Development of an Enhanced Thermodynamic Database for the Pitzer Model in ESP: The Fluoride and Phosphate Components

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Abstract

In this report the development of an enhanced database of thermodynamic modeling parameters for the $Na-OH-NO_3-NO_2-SO_4-CO_3-F-PO_4-H_2O$ system is presented. The model development emphasizes the chemical reactions involving the fluoride and phosphate components and is based upon the thermodynamic model of Pitzer and coworkers. Extensive comparisons of the model with experimental data in common-ion ternary and more complex solutions are presented to establish the validity of the final model. Comparisons are also made with the current version of the Environmental Simulation Program (ESP V6.4) using both the public and certain special databases developed for these chemical systems. On an overall basis the new model gives a quite satisfactory representation of the experimental data for these chemical systems. The limitations of the current model, which are principally due to a lack of experimental data for certain systems, is also discussed. It is anticipated that this database will form the foundation for the new version of ESP that includes the Pitzer model. The new version of the Pitzer model is slated for release for beta testing at the end of this fiscal year (9/01). Initial applications of this new model are also presented which illustrate the improved predictions of the new model parameterizations for the Sr/TRU separation process.

Table of Contents

Figures

Tables

1.0 Introduction

In FY00, thermodynamic modeling was used to help define the specific chemical processes responsible for the Sr/TRU separation process (Felmy 2000). This modeling activity emphasized the use of the Pitzer thermodynamic model, principally as a result of deficiencies that were noted in the application of the current version of ESP. The deficiencies were important with respect to Sr/TRU separations since they involved the precipitation of $SrCO_3(c)$ and the solubility of actinide hydroxides, which were found to be erroneously predicted (see examples in Figures 1 and 2). In addition, certain inaccuracies were also noted with respect to other major electrolyte components. Unfortunately, the currently available database for Pitzer modeling parameters is based principally upon binary solution data and lacks the necessary common-ion ternary information required to obtain the necessary accuracy in model predictions.
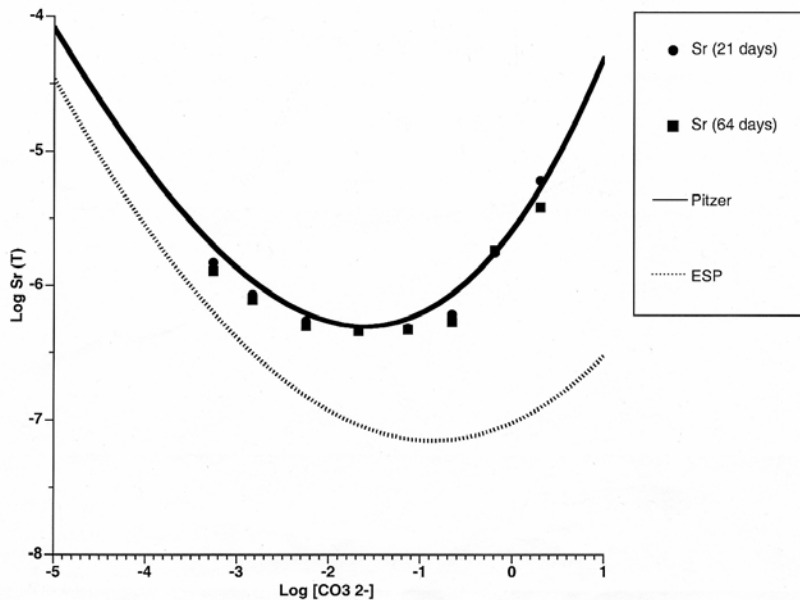
Figure 1. Experimental and calculated solubilities of $SrCO_3$(crystalline, c) in Na_2CO_3 solutions. The Pitzer model includes new thermodynamic data for the strontium dicarbonate complex $(Sr(CO_3)_2^{2-})$. The ESP model lacks thermodynamic data for all strontium carbonate aqueous species. Experimental and thermodynamic data developed by Felmy et al. (1998) with support form the Environmental Management Sciences Program.
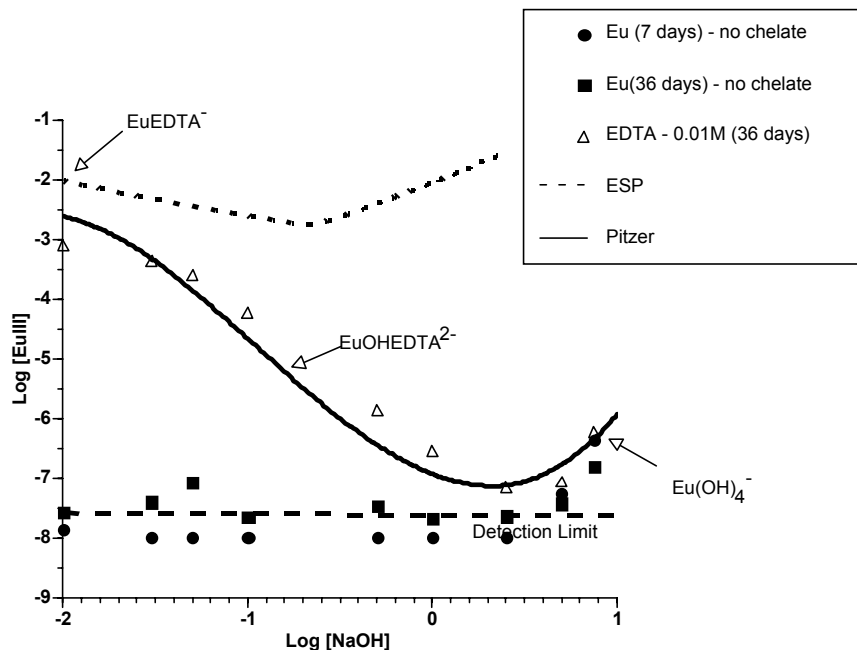
Figure 2. Experimental and Calculated Solubilities of Eu(OH)$_3$(c) in NaOH solutions in the presence and absence of 0.01m EDTA. The Pitzer model includes new thermodynamic data for the mixed metal-ligand-hydroxide complexes (i.e. EuOHEDTA^{2-}). In addition, the ESP model contains an erroneously high value for the stability constant for the Eu(OH)$^{4-}$ species. Experimental and thermodynamic data developed by Felmy et al. (2001) with support form the Environmental Management Sciences Program.

Including modeling parameters for common-ion ternary systems is important since electrolyte behavior can vary significantly for solutions at the same electrolyte concentration and stoichiometric ionic strength.

As an example, the solubility of NaNO$_3$(c) in mixed NaNO$_3$-NaOH solutions (Figure 3), shows the classic behavior for a dissociated electrolyte in that the addition of Na$^+$ through NaOH results in a significant and almost stoichiometric depression in the solubility of NaNO$_3$ as a result of the common-ion effect.

This contrasts to the observed solubilities in the mixed NaNO$_3$-NaNO$_2$ system (Figure 4) which show an initial lowering of the NaNO$_3$ solubility upon addition of NaNO$_2$ but then a leveling off in the solubility at higher added NaNO$_2$ concentrations. In terms of thermodynamic models, this lack of a common-ion effect is most easily modeled in terms of ion pair formation in that the added NaNO$_2$ remains associated as a NaNO$_2$(aq) neutral species with less "free" Na$^+$ to suppress the solubility of NaNO$_3$(c). In terms of model accuracy these interactions are important to include since the observed solubility of NaNO$_3$ is quite different between the two electrolytes. For example, at 10 molal (m) added electrolyte the solubility of NaNO$_3$ in NaOH is approximately 2 molal

whereas in NaNO$_2$ it is approximately 11m. Predicting such difference in solubility in the common-ion ternary systems even at the same stoichiometric ionic strength are one of the principal objectives of this study.
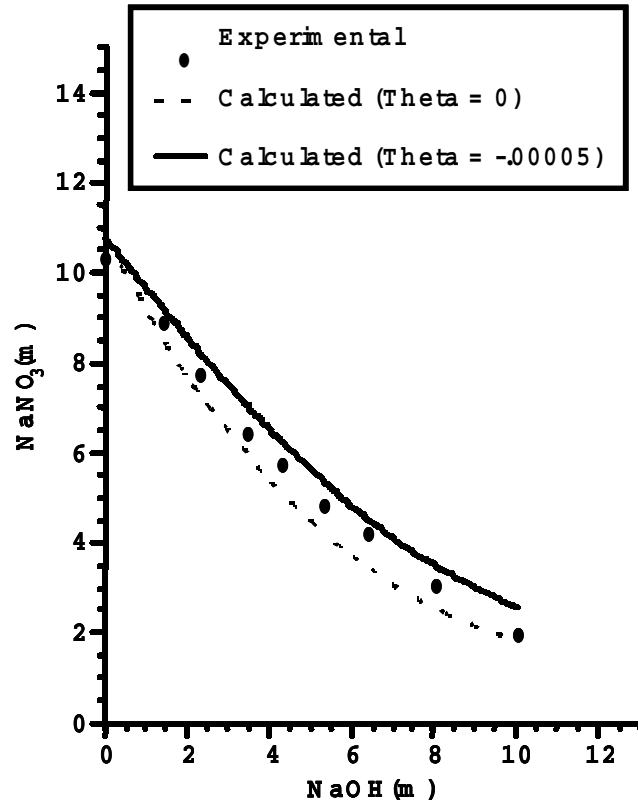
Figure 3. The solubility of NaNO$_3$(c) in NaOH exhibiting a strong common-ion effect on the solubility, Felmy et al. (1994). The parameter "theta" represents NO$_3^-$OH interactions in the Pitzer thermodynamic model (see next section).
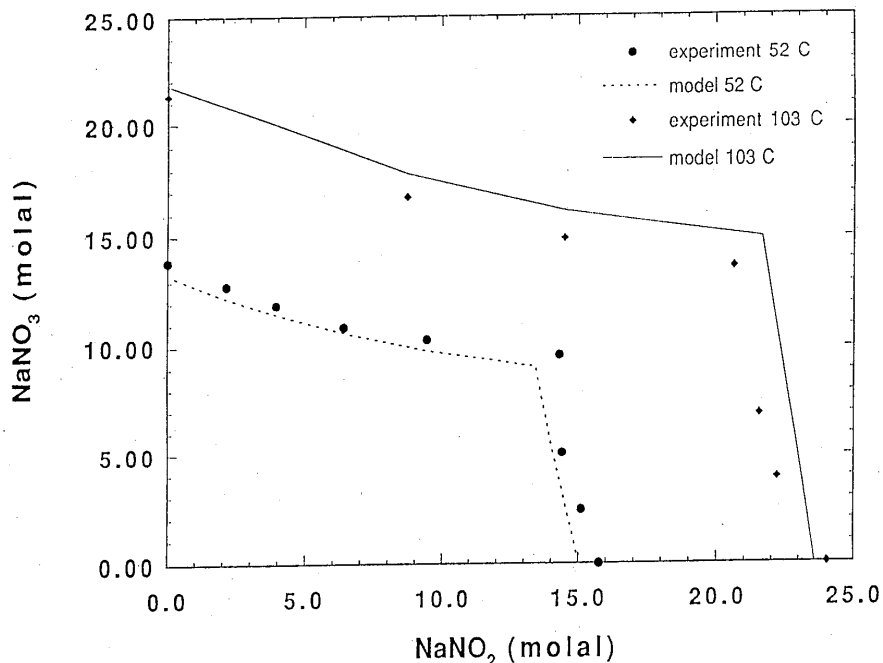
Figure 4. The solubility of NaNO$_3$(c) in NaNO$_2$(c) exhibiting a lack of a common-ion effect on the solubility. The reduced common-ion effect is modeled by assuming the formation of ion pairs in solution (e.g. NaNO$_2$(aq)), Felmy et al. (1994).

Fortunately, an extensive database of Pitzer model parameters is being developed with funding support from the Environmental Management Sciences Program, and other recent literature sources have presented enhanced databases of Pitzer parameters including the important fluoride and phosphate components. However, these recent advances need to be incorporated into a larger and thermodynamically consistent database.

With these factors in mind, this project has focused on the development of an enhanced database of Pitzer model parameters for the Na-OH-NO$_3$-NO$_2$-SO$_4$-CO$_3$-F-PO$_4$-H$_2$O system. Emphasis is placed on the parameters for the fluoride and phosphate systems as well as maintaining thermodynamic consistency with other data sets of Pitzer parameters. An example of the improved predictions of this new model with respect to Sr/TRU separations is also given following the description of the new model.

2.0 Thermodynamic Model Development

The aqueous thermodynamic model used in this study is the ion-interaction model of Pitzer and coworkers. (Pitzer, 1973; Pitzer, 1991) This model emphasizes a detailed description of the specific ion interactions in the solution. The effects of the specific ion interactions on the excess solution free energy are contained within the expressions for the activity coefficients. The activity coefficients can be expressed in a virial-type expansion as

$$\ln \gamma_i = \ln \gamma_i^{DH} + \sum_j \beta_{ij}(I)\, m_j + \sum_j \sum_k C_{ijk}\, m_j m_k + \ldots \tag{1}$$

where m is the molality and γ_i^{DH} is a modified Debye-Hückel activity coefficient that is a universal function of ionic strength. $\beta_{ij}(I)$ and C_{ijk} are specific for each ion interaction and are a function of ionic strength. Pitzer gives explicit phenomenological expressions for the ionic-strength dependence of β. (Pitzer, 1973; Pitzer, 1991). The third virial coefficient, C, is taken to be independent of ionic strength. The form of β is different for like, unlike, and neutral ion interactions. The following are the complete set of parameters defining the non-ideal behavior of electrolytes solutions:

β_{ij}^0, β_{ij}^1, β_{ij}^2, and C_{ij}^ϕ for each cation-anion pair

ϕ_{ij} for each cation-cation and anion-anion pair

ψ_{ijk} for each cation-cation-anion or anion-anion-cation triplet

λ_{ni} amd ξ_{nij} for ion-neutral and ion-ion-neutral interactions.

A detailed description of the exact form of Eq. (1) is given elsewhere. (Felmy and Weare, 1986; Felmy et al. 1989; Harvie et al. 1984).

2.1 Model Parameterization

Our overall approach was to begin with the extensive model development of binary (i.e. cation-anion) Pitzer parameters for the Na-OH-NO$_3$-NO$_2$-SO$_4$-CO$_3$-F-PO$_4$-H$_2$O system developed by Felmy et al. (1994) over the temperature range 25 - 100^{0}C. This model includes all of the essential *binary* ion-interactions (i.e. Na$^+$-OH$^-$, Na$^+$-NO$_3^-$, …), and important ion associations (i.e. formation of NaNO$_3$(aq) and NaNO$_2$(aq) ion pair found in binary systems. A complete description of these model parameters along with extensive comparisons with the existing osmotic and solubility data is given in Felmy et al. (1994). All of the ion-interaction parameters in this model were fit to the following temperature dependent expression:

$$P(T) = a_1 + a_2T + a_3/T + a_4 \ln T + a_5/(T-263) + a_6T^2 + a_7/(680-T) + a_8/(T-227), \quad (2)$$

where P(T) is a temperature-dependent ion-interaction parameter or standard chemical potential and T is in degrees Kelvin. To enhance this database we began with the recent work on the Na-F-PO$_4$-OH-Cl-H$_2$O system published by Weber et al. (2000). This study utilized the Pitzer thermodynamic model but used a different temperature dependent expression than eqn (2) and also accepted slightly different standard chemical potentials for certain basis species (including H$_2$O(l)) in the model. These two factors required that the original model parameterizations proposed by Weber et al. (2000) be recalculated to fit the temperature dependence in eqn(1) and maintain thermodynamic consistency. At the same time a literature review was initiated to obtain experimental solubility data for other common-ion ternary systems important in the overall Na-OH-NO$_3$-NO$_2$-SO$_4$-CO$_3$-F-PO$_4$-H$_2$O system but not addressed in the simpler Na-F-PO$_4$-OH-Cl-H$_2$O system examined by Weber et al. (2000). Table 1 presents a summary of all of the common-ion ternary systems found in the overall Na-OH-NO$_3$-NO$_2$-SO$_4$-CO$_3$-F-PO$_4$-H$_2$O system as well as an indication of which systems have previously been parameterized, which systems have not been treated, and which systems where experimental data are unavailable.

Table 1. Summary of the common-ion ternary systems in the Na-OH-NO$_3$-NO$_2$-SO$_4$-CO$_3$-F-PO$_4$-H$_2$O system with the status of previous model development efforts and current data availability. (F) represents the work of Felmy et al. (1994), (GM) that of Greenberg and Møller (1989), and (W) Weber et al. (2000). The numbers in parenthesis represent the temperatures in degrees celsius for which data is available in the literature.

Previously Modeled	Not Previously Modeled
NaOH – NaNO$_3$ (F)	NaNO$_3$ – Na$_2$SO$_4$ (25-100)
NaOH – NaNO$_2$ (F)	NaNO$_3$ – Na$_2$CO$_3$ (25)
NaOH – Na$_2$SO$_4$ (GM)	NaNO$_3$ – NaF (25)
NaOH – Na$_2$CO$_3$ (GM)	NaNO$_3$ – Na$_3$PO$_4$ (none)
NaOH – NaF(W)	NaNO$_2$ – Na$_2$SO$_4$ (none)
NaOH – Na$_3$PO$_4$(W)	NaNO$_2$ – Na$_2$CO$_3$ (25)
NaNO$_3$ – NaNO$_2$ (F)	NaNO$_2$ – NaF(none)
Na$_2$SO$_4$ – Na$_2$CO$_3$ (GM)	NaNO$_2$ – Na$_3$PO$_4$ (25)
NaF – Na$_3$PO$_4$ (W)	Na$_2$SO$_4$ – NaF (25,35)
	Na$_2$SO$_4$ – Na$_3$PO$_4$(25,150)
	Na$_2$CO$_3$ – NaF (25,50)
	Na$_2$CO$_3$ – Na$_3$PO$_4$ (25-100)

All of the available literature data identified in Table 1 were then tabulated and converted from the originally reported units (usually weight percent) to molality for comparison with thermodynamic models. The thermodynamic models used for this comparison included the previously described Pitzer model (combined thermodynamically consistent Felmy-Weber model) and the ESP model. The model comparisons and parameterizations are described in detail below beginning with the NaNO$_3$-Na$_2$CO$_3$-H$_2$O system and ending with the NaF-Na$_3$PO$_4$-H$_2$O system. Tables 2, 3, and 4 contain a complete listing of all of the model parameters developed as part of this study.

Table 2. Coefficients for the temperature dependent expression for the binary Pitzer ion-interaction parameters. All numbers are significant. The coefficients a5, a7, and a8 (eqn (2)) were not required.

Ions		a_1	a_2	a_3	a_4	a_6
Na^+ - OH^-	B^0	-6.6052702e-01	4.5522681e-03	0	0	-6.8613774e-06
	β^1	0	0	0	0	2.8379182e-06
	$C^\varnothing$	1.0462530e-01	-5.634757e-04	0	0	7.5964898e-07
Na^+ - F^-	B^0	4.69412401e+00	0	-2.4680108997e+02	-6.7280111225e-01	0
	β^1	6.359551397e+01	0	-2.8329985180e+03	-9.4510005287e+00	0
	$C^\varnothing$	5.8256139127e-01	0	-2.4398622636e+01	-8.689758235e-02	0
Na^+ - PO_4^{3-}	B^0	-3.101961e-01	1.58428e-03	0	0	0
	β^1	-3.0422189894e+01	2.08543552e-01	0	0	-3.1104e-04
Na^+ - HPO_4^{2-}	B^0	3.548478825e+01	0	-1.8258508149e+03	-5.1585440858e+00	0
	β^1	1.2849586005e+02	0	-6.0230164212e+03	-1.8770048134e+01	0
	$C^\varnothing$	-1.5990158235e+01	0	7.9916048666e+02	2.3378123473e+00	0

Table 3. Coefficients for the temperature dependent expression for the dimensionless standard chemical potentials for solids and aqueous species added to the model. All numbers are significant. The coefficients a5, a7, and a8 (eqn (2)) were not required.

Species	a_1	a_2	a_3	a_4	a_6
HPO_4^{2-}	-5.0495533734e+02	4.0949002466e-01	0	0	-6.35380022e-04
$Na_3PO_3 \cdot \frac{1}{4}NaOH \cdot 12H_2O$	-1.677370757e+06	-1.061229989e+03	3.229103564e+7	3.2150164699e+5	5.8225576757e-01
$Na_7F(PO_4)_2 \cdot 19H_2O$	4.7879241203e+04	5.1234901666e+01	-7.286403216e+5	-1.069564763e+4	-3.692974789e-02
$NaF(c)$	-2.2534008957e+02	3.876692592e-02	0	0	-6.074992249e-05
$NaF \cdot Na_2SO_4(c)$	-7.3577286e+02	4.4e-03	0	0	0
$NaNO_3 \cdot Na_2SO_4 \cdot H_2O$	-7.547e+02	0	0	0	0
$Na_2HPO_4 \cdot 12H_2O$	3.2244900418e+04	21.094416232	-4.601007811e+5	-6.754307214e+3	-3.495703892e-3

Table 4. Common-ion ternary Pitzer ion-interaction parameters. All values are for the a1 parameter in the temperature dependent expression and are therefore independent of temperature as described in the text.

	θ	ψ	Additional
NaF·NaOH	0.1193	-0.035	-
NaF·NaNO$_3$	0.15	-0.036	-
NaF·Na$_2$CO$_3$	0.13	-0.05	-
Na$_3$PO$_4$·NaOH	0.13	-0.013	-
Na$_3$PO$_4$·NaNO$_2$	0.06	0.05	-
NaNO$_3$·Na$_2$CO$_3$	0.14	-	-
NaNO$_3$·Na$_2$SO$_4$	0.20	-0.025	-
NaNO$_2$·Na$_2$CO$_3$	0.12	-	$\lambda_{NaNO2·CO3} = 0.05$

2.1.1 NaNO₃-Na₂CO₃-H₂O

The comparisons between model and experimental data for the $NaNO_3$-Na_2CO_3-H_2O system, Figure 5, show the expected trends for models that have been constructed solely from binary data. These trends consist of good agreement between model and experiment in the end point regions where the thermodynamics of a single electrolyte dominate the system and poorer agreement in the intermediate regions where both electrolytes are important. The absolute differences are significant, almost a factor of two in the worst case. Such systems are however easily modeled by including mixing terms within the Pitzer formalism (i.e. in this case only $\phi(NO_3^--CO_3^{2-})$, see Table 4) was required to obtain a quite satisfactory representation of the experimental results.

The System $NaNO_3$-Na_2CO_3-H_2O at 25^0C.
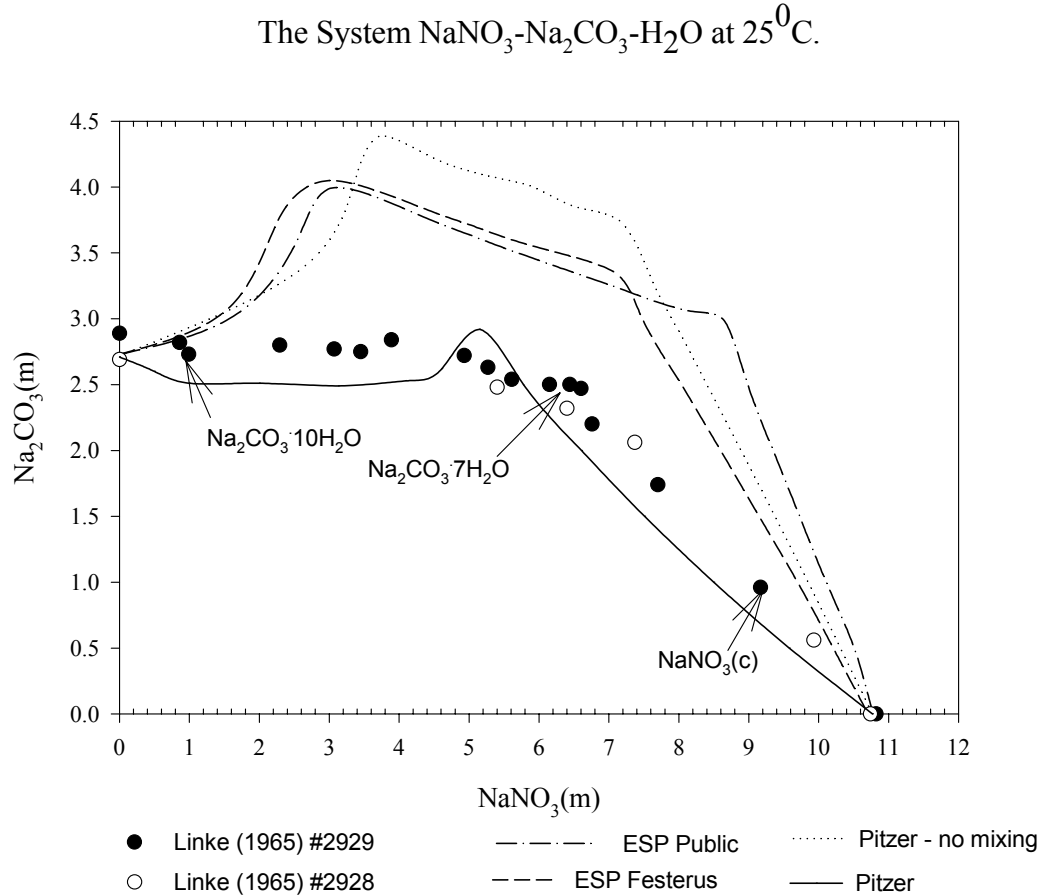
Figure 5. Solubility relations in the $NaNO_3$-Na_2CO_3-H_2O system at $25^{\circ}C$. ESP Festerus refers to the special database developed for the ESP model by Sterner et al. (1996).

2.1.2 NaNO₃-Na₂SO₄-H₂O

The comparisons between model and experiment for the $NaNO_3$-Na_2SO_4-H_2O system follow similar trends to those observed for the $NaNO_3$-Na_2CO_3-H_2O system with the main difference being that the double salt $NaNO_3.Na_2SO_4.H_2O$ forms in the intermediate composition region. Thermodynamic data for this phase are not available in either the Pitzer or ESP models and both models correspondingly overpredict the solubilities in this chemical system. In order to satisfactorily represent these data within the Pitzer model required adjusting both mixing terms (i.e. $\phi(NO_3^--SO_4^{2-})$, and $\psi(Na^+-NO_3^--CO_3^{2-})$) as well as the standard chemical potential for the formation of the $NaNO_3.Na_2SO_4.H_2O$ double salt.
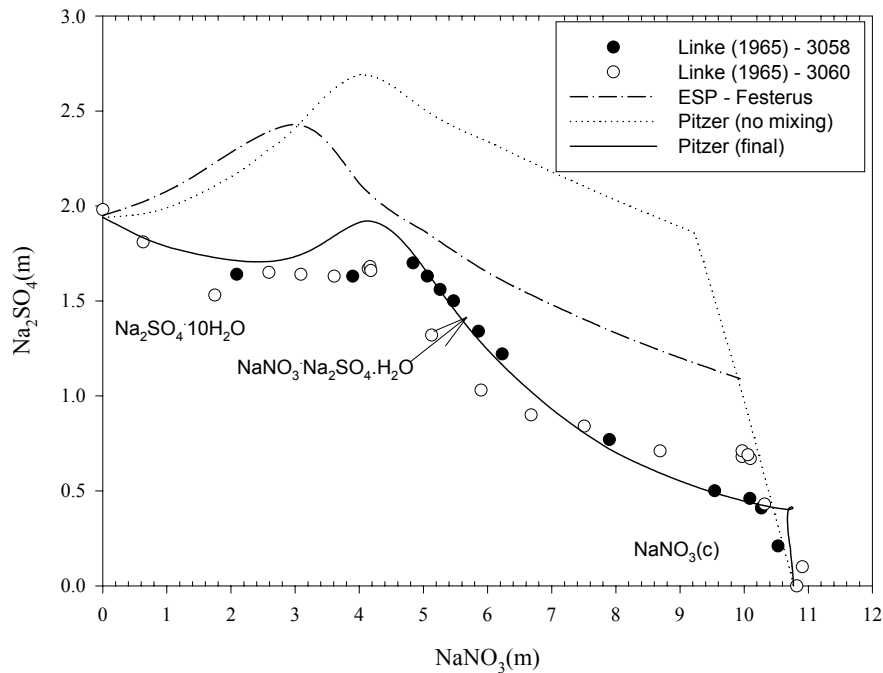
Figure 6. Solubility relations in the NaNO3-Na2SO4-H2O system at 250°C. The double salt (NaNO3.Na2SO4.H2O) forms in the intermediate concentration range.

2.1.3 NaNO$_2$-Na$_2$CO$_3$-H$_2$O

A comparison between the model predictions and experimental data for the NaNO$_2$-Na$_2$CO$_3$-H$_2$O system, Figure 7, also shows the expected trends. However, in this chemical system the association reaction between Na$^+$ and NO$_2^-$ is sufficiently strong that in the intermediate composition region NaNO$_2$(aq) ion pair formation is predicted to effectively ties up the majority of the soluble NO$_2^-$. Therefore, in order to satisfactorily model the experimental data required including a mixing term between the ion pair NaNO$_2$(aq) and CO$_3^{2-}$ (i.e. λ(NaNO$_2$(aq)-CO$_3^{2-}$) as well as ϕ(NO$_2^-$-CO$_3^{2-}$) (see Table 4). The final representation of the experimental data in the Pitzer formalism is satisfactory.
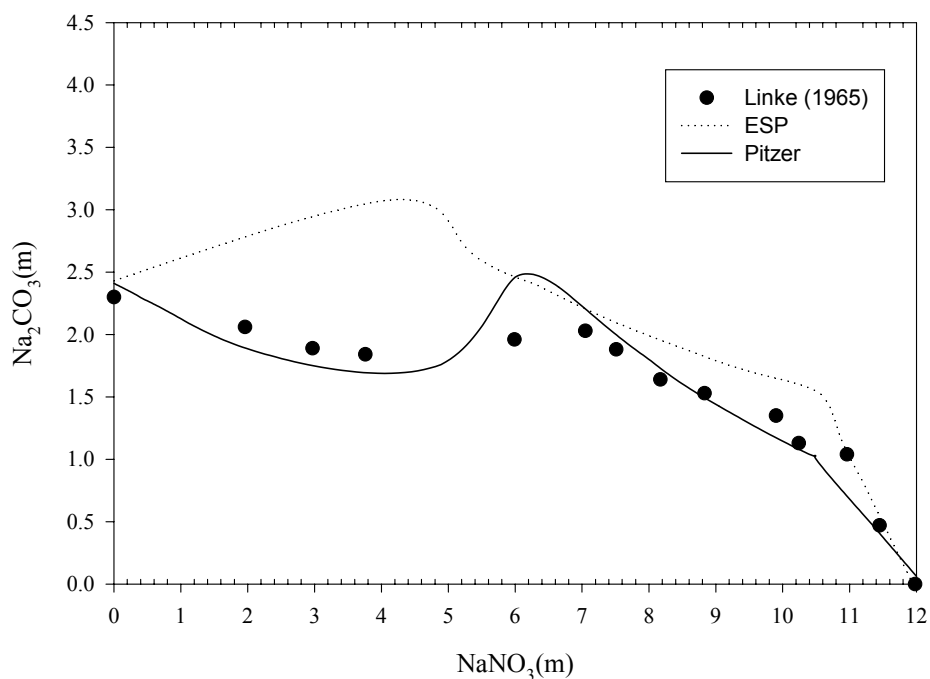
Figure 7. Solubility relations in the NaNO$_2$-Na$_2$CO$_3$-H$_2$O system at 23°C.

2.1.4 NaF-NaOH-H₂O

The NaF-NaOH-H₂O system was treated in detail by Weber et al. (2000). Utilizing their model parameterizations offers a fully satisfactory prediction of the experimental data for this chemical system. This application demonstrates the true value of being able to utilize the Pitzer approach with parameters taken directly from literature sources. Interestingly, the ESP model also gives quite satisfactory predictions of the solubility relations for this system even though a different phenomenology is invoked (i.e. the ESP model includes a series of Na-F ion pairs).
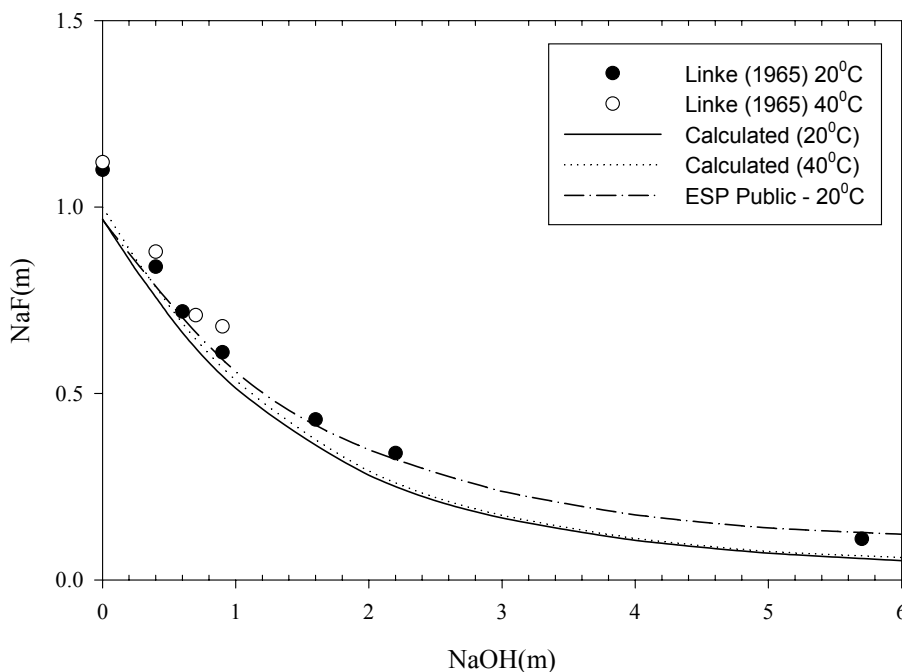
Figure 8. Solubility relations in the NaF-NaOH-H₂O system at 20 and 40°C.

2.1.5 NaF-Na$_2$SO$_4$-H$_2$O

The modeling calculations and experimental data for the NaF-Na$_2$SO$_4$-H$_2$O system, Figure 9, shows the importance of including double salts in the thermodynamic models. The ESP model includes the double salt, NaF·Na$_2$SO$_4$, and accurately predicts the solubility relations at 25°C and gives a fair representation of the observed solubilities at 35°C, even though no temperature dependence of the solubility product is included. The double salt is not included in the initial Pitzer model and its absence results in an overprediction of the solubilities in this system (dotted lines in Figure 9). Inclusion of this phase in the Pitzer model, including a linear representation of the temperature dependence, without adjusting any other parameters gives a very satisfactory fit to the experimental data.
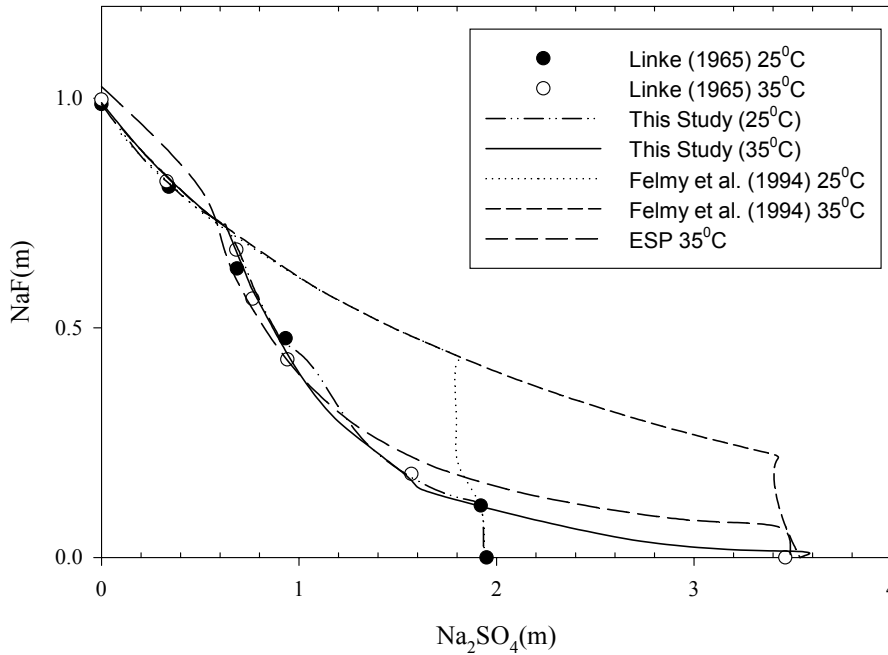
Figure 9. Solubility relations in the NaF-Na$_2$SO$_4$-H$_2$O system at 25 and 350°C. Thermodynamic data for the double salt (NaF.Na$_2$SO$_4$) were not included in the original models of Felmy et al. (1994) or Weber et al. (2000).

2.1.6 NaF-NaNO$_3$-H$_2$O

The solubility relations for the NaF-NaNO$_3$-H$_2$O system also show the expected predictions of binary only models in the absence of double salt formation. The initial Pitzer model and the ESP model both give reasonable predictions at the end points and then deviate in the intermediate mixed concentration region. The experimental data are easily represented with the Pitzer model by including the appropriate mixing terms (ϕ and ψ), see Table 4.
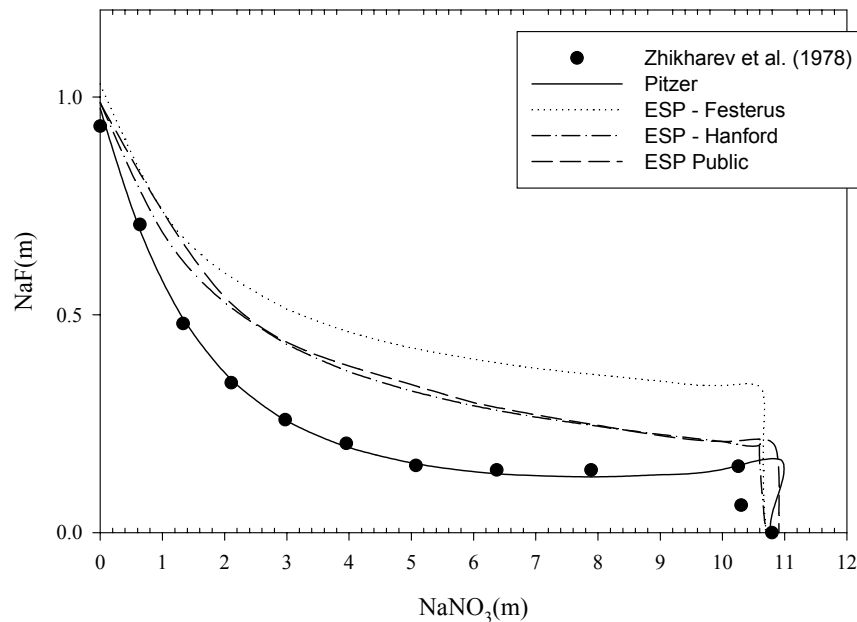
Figure 10. Solubility relations in the NaF-NaNO$_3$-H$_2$O system at 25°C.

2.1.7 NaF-Na$_2$CO$_3$-H$_2$O

The solubility relations for the NaF-Na$_2$CO$_3$-H$_2$O system are fairly straightforward. The initial Pitzer model without mixing terms actually gives good predictions of the solubility data at 25°C but deviates at high Na$_2$CO$_3$ concentration at 50°C. The deviation at 50°C results from the much higher Na$_2$CO$_3$ solubilities at this temperature which results in the mixing terms between fluoride and carbonate being much more significant. The experimental data is easily represented by determining these parameters, Table 4.

Figure 11. Solubility relations in the NaF-Na$_2$CO$_3$-H$_2$O system at 25 and 500°C. The designation, Weber, refers to the combined model of Weber et al. (2000) and Felmy et al. (1994).

2.1.8 Na$_3$PO$_4$-Na$_2$CO$_3$-H$_2$O

The Na$_3$PO$_4$-Na$_2$CO$_3$-H$_2$O system is the first system examined which contained phosphate. Although the most recent versions of ESP give satisfactory predictions for this chemical system, this is not the case for the combined Felmy-Weber Pitzer model. Utilizing the model parameterizations for Na-PO$_4$ given by Weber et al. (2000) gives reasonable predictions only over a limited concentration region at low Na$^+$ molalities (<2m), Figure 12. At higher Na$^+$ concentrations the predicted solubilities increase sharply, the free energy becomes non-convex, and there is no predicted two phase region where both natron (Na$_2$CO$_3$.10H$_2$O) and trisodium phosphate (Na$_3$PO$_4$.1/4NaOH.12H$_2$O) are stable. The problem is related to a large and negative value for one of the ion-interaction parameters, C$^\phi$(Na$^+$-PO$_4^{3-}$), in the initial model parameterizations of Weber et al. (2000). The parameter C$^\phi$ is multiplied in the activity coefficient expression by two terms that have the combined approximate functionality of the ionic molalities squared. This product thus increases rapidly at high concentration and when further multiplied by

16

a coefficient (C^ϕ) which is also relatively large results in the extremely poor agreement between model and experiment found at high Na^+ concentrations. This problem was not reported in the original work of Weber et al. (2000) presumably owing to the lower Na^+

concentrations in their study. Although it is possible to fit common-ion ternary parameters that can satisfactorily explain this particular data set, the calculated mixing terms are extremely large and positive in order to suppress the effect of the large C^ϕ term. Using such model parameterizations is fundamentally unwise since the pairing off of large terms of opposite sign, multiplied by a molality squared product, invariably results in dramatic model failure in some mixed solution concentration region where the two terms do not cancel out. The most reliable approach was to re-determine the Na^+-PO_4^{3-} ion-interaction parameters. The most useful experimental data from which to determine these parameters is the binary osmotic/vapor pressure data for the Na_3PO_4-H_2O system. Tabulating, recalculating, and analyzing all of the experimental data for Na_3PO_4 solutions at different temperatures is a somewhat time consuming exercise. Fortunately, Weber et al. (2000) had previously accurately fit these data sets and accurately reproduced the experimental results. Therefore, the approach taken in this study was to utilize the model of Weber et al. (2000) to calculate osmotic coefficients for Na_3PO_4 solutions and then use these generated data sets to test alternate models for the Na_3PO_4 binary parameters. These generated data sets were limited to the original range of concentrations examined in the

vapor pressure studies (i.e. < 1molal) owing to the limited solubility of trisodium phosphate. This essential limitation to lower total Na_3PO_4 concentration meant that it was impossible to determine an unambiguous value for C^{ϕ} and this term was set to zero
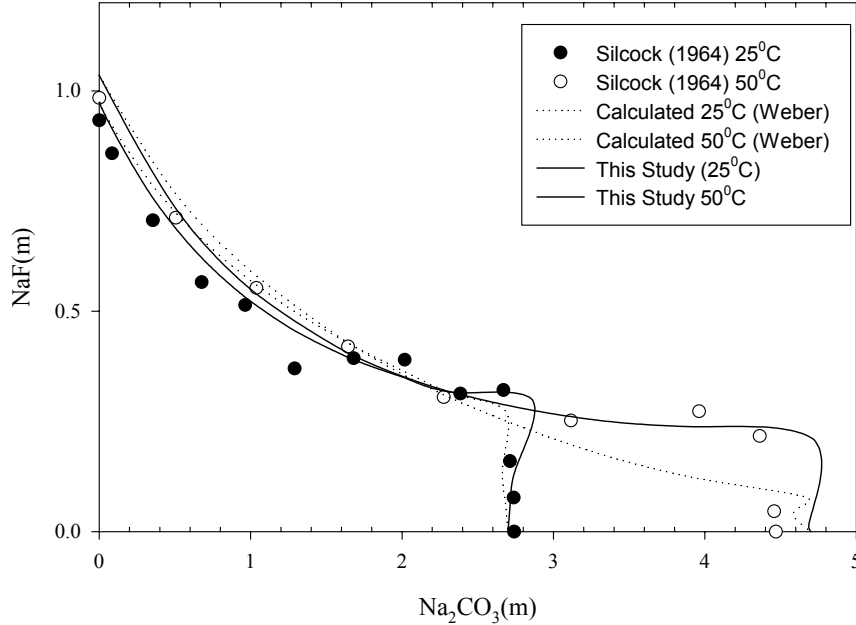

Figure 12. Solubility relations in the Na_2CO_3-Na_3PO_4-H_2O system at 250°C. The designation, Weber, refers to the co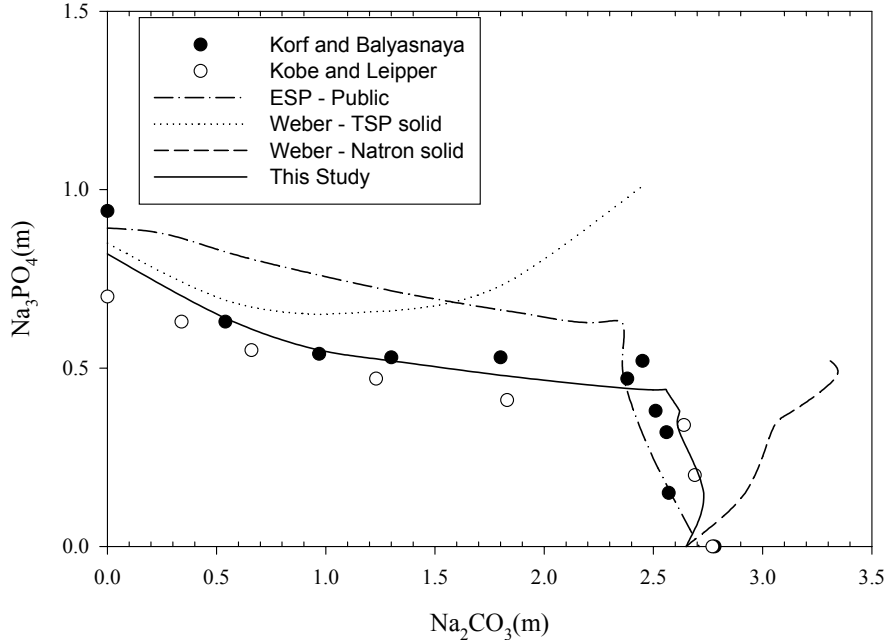mbined model of Weber et al. (2000) and Felmy et al. (1994). The data designated as Korf and Balyasnaya and Kobe and Leipper refer to citations in Linke (1965).

in our final analysis. The remaining binary Na_3PO_4 parameters (β^0, and β^1) where then determined by fitting the generated osmotic data. An example of the agreement of the calculations using these two parameter sets is shown in Figure 13. Clearly, the new model parameterization reproduces the same calculated osmotic coefficients as the original Weber et al. (2000) model. However, the elimination of the C^{ϕ} term results in a much more stable and reliable thermodynamic model. This fact can be clearly seen in Figure 12, solid line, which represents the new model predictions with no adjusted parameters. The new predictions are essentially identical to the experimental results.

18

Figure 13. Calculated osmotic coefficients for Na_3PO_4 solutions at 25 and 100°C.

2.1.9 Na_3PO_4-$NaNO_2$-H_2O

The solubility relations for the Na_3PO_4-$NaNO_2$-H_2O system, Figure 14, are relatively straightforward as only two solid phases form, TSP ($Na_3PO_4 \cdot 1/4NaOH \cdot 12H_2O$) and $NaNO_2$(c). As was true for the Na_3PO_4-Na_2CO_3-H_2O system the Pitzer model parameterization of Weber et al. (2000) gave very poor predictions for this chemical system at high Na^+ concentration (dotted line in Figure 14). Our new parameterization works quite well for this chemical system with calculated mixing terms that are of very reasonable magnitude (Table 4). The final Pitzer model gives a very satisfactory representation of the experimental data. The ESP model overpredicts the solubilities for this chemical system.
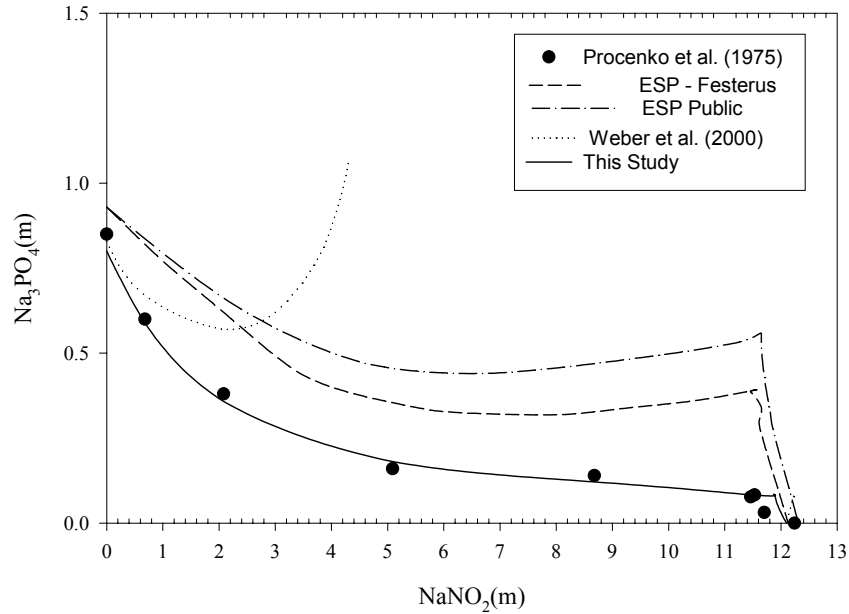
Figure 14. Solubility relations in the $NaNO_2$-Na_3PO_4-H_2O system at 25°C.

2.1.10 Na₃PO₄-NaOH-H₂O

The solubility relations in the Na_3PO_4-NaOH-H_2O system are very complex with numerous phases including: $Na_3PO_4 \cdot 1/2H_2O$, $Na_3PO_4 \cdot 6H_2O$, $Na_3PO_4 \cdot 1/4NaOH \cdot 12H_2O$, $Na_3PO_4 \cdot 12H_2O$, $Na_2HPO_4 \cdot 12H_2O$, $Na_2HPO_4.8H_2O$ forming (Wendrow and Kobe 1952). The exact composition of these phases in terms of the number of waters of hydration and the amount of NaOH incorporated into the structure is still somewhat uncertain (Weber et al. 2000). The stability fields for these different phases are also highly depend upon temperature and NaOH concentration. The less hydrated phases ($Na_3PO_4 \cdot 1/2H_2O$, $Na_3PO_4 \cdot 6H_2O$) being stable only at very high NaOH concentration, i.e. >10m at 25°C but having stability fields that expand with temperature. Owing to time and funding constraints it was impossible to fully treat the phase equilibrium in this chemical system. The phases included in the current version of the chemical model include only those phases treated by Weber et al. 2000 (i.e. $Na_3PO_4 \cdot 1/4NaOH \cdot 12H_2O$ and $Na_2HPO_4 \cdot 12H_2O$). At 25°C these are also likely to be the phases most important in analyzing tank chemistry but their stability fields are reduced with temperature and the entire phase diagram should be eventually incorporated into the model simulations. The subset of the Na_3PO_4-NaOH-H_2O system that we have examined is illustrated in Figure 15. The experimental concentration region represented covers much of the chemical equilibrium relations below approximately 10m NaOH and extending to about 60°C. Only two comparisons between models and experimental data are shown in Figure 15. The first calculation uses only Weber et al.'s original parameterization of the Pitzer model (dotted lines) and, as expected, begins to fail at higher Na^+ concentration. The other model representation is of our final thermodynamic model for which the parameters are illustrated in Tables 2-4. The mixing terms (i.e. PO_4-OH) were fit to the higher NaOH concentration data for which the final model gives very satisfactory predictions. However, the model fails to accurately predict the large increases in phosphate concentration at 40 and 60°C at lower NaOH concentrations. All attempts to simultaneously fit both the lower concentration NaOH data and the higher concentration NaOH data failed. The large increases in solubility could not be predicted without including large negative interaction parameters between Na^+ and PO_4^{3-}, however such large parameters then overpredicted the solubilities

at high NaOH concentration. The decision was made to focus on the higher NaOH concentration data since previous experience has shown that such large increases in solubility usually result from the formation of polynuclear species. Unfortunately, there are no current experimental data to confirm or deny such hypothesis. Clearly, more information on the chemical speciation of phosphate is needed for the Na_3PO_4-NaOH-H_2O system.

Figure 15. Solubility relations in the NaOH-Na_3PO_4-H_2O system at 25, 40, and $60^{\circ}C$.
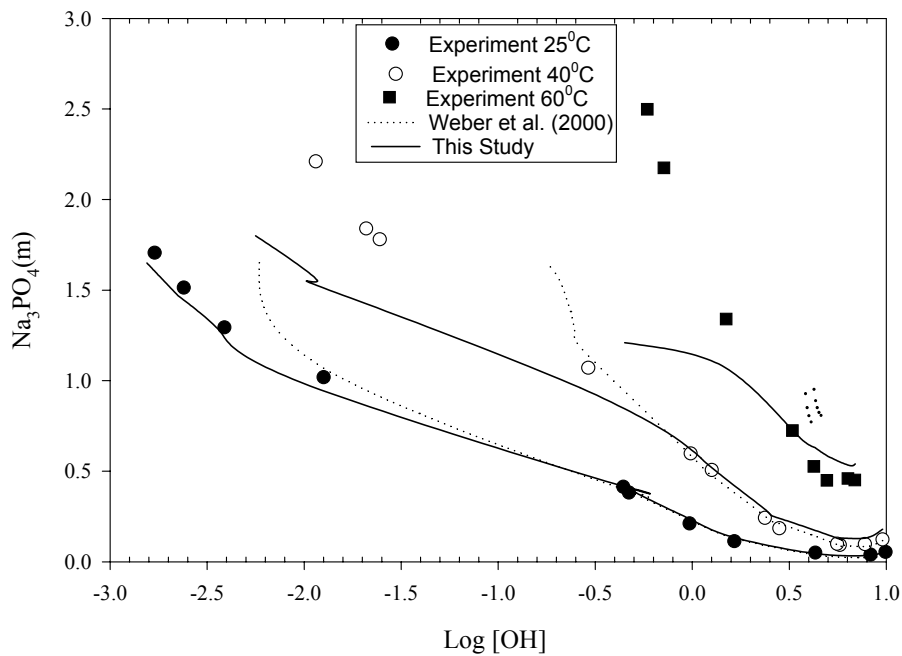
2.1.11 Na_3PO_4-NaF-H_2O

The NaF-Na_3PO_4-H_2O system has been of considerable interest in waste tank applications as a result of the relatively insoluble nature of the precipitates that can form in this system and their potential for plugging transfer lines and affecting filtration processes. Several investigators have studied this chemical system over the years beginning with the work of Mason and Ashcraft (1939). Unfortunately, unanimous agreement on the nature of the precipitates and the exact equilibrium concentrations has not been achieved. Figure 16 presents examples of results of previous investigations of the NaF-Na_3PO_4-H_2O system at $25^{\circ}C$. The data of Roslyakova et al. (1979) are

significantly lower than the other values and report the formation of a solid solution rather than the usually identified $Na_7F(PO_4)^.19H_2O$ precipitate. Also, the original source of the data reported as "Beahm et al." in Figure 16 are still somewhat uncertain. These data were taken from a viewgraph included in a packet of material tabulated from a salt cake workshop at Hanford. No other information on the source was included with the viewgraph. These data were included since they correspond to the predicted solubilities of Weber et al. (2000).
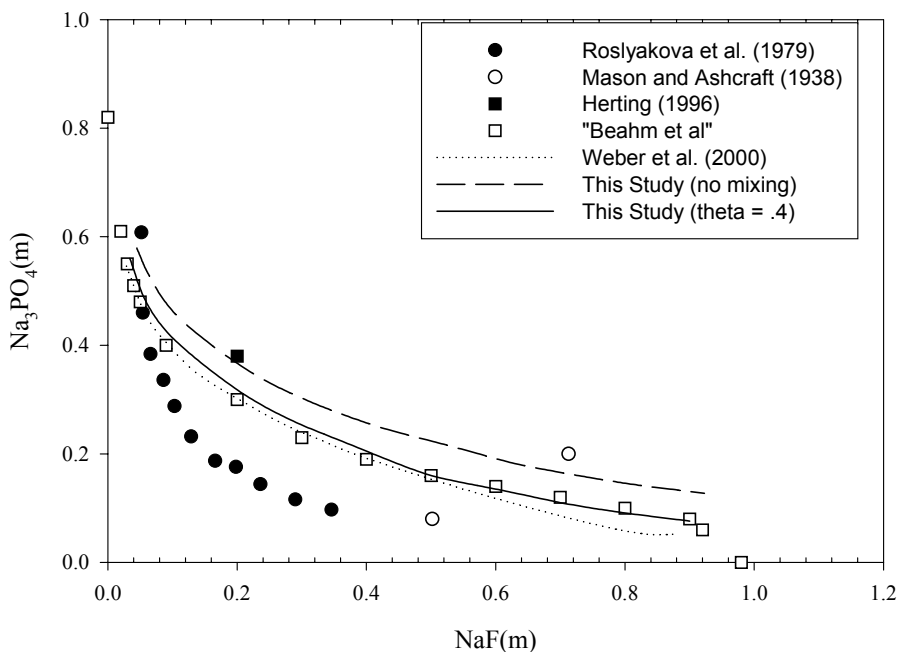
Figure 16. Solubility relations in the $NaF-Na_3PO_4-H_2O$ system at 250°C. The designation "Beahm et al." is described in the text.

The Pitzer model without F/PO_4 mixing terms yields solubility predictions that are somewhat higher than the original model of Weber et al. (2000), which included a very large and positive value for $\phi(F^--PO_4^{3-})$ of 0.55. Similarly, in order to match the predicted solubilities of Weber et al. (2000) required the inclusion of a large and positive value for $\phi(F^--PO_4^{3-})$. Given this situation, it was decided to test the model without including mixing terms on a wider range of data sets at different temperatures to better evaluate the possible need for the $\phi(F^--PO_4^{3-})$ mixing term. The most comprehensive set of data available for this comparison is the work of Herting (1996) who examined the solubility of $Na_7F(PO_4)^.19H_2O$ from 15°C to 75°C and at different solution compositions

including: dilute water, 1M NaOH, and a complex 5M Na solution (i.e. 1M NaOH + 2M NaNO$_3$ + 2M NaNO$_2$). The agreement between model and experiment, Figure 17, shows that on an overall basis the final thermodynamic model, without the large F$^-$-PO$_4^{3-}$ mixing terms gives quite good agreement with the experimental data of Herting (1996). In fact, two of the solubility points reported by Herting (1996) at 65 and 75°C and in the 5M Na solution did not show congruent dissolution of the solid phase and had considerably lower F concentrations than expected. Interestingly, these were the only two solubility points for which our thermodynamic model predicted a two phase stability region (NaF(c) + Na$_7$F(PO$_4$)$\cdot$19H$_2$O) accounting for the previously unexplained lack of congruent dissolution. Such predictions of previously unexplained data variations give considerable confidence in the thermodynamic model predictions.
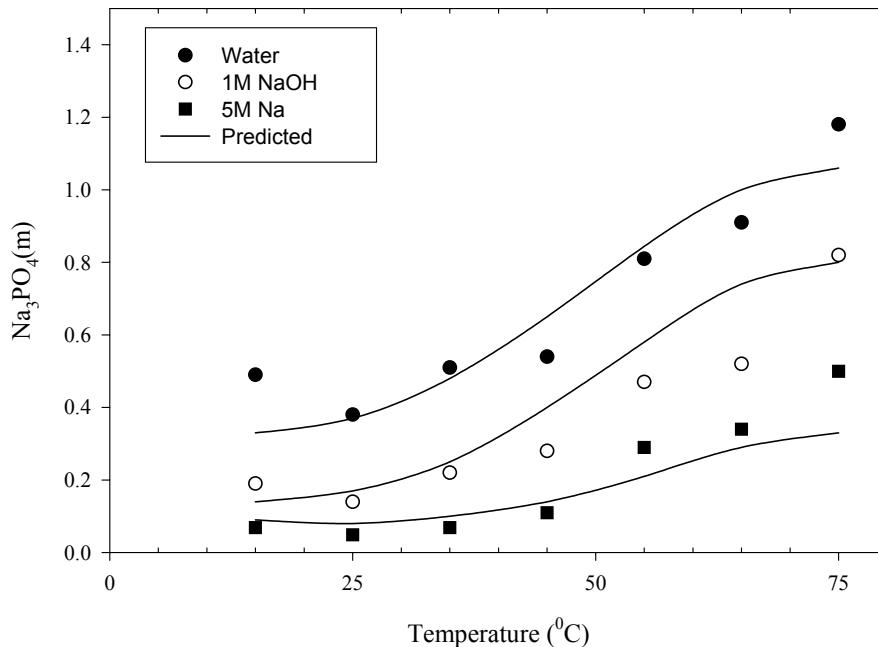

Figure 17. Solubility relations in the NaF-Na$_3$PO$_4$-H$_2$O system at different temperatures. Experimental data of Herting (1996).

3.0 Impact of New Model Parameters

Development of new modeling parameters for the Pitzer option in the ESP program has long range impacts to the Hanford site in numerous application areas that may not be fully realized for years to come. However, as an illustrative example of the effect these new parameters we performed modeling simulations for the major electrolyte components of a diluted tank AN-102 solution (labeled HD) to contrast the predictions of the Pitzer models with and without the new model parameters. The HD sample is approximately 6M in Na with high concentrations of nitrate, nitrite, and carbonate as well as containing significant concentrations of fluoride, phosphate, and aluminate. Table 5 gives a few examples of changes in the equilibrium model calculations.

Table 5. Impact of new model parameters on chemical equilibrium calculations for a diluted tank AN-102 sample.

Calculation	Impact
$NaNO_3$ saturation state	Reduced 14%
$Na_2CO_3^.H_2O$ saturation state	Reduced 193%
$Na_2CO_3.2Na_2SO_4$ saturation state	Reduced 428%
$Na_7F(PO4)_2^.19H_2O$	Calculated to be in equilibrium with the solution, previously not included in the model calculations.

Clearly, the identification of phases likely to precipitate in the tank solutions is the most significant impact of the new modeling calculations. However, it also needs to be pointed out that improving the major electrolyte model also impacts the calculations for all components of the model. For example, a recent calculation on the solubility of $SrCO_3(c)$ in a diluted tank AN-102 solutions showed a 25% change in the final equilibrium solution composition. This change improved the final agreement between model and experiment and resulted from an improved calculation of the carbonate ion activity. So the impact of improving the major electrolyte model is fundamentally important for all modeling calculations.

4.0 Model Limitations

Although the present Pitzer model has been significantly enhanced for predicting the solubility relations in the Na-OH-NO_3-NO_2-SO_4-CO_3-F-PO_4-H_2O system the current model parameterizations cannot be completed owing to a lack of experimental data. This lack of experimental data is detailed below.

First, experimental solubility data for three common-ion ternary systems are unavailable. These systems are: $NaNO_3$-Na_3PO_4-H_2O, $NaNO_2$-Na_2SO_4-H_2O and $NaNO_2$-NaF-H_2O. The model parameters describing the aqueous ion-interactions (e.g. $\phi(NO_3^-$-$PO_4^{3-})$) are currently set to zero in the current version of the model. In addition, the possible formation of double salts in these chemical systems is unknown. Second, experimental data for four chemical systems ($NaNO_3$-NaF, $NaNO_2$-Na_2CO_3, $NaNO_2$-Na_3PO_4, and $NaNO_3$-Na_2CO_3) is limited to $25^\circ C$. This factor obviously limits the accuracy of the model at higher temperatures. Third, the model does not describe the phosphate solubility data at very high phosphate (see Figure 15). The chemical speciation of phosphate in these solutions should be examined to determine if phosphate polymerization reactions have occurred. Finally, there is one chemical system for which the available experimental data are not well predicted and the experimental data do not correlate with data for similar chemical systems. This chemical system is the Na_2SO_4-Na_3PO_4-H_2O system, Figure 18. The experimental solubilities in this chemical system are much lower than for the corresponding Na_2CO_3-Na_3PO_4-H_2O system and are impossible to parameterize without invoking very large and positive mixing terms between sulfate and phosphate. This situation is usually indicative of either the formation of an unidentified double salt, which are common for the sulfate containing systems, or errors in the experimental measurements. In any event, this chemical system should be re-examined to determine if the currently available solubility data and phase identification information are reliable.
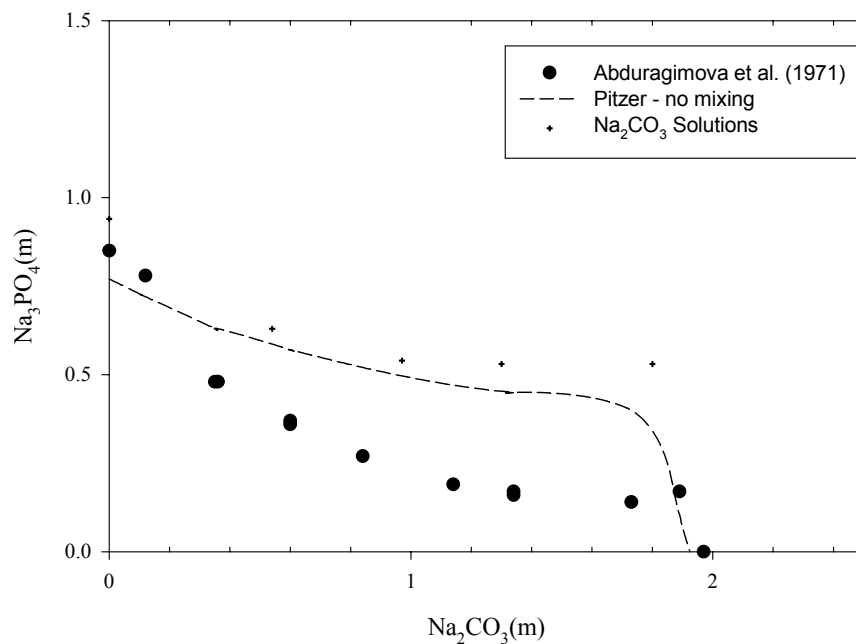
Figure 18. Solubility relations for the Na_2SO_4-Na_3PO_4-H_2O system at 250°C. Experimental data do not correlate with similar data for Na_2CO_3 and no insoluble double salt was reported.

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