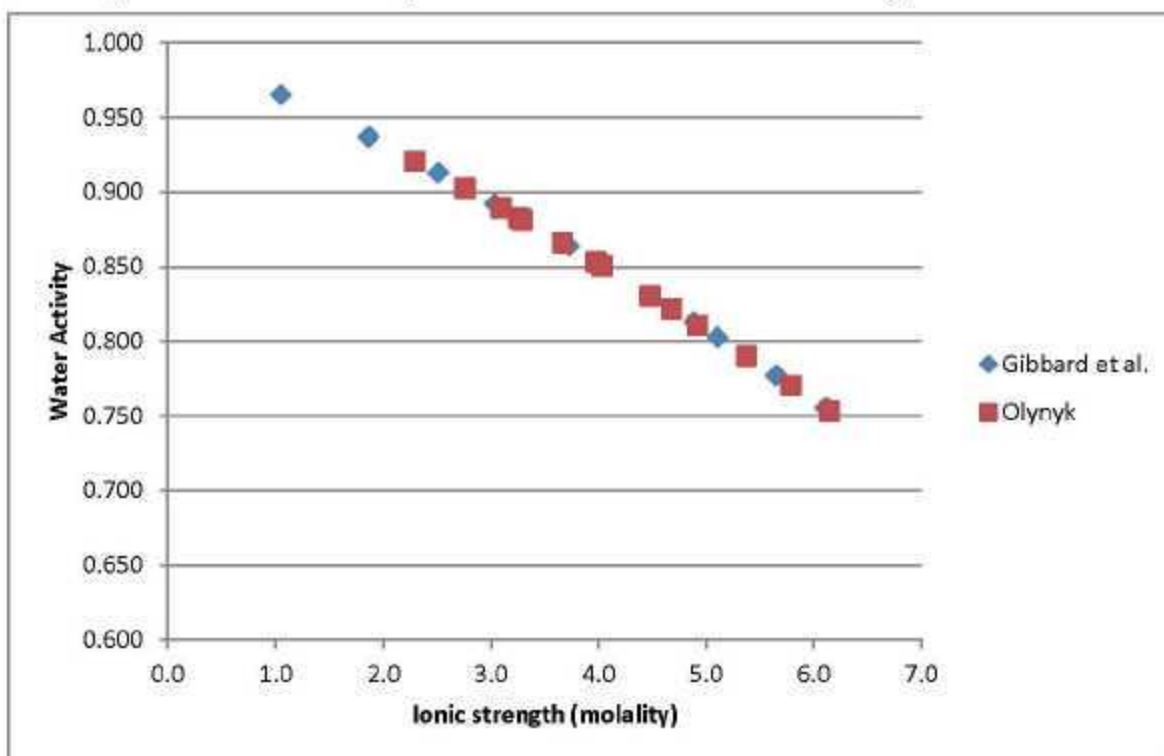
There are three datasets available at 298.15 K for the NaNO₂ system. Of the three, only the dataset of Galleguillos (Galleguillos et al. 2010) has data at temperatures other than 298.15 K. The data collected at 298.15 K is plotted in Figure 3. As can be seen in Figure 3, the Galleguillos data is slightly inconsistent with the other two datasets at 298.15 K. Nonetheless, the Galleguillos dataset will be used in modeling because it is the only dataset available at any temperature other than 298.15 K, and because the discrepancy at 298.15 K was not large (Figure 3). Given the uncertainty in the quality of the Galleguillos NaNO₂ dataset, additional data for the NaNO₂ system at temperatures other than 298.15 K would greatly improve the confidence of our model to predict the water activity of waste with large concentrations of NaNO₂, particularly at elevated temperature.

Figure 3. Water Activity as a Function of NaNO₂ Ionic Strength at 298.15 K.

4.1.3 NaCl

There are two NaCl datasets available (Gibbard et al., 1974, Olynyk and Gordon, 1943) with data points at 298.15 K, plotted in Figure 4. As can be seen in Figure 4, there is good agreement between these two datasets at 298.15. Therefore, it is assumed that these are both good datasets at other temperatures as well. A third dataset (Hubert et al., 1995) has data points that range from 294 K to 368 K. Their data points at 299 K are very close to the data at 298.15 K of the other two datasets. Thus, the Hubert et al. (1995) dataset is also used in this study.

Appelblat and Korin (1998) report one data point at 298.15 K, and this data point is also consistent with the other data at 298.15 K. At an ionic strength of 6.15 molal, Appelblat and Korin (1998) report a water activity of 0.751, whereas the other datasets have a water activity near 0.755. Thus, the Appelblat and Korin data is also assumed to be acceptable data and is used in this study. The rest of the data reported by Appelblat and Korin (1998) is at temperatures or composition regions that are not comparable to other datasets so cannot be cross checked.

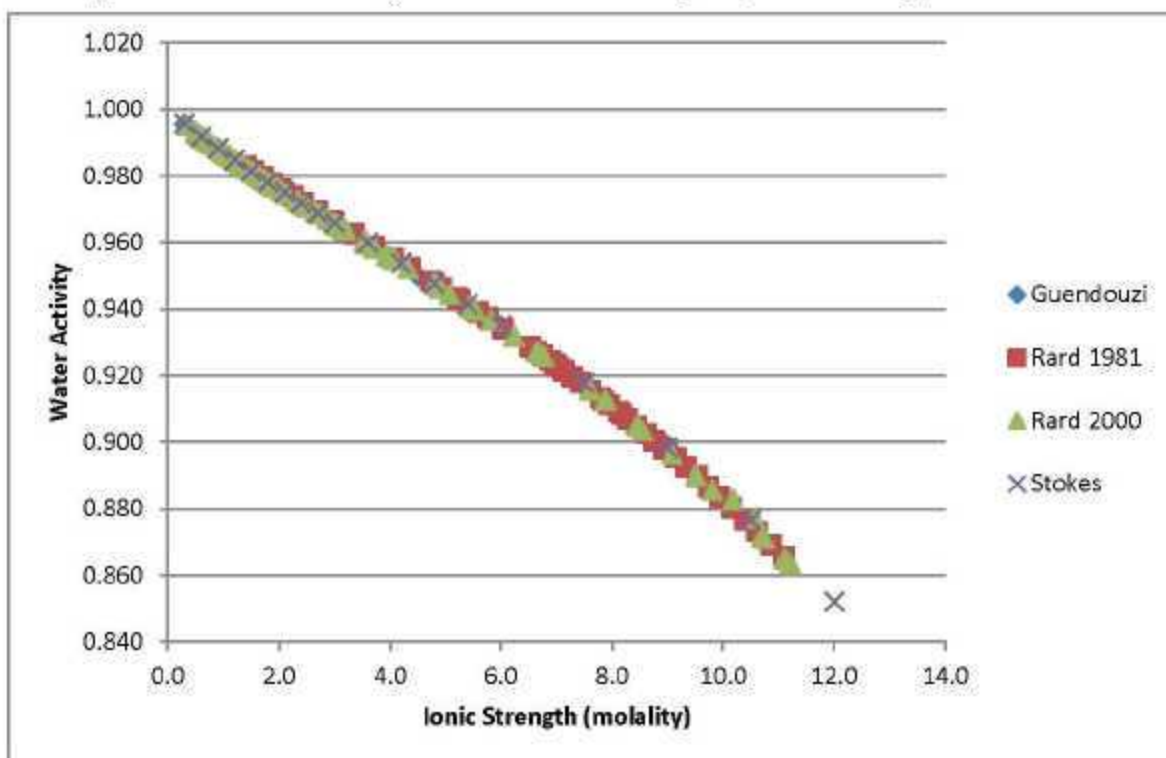
Figure 4. Water Activity as a Function of NaCl Ionic Strength at 298.15 K.

4.1.4 Na_2CO_3

There are only two datasets available for Na_2CO_3 (Robinson and Macaskill, 1979; Taylor, 1955). Neither of these datasets covered the same temperature range. Thus, these datasets were assumed to be acceptable, based on the lack of conflicting evidence. There are other datasets in the literature for the Na_2CO_3 system, but we have not been able to gain access to them in time for the present revision of this report. This report will be updated with the new datasets when the authors have obtained copies of those studies.

4.1.5 Na_2SO_4

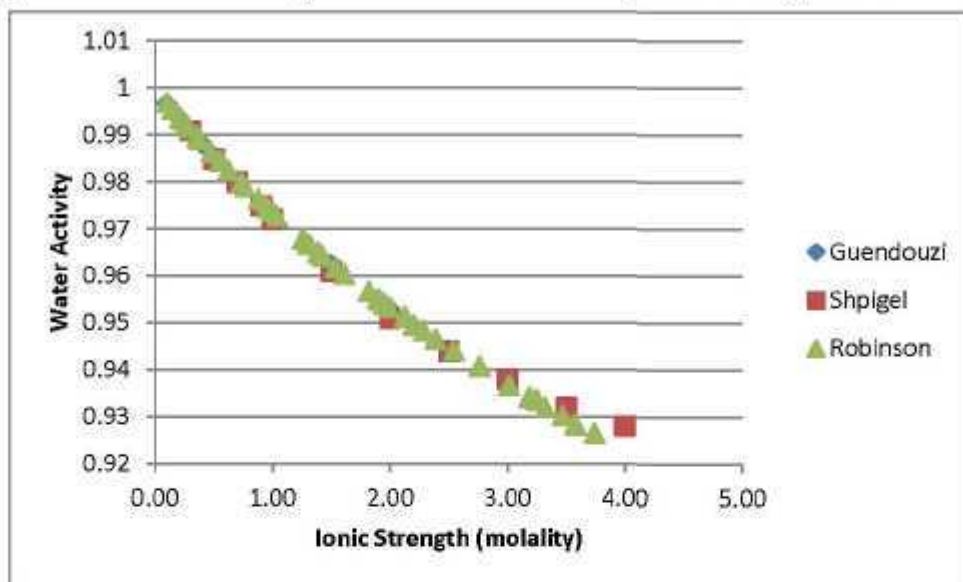
There are four datasets (Guendouzi et al., 2003; Rard and Miller, 1981; Rard et al., 2000; Robinson et al., 1941) available in the Na_2SO_4 system with data at 298.15 K. Figure 5 plots these data and shows that all four are consistent with each other. There is additional data, reported by Gibson et al. (1933), with data at 300 K. These data at 300 K are not appreciably different than the data at 298.15 K shown in Figure 3, as expected for such a small temperature change. Thus, all five of these datasets are considered self consistent and will be used in this study.

Figure 5. Water Activity as a Function of Na₂SO₄ Ionic Strength at 298.15 K.

The data in Leopold et al. (1927) does not appear to be consistent with other datasets. The Leopold et al. (1927) data changes both ionic strength and temperature because they measured the water activity in solutions that are at saturation with respect to sodium sulfate. At 298.15 K, Leopold et al. (1927) predicts a saturation vapor pressure of 0.860, which is very close to the 0.866 reported by Rard (1981) and the value of 0.865 reported by Rard et al. (2000). However, the ionic strengths at saturation are very different between the Rard et al. (1981; 2000) and the Leopold et al. (1927) data (9.5 molal versus 11.1 molal in Rard, 1981). Thus, there appears to be an error in the concentration at saturation reported by Leopold et al. (1927) and, therefore, these data were excluded from the study.

4.1.6 KNO₃

There are three datasets (Guendouzi et al., 2003; Shpigel et al., 1967; Robinson, 1935) for the KNO₃ system that has data at 298.15 K. Because the Shpigel dataset was smoothed, it is used for comparison only. These four datasets are plotted in Figure 6, below. As can be seen in this figure, all four datasets are self-consistent. Thus, the data from all four datasets will be used for model development. A fourth dataset also has three data points at 298.15 K (Kangro et al., 1962), which were too few to plot in Figure 6, but also were consistent with the other datasets. Kangro et al. (1962) also reported three data points at 293.15 K, which were assumed to be consistent with the other data because this same study had consistent data at 298.15 K.

Figure 6. Water Activity as a Function of KNO_3 Ionic Strength at 298.15 K.

5 FUTURE WORK

In this report literature data is presented, analyzed, and examined for its suitability for use in calculating water activity under Hanford relevant temperature and solute concentration conditions. The goal of this effort will be to use water activity in calculating solubility of Hanford tank waste solid phases. Suitability was based on agreement between water activity as a function of ionic strength, for single solutes, as examined among multiple data sources. A total of six single solutes were examined.

In future follow-on work, these datasets will be used to develop models of water activity versus ionic strength and temperature. These models will enable solutions made from mixtures of solutes to calculate water activity based on single solute water activity data versus concentration and temperature. The ultimate objective of this ongoing task will be to extend these single solute water activities to multiple, mixed, solute systems to calculate solids formation in Hanford operations based on a predictive model. In future work this formalism and application will be extended to additional solutes, as well as incorporating ternary and higher mixed solute solutions to develop model parameterizations for Hanford-relevant wastes. Additional solutes to be examined in the future include: NaOH, NaF, Na₂C₂O₄, Na₃PO₄, KOH, KNO₂, KCl, K₂CO₃, KF, and K₂SO₄, as well as ternary solids such as NaAl(OH)₄.

6 REFERENCES

6.1 GENERAL REFERENCES

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