A CHEMICAL MODEL FOR THE MAJOR ELECTROLYTE COMPONENTS OF THE HANFORD WASTE TANKS:
THE BINARY ELECTROLYTES IN THE SYSTEM:
Na-NO₃-NO₂-SO₄-CO₃-F-PO₄-OH-Al(OH)₄-H₂O

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Richland, Washington 99352

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A Chemical Model for the Major Electrolyte Components of the Hanford Waste Tanks:

The Binary Electrolytes in the System:
Na-NO₃-NO₂-SO₄-CO₃-F-PO₄-OH-Al(OH)₄-H₂O

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James R. Rustad
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Richland, WA 99352

Abstract

An aqueous thermodynamic model is developed, based on the equations of Pitzer, which accurately model the major binary electrolytes in the Na-NO₃-NO₂-SO₄-CO₃-F-PO₄-OH-Al(OH)₄-H₂O chemical system. This model was developed both from existing data in the literature, and from new osmotic and solubility measurements made as part of this study. Some of the new experimental data developed as part of this study include measurements of osmotic coefficients for NaNO₃, NaNO₂, and Na₃PO₄ at both 50 and 100°C as well as selected measurements of NaF at 100°C. In addition, the solubility of gibbsite was measured in mixed NaOH-NaNO₃ solutions to determine the reliability of existing thermodynamic models of aluminum hydroxide solubility when applied to concentrated nitrate.

In general the final model proposed here is valid from dilute solution to salt saturation over the temperature range 25-100°C. The accuracy of the model is tested by comparisons of the model predictions with experimental data in selected common-ion ternary systems. When necessary a few common-ion ternary ion interaction parameters for the Pitzer model were developed.

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Introduction

The Hanford waste tanks contain high concentrations of several electrolytes including NaNO₃, NaNO₂, NaOH, Na₃PO₄, Na₂CO₃ and NaAl(OH)₄, as well as lesser amounts of NaF and Na₂SO₄. To develop effective remediation strategies for the tanks as well as develop an understanding of the processes responsible for tank sludge dissolution requires the capability to predict changes in the major electrolytes chemistry that will occur during these remediation processes. Understanding the chemistry of the major electrolytes is also important in developing a predictive capability for important minor components, such as Cs and Sr, since the chemistry of the minor components is greatly affected by the major electrolytes.

To predict the changes in major electrolyte chemistry, such as precipitation/dissolution of solid phases, requires developing an accurate thermodynamic model for these components. The ion-interaction model of Pitzer, which is valid to high ionic strength, was used in this study. In the Pitzer model, or any aqueous thermodynamic model, the most important ion-interactions are those between cations and anions. These interactions are most easily and accurately determined from binary salt data (i.e., NaNO₃-H₂O, NaNO₂-H₂O) and these binary electrolytes are the focus of this study. The accuracy of this model, or any model, is critically dependent on the experimental data on which the model is based. The model presented here is based both on data taken from the literature and new experimental data developed as part of this study.

The experimental studies that were conducted were primarily osmotic coefficient studies of NaNO₃, NaNO₂, Na₃PO₄ solutions at 50 and 100°C and selected measurements of NaF solutions at 100°C. Isopiestic measurements are one of the best methods of determining the thermodynamic properties of binary electrolyte solutions at high concentration owing both to the precision of the measurements and to the large changes in water activity, that can occur in these solutions. Selected solubility studies of gibbsite in mixed NaOH-NaNO₃ solutions were also conducted to test the reliability of existing thermodynamic models developed in chloride solutions on the high nitrate solutions of importance in this study.
The remainder of this paper contains a brief description of the experimental procedures, a description of the development of the aqueous thermodynamic model for each binary electrolyte, and a final section comparing the model calculations with experimental data from selected common-ion ternary systems. This latter section is especially important because it represents a partial validation of the thermodynamic model in systems more complex than those used in model parameterization.

Experimental Procedures

Isopiestic measurements

The isopiestic apparatus and experimental procedures used in this study are similar to those described by Grotheim et al. (1988). Briefly, isopiestic equilibrium was established between 12 vitrous carbon cups placed inside a stainless steel container. The measurements on NaNO₃ and NaNO₂ were conducted simultaneously. Four of the cups contained NaNO₃, four cups contained NaNO₂, and four cups contained the reference solution CaCl₂. The measurements on Na₃PO₄ and NaF were conducted separately with six cups containing either Na₃PO₄ or NaF, four contained the reference salt, in this case KCl, and two cups remained empty in order to obtain more accurate wafer weight corrections (see below). Each of the cups was weighed empty, with added salt, and after placing a silicon rubber gasket on each cup. The stainless steel container was constructed so as to allow the wafers to be sealed on top of the cups before the cups were removed from the stainless steel vessel.

Equilibration periods generally extended from four days to one week depending on the temperature and salt concentration. After equilibration the cups were sealed inside the vessel and removed for weighing on a five place balance. After this weighing the wafers were removed, dried with a paper towel, and reweighed in order to correct for any wafer weight gain during equilibration. The wafer weight gain correction was generally minor at high concentration but became significant at lower concentration when water could condense on the bottom of the wafer following cooling. Therefore, to obtain more accurate wafer weight corrections, for the relatively low concentration
NaF and Na$_3$PO$_4$ solutions, two empty cups were placed inside the apparatus and carried along as effective blanks for determining wafer weight corrections.

Osmotic coefficients were then calculated from the isopiestic molalities and the water activities calculated for the reference salts from the data compiled for CaCl$_2$ by Ananthaswamy and Atkinson (1985).

For a detailed description of the development of the isopiestic method the reader is referred to Rard and Platford (1991).

**Gibbsite solubility studies**

The experimental procedures used in this study followed as closely as possible the procedure of Wesolowski (1992). Briefly, the gibbsite starting material was repeatedly washed with water and centrifuged until a clear centrate was obtained. The remaining gibbsite was then resuspended in 1N HCl and placed on a shaker for six days. This acid treatment step was designed to remove very fine particles or highly soluble amorphous material. Following the acid treatment, the gibbsite was soaked in 1N NaOH for one day to saturate any Na$^+$ adsorption sites. The remaining material was then separated and air dried. Approximately 2 g of gibbsite was then weighed and placed in a 50-ml centrifuge tube with 30 ml of the mixed NaOH-NaNO$_3$ solution. The suspensions were maintained at room temperature (~22-23°C) and sampled after 6, 63, and 419 days of equilibration.

Sampling consisted of centrifugation at 2000 g for 7 to 10 minutes followed by filtration through Amicon-type F-25 Centriflo membrane cones with an approximate pore size of 0.0018 μm. The filters were pretreated by soaking and rinsing in deionized water. A small aliquot of the sample was then passed through each filter to saturate any possible adsorption sites (this aliquot was discarded), followed by sufficient solution to analytically determine Al. Total Al was analyzed by inductively coupled plasma spectroscopy (ICP).
Thermodynamic Model

The aqueous thermodynamic model of Pitzer (1979), which is valid to high ionic strength, was utilized throughout this study to account for the variations in the activity coefficients of neutral and dissolved species. The exact equations used have been described in detail elsewhere (see Felmy and Weare 1986; Felmy et al. 1989; Pitzer 1979). In this study the most important ion-interaction parameters are \( \beta^0 \), \( \beta^1 \), and \( C^4 \) that describe binary ion-interactions like \( \text{Na}^+\text{NO}_3^- \), and to a lesser extent, common-ion ternary interaction parameters, \( \Theta \) and \( \psi \), like \( \text{OH}^-\text{NO}_3^- \), as a function of temperature.

All of the ion-interaction parameters and standard chemical potentials developed or utilized in this study were fit to the following empirical temperature dependent expression (see Møller 1988),

\[
P(T) = a_1 + a_2T + a_3/T + a_4\ln T + a_5/(T-263) + a_6T^2 + a_7/(680.-T) + a_8/(T-227)
\]

where \( P(T) \) is a temperature-dependent ion-interaction parameter or standard chemical potential. The necessary coefficients in eqn(1) for the Debye-Huckel \( A^e \) term and the standard chemical potential of \( \text{H}_2\text{O(l)} \) were taken from Greenberg and Møller (1989). The coefficients for eqn(1) for \( \text{Na}_2\text{SO}_4 \) ion-interaction parameters were also taken from Greenberg and Møller (1989). The parameters of \( \text{NaOH} \) were recalculated from the data of Pabalan and Pitzer (1987). A complete listing of the other coefficients of eqn (1) used in this study is given in Tables 1 and 2. The next section describes the methodology for calculating these parameters and presents a comparison between the model calculations and experimental data for each electrolyte. The objective of the model parameterization was to develop the simplest thermodynamic model that would explain all of the existing osmotic and solubility data on these electrolytes over the temperature range 25-100°C.
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Binary Electrolytes

The chemical behavior of the electrolytes examined here is quite different, especially regarding the formation of ion association species. The inclusion of ion association species in an aqueous thermodynamic model is dependent on the electrolyte concentration, temperature, and strength of the interactions. In general the fraction of the electrolyte associated increases with electrolyte concentration and temperature. This fact is especially important in this study because of the relatively high temperatures (as high as 100°C) and electrolyte concentration (as high as 20 m in NaNO₃) which were modeled.

NaNO₃

In developing the model for NaNO₃ osmotic data at 25, 50, 75, and 100°C were fit to the Pitzer thermodynamic model. Several attempts were made to accurately model these data, but they could not be accurately modeled (fit) at all four temperatures without including an ion association species because of the very high concentration of NaNO₃. Figure 1 shows our modeling calculations of the percent of the total NaNO₃ in solution present as an ion association species. NaNO₃ shows the expected trend of increasing association with increasing electrolyte concentration and temperature. The agreement of this thermodynamic model with the experimental data on osmotic coefficients at 25, 50, 75, and 100°C is shown in Figure 2. It should be noted that this model is valid to saturation with NaNO₃(c) and will thus accurately predict the solubility of NaNO₃(c) over the temperature range 25-100°C (see Figure 3). Also of note is the dashed curve in Figure 2 (d) which shows the predicted osmotic coefficients calculated with the recently published Pitzer ion-interaction parameters of Voigt et al. (1990) who did not include an ion association species in their analysis. The model of Voigt et al. is accurate to only approximately 8 m. In our analysis the introduction of a NaNO₃(aq) ion association species was required to extend the Pitzer ion-interaction model to NaNO₃ concentrations greater than eight molal at 100°C. However, at 25°C the osmotic data on NaNO₃ could be accurately
Figure 1. Calculated percentage of the total NaNO₃ in solution present as an ion association species.
Figure 2. Experimental and calculated osmotic coefficients for NaNO₃ solutions at (a) 25°C, (b) 50°C, (c) 75°C, (d) 100°C. Experimental data at 25°C of Wu and Hamer (1980), 75°C from Shipigel and Mishchenko (1967), 50 and 100°C this study.
Figure 3. Experimental and calculated NaNO₃ solubilities as a function of temperature. Experimental data from Linke (1965).
modeled without an ion association species (although our final model predicts a finite amount of association, Figure 1) even to concentrations approaching 11 molal. Again, this follows the expected trend in ion association with respect to temperature and electrolyte concentration.

**NaNO₂**

In the case of NaNO₂ introduction of an ion association species was required even at 25°C. The best fit ion interaction model without ion association, dashed line in Figure 4(a), gives only a qualitatively accurate representation of the experimental osmotic data. However by including an ion association species in the analysis an accurate model of the experimental osmotic coefficients is obtained, solid curve in Figure 4(a). A comparison of this final thermodynamic model for NaNO₂ with the experimental data on osmotic coefficients at 50 and 100°C is shown in Figures 4(b) and 4(c), respectively. The model gives an accurate representation of all of these experimental data even to saturation with NaNO₂ and accurately predicts the solubility of NaNO₂(c) over the temperature range 25-100°C (see Figure 5). Also of note is the dashed curve in Figure 4(c), which shows the best fit Pitzer model without ion association species at 100°C. As expected, owing to the increased importance of ion association with temperature, this model gives an even poorer representation of the experimental data than the model without association at 25°C, Figure 4(a).

**Na₂CO₃**

In the case of Na₂CO₃ accurate experimental osmotic data were available only to 45°C. Na₂CO₃ is not as soluble as NaNO₃ or NaNO₂ and, as a result, the experimental data could be accurately modeled without the inclusion of an ion association species. The prediction of our thermodynamic model with the experimental data on osmotic coefficients at 35 and 45°C is shown in Figure 6. The parameters for this model are in good agreement with previous models of this system proposed by Peiper and Pitzer (1982). In determining our final model the solubility data for natron (Na₂CO₃·10H₂O), sodium heptahydrate (Na₂CO₃·7H₂O) and thermonatrite (Na₂CO₃·H₂O) were also included (see Figure 7). Additional osmotic data on Na₂CO₃ solution
Figure 4. Experimental and calculated osmotic coefficients for NaNO₂ solutions at (a) 25°C, (b) 50°C, and (c) 100°C. Experimental data for 25°C from Staples (1981), data for 50 and 100°C determined in this study.
Figure 5. Experimental and calculated NaNO₂ solubilities as a function of temperature. Experimental data from Linke (1965).
Figure 6. Experimental and calculated osmotic coefficients for Na₂CO₃ solutions at 35 and 45°C. Experimental data from Peiper and Pitzer (1982).
Figure 7. Experimental and calculated solubilities for Na₂CO₃ solutions. Experimental data from Linke (1965).
are needed at higher temperatures (50-100°C) to extend the model for Na₂CO₃ to 100°C.

**Na₃PO₄**

Ion-interaction parameters for Na₃PO₄ solutions are available only at 25°C (Pitzer 1979). In order to extend the validity of the Pitzer model for Na₃PO₄ solutions to higher temperatures, osmotic measurements were made on Na₃PO₄ solutions at 50 and 100°C. Since these osmotic measurements extended to only approximately one molal, no ion-association species were included in the model. In addition, owing to the relatively low Na₃PO₄ molalities, the value of C⁴ could not be accurately determined and was therefore fixed at the 25°C value given by Pitzer (1979). Only the values of β⁰ and β¹ were adjusted in this analysis. The agreement between this relatively simple model and the experimental data at 50 and 100°C is shown in Figure 8. A comparison of the experimental and calculated (fit) solubilities for the Na₃PO₄·xH₂O solid phases is presented in Figure 9.

**NaF**

Ion-interaction parameters for NaF are available at 25°C and the first derivatives of these parameters with respect to temperature, determined from heat of solution data, are also available. To test the reliability of this model, osmotic measurements of NaF solutions at higher temperatures were attempted. Unfortunately, osmotic measurements of NaF solutions at higher temperatures proved difficult because of problems in accurately weighing the hydroscopic salt and especially to the relatively dilute solutions involved (<1m). In such dilute solutions even very small errors in salt weights can have a large effect on the calculated osmotic coefficients. A comparison between the experimental and calculated osmotic coefficients for NaF, Figure 10, shows that the currently available temperature corrections for the NaF ion-interaction parameters appear to be reasonable, at least to 100°C. Given the large errors in the osmotic measurements, no further analysis of these data appeared warranted.
Figure 8. Experimental and calculated osmotic coefficients for Na₃PO₄ solutions at 50 and 100°C. Experimental data determined as part of this study.
Figure 9. Experimental and calculated Na$_3$PO$_4$-$x$H$_2$O solubilities as a function of temperature.
Figure 10. Experimental and calculated osmotic coefficients for NaF solutions at 100°C. Experimental data determined as part of this study.
The solubility of gibbsite \((\text{Al(OH)}_3)\) in mixed \(\text{NaOH-NaNO}_3\) solutions over a wide range of electrolyte composition extending to \(\text{NaNO}_3\) saturation was examined. \(\text{NaOH}\) and \(\text{NaNO}_3\) are two of the principal electrolyte components present in the tanks which could affect the solubility of aluminum hydroxide compounds. Hence, the \(\text{NaOH-NaNO}_3\)-\(\text{H}_2\text{O}\) system is the simplest chemical system that should be representative of the more complex mixed electrolytes present in the tanks, at least regarding the solubility of aluminum hydroxide compounds. Data gathered in the simpler \(\text{NaOH-NaNO}_3\)-\(\text{H}_2\text{O}\) system can also be used to develop and parameterize thermodynamic models for predicting changes in solubility for aluminum hydroxide and more complex aluminum silicate compounds.

The solubility of gibbsite in mixed \(\text{NaOH-NaNO}_3\) solutions, Figure 11, as expected, clearly shows the dependence of gibbsite solubility on the \(\text{NaOH}\) concentration. This effect is well known and has been accurately modeled by Wesolowski (1992) in mixed \(\text{NaOH-NaCl}\) solutions. Of interest in this study is the fact that the observed solubilities of gibbsite are practically independent of the \(\text{NaNO}_3\) concentration and, with the exception of the 3.0M \(\text{NaOH}\) solutions, the solutions attained equilibrium relatively rapidly (i.e. <6 days). However, the 3M \(\text{NaOH}\) solutions took considerably longer to equilibrate with significant increases in solubility occurring between 63 and 419 days of equilibration. This slow attainment of equilibrium was not significantly affected by the \(\text{NaNO}_3\) concentration and appears to be a result primarily of the fact that to equilibrate 3M \(\text{NaOH}\) with gibbsite requires transfer of significant mass of Al from solid to solution. At the conclusion of the 419-day sampling the remaining solid phase was examined by X-Ray Diffraction and determined to be crystalline gibbsite. There was no trace of other solid phases being present in the samples.

Wesolowski (1992) presented a complete aqueous thermodynamic model for the solubility of gibbsite in the system \(\text{Na-K-Cl-OH-Al(OH)}_3\)-\(\text{H}_2\text{O}\) from 0 to 100°C using the aqueous thermodynamic model of Pitzer. In this study we have refit the Pitzer ion-interaction parameters and standard chemical potentials given by Wesolowski (1992) and Palmer and Wesolowski (1992) for gibbsite and \(\text{Al(OH)}_4^-\) to our ...
Figure 11. Experimental Gibbsite Solubilities in NaOH-NaNO₃ Solutions at 22-23°C.
temperature-dependent expression (eqn 1).

This model is relatively simple in that ternary interactions between major constituents such as NO\textsubscript{3}^-\text{-Al(OH)}\textsubscript{4}^- and Na\textsuperscript{+}-NO\textsubscript{3}^-\text{-Al(OH)}\textsubscript{4}^- are ignored. Figure 12 shows a comparison of the calculated gibbsite solubilities with the experimental data using this relatively simple model. These results show that the model works quite well as long as the concentration of NaNO\textsubscript{3} does not exceed approximately 2m. At NaNO\textsubscript{3} concentrations greater than 2m the model begins to significantly over predict the solubility of gibbsite in the concentrated solutions. This overprediction is the direct result of missing common ion ternary ion-interaction parameters involving NO\textsubscript{3}^- (i.e. either NO\textsubscript{3}^-\text{-Al(OH)}\textsubscript{4}^- or Na\textsuperscript{+}-NO\textsubscript{3}^-\text{-Al(OH)}\textsubscript{4}^-). As a result, the gibbsite solubility data in NaOH-NaNO\textsubscript{3} solutions were fit with these common-ion ternary ion-interaction parameters adjusted. The resulting parameter values are quite reasonable, \(\theta\text{NO}_3^-\text{-Al(OH)}_4^- = 0.038\) and \(\psi\text{Na}^+\text{-NO}_3^-\text{-Al(OH)}_4^- = 0.0066\) when compared to the corresponding values for OH^-\text{-Al(OH)}\textsubscript{4}^- (see Table 1). This final model gives excellent agreement with all of the experimental data.

**Mixed Systems**

In this section the model developed from the binary electrolyte data will be applied to systems more complex than those used for model parameterization. Data for three of the most concentrated mixed systems were selected for study. These systems are the NaNO\textsubscript{3}-NaNO\textsubscript{2}-H\textsubscript{2}O system, which reaches concentrations as high as 36m at 100°C; the NaNO\textsubscript{3}-NaOH-H\textsubscript{2}O system; and the NaNO\textsubscript{2}-NaOH-H\textsubscript{2}O system.

The experimental and calculated solubilities for NaNO\textsubscript{2} and NaNO\textsubscript{3} in the NaNO\textsubscript{3}-NaNO\textsubscript{2}-H\textsubscript{2}O system at 50 and 100°C, Figure 13, shows excellent agreement between model and experiment, even to very high concentration. This application represents an excellent test of the model in a very concentrated mixed system. There were no adjusted parameters in these calculations.
Figure 12. Experimental and calculated gibbsite solubilities in NaOH-
NaNO₃ solutions. The dashed curve represents calculations with \( \theta \text{NO}_3^- - \text{Al(OH)}_4^- \) and \( \psi \text{Na}^+ - \text{NO}_3^- - \text{Al(OH)}_4^- \) set to zero. The solid curve represents calculations with \( \theta \text{NO}_3^- - \text{Al(OH)}_4^- = .038 \) and \( \psi \text{Na}^+ - \text{NO}_3^- - \text{Al(OH)}_4^- = .0066 \).
Figure 13. Experimental and calculated solubilities for NaNO₃ and NaNO₂ in the NaNO₃-NaNO₂-H₂O system at 50 and 100°C. Experimental data from Linke (1965).
Figure 14. Experimental and calculated solubilities for NaNO₃ in NaOH solutions at 25°C. Experimental data from Plekhotkin and Bobrovskaya (1970).
Figure 15. Experimental and calculated solubilities for NaNO₂ in NaOH solutions at 25°C. Experimental data from Linke (1965).
C. REFERENCES


