

Development of Accurate Not Concentration Restricted Models for Predicting Solution Properties and Solid-Liquid Equilibrium in Binary Nitrate Systems from Low to Very High Concentration (up to $\approx 30 \text{ mol.kg}^{-1}$) at $T = 25^\circ\text{C}$

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Introduction

Aqueous geochemical models that predict solid and gas equilibria over a broad range of water compositions and temperatures are powerful tools for studying the geochemistry of natural waters, solving environmental problems and optimizing industrial processes. The Pitzer ion interaction model has been widely accepted as the most effective approach to predict chemical behaviour in concentrated solutions; however, the description of natural waters requires a large compilation of interaction parameters. These parameters are derived from experimental data such as isopiestic, electrochemical, and solubility measurements on simpler systems. An accurate parameterization of a solution and solid-liquid equilibria model for binary systems is essential for the development of accurate models for complex systems. In this study, a large number of binary systems have been evaluated to understand issues that could potentially compromise the representation of more complex solutions. The results revealed that the concentration range, within which Pitzer parameters are derived, and the choice of aqueous species that are included in the model are of most importance.

In this study we developed well validated Pitzer ion interactions approach based thermodynamic models for solution behavior and solid-liquid equilibrium in 17 nitrate binary systems [of the type 1-1 ($\text{HNO}_3\text{-H}_2\text{O}$, $\text{LiNO}_3\text{-H}_2\text{O}$, $\text{NaNO}_3\text{-H}_2\text{O}$, $\text{KNO}_3\text{-H}_2\text{O}$, $\text{RbNO}_3\text{-H}_2\text{O}$, $\text{CsNO}_3\text{-H}_2\text{O}$, and $\text{NH}_4\text{NO}_3\text{-H}_2\text{O}$), of the type 2-1 ($\text{Mg}(\text{NO}_3)_2\text{-H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2\text{-H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2\text{-H}_2\text{O}$, and $\text{UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$), 3-1 ($\text{Cr}(\text{NO}_3)_3\text{-H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3\text{-H}_2\text{O}$, $\text{La}(\text{NO}_3)_3\text{-H}_2\text{O}$, $\text{Lu}(\text{NO}_3)_3\text{-H}_2\text{O}$), and 4-1 ($\text{Th}(\text{NO}_3)_4\text{-H}_2\text{O}$)] from low to very high concentration at $T = 25^\circ\text{C}$.

Parameterization Over Entire Concentration Range

In evaluating and using model parameters, it is imperative to ensure that any parameters used were derived within the concentration range of interest for the study. For a system that is parameterized over a limited concentration range, model predictions may deviate substantially from the experimental data outside this range. Further evaluations of parameters within a chemical system will be hampered if any of the data points used in evaluating new parameters fall outside this concentration range. In particular, the new introduced parameters may be biased to compensate for inaccuracies in the original model rather than real chemical effects. It is possible to reduce the potential for introducing such systematic errors into an analysis by ensuring that the parameterization for binary systems is valid up to the solubility limit, and even to supersaturated conditions, if possible.

Evaluation of Pitzer Parameters

To parameterize models for binary systems we used all available raw experimental osmotic coefficients data (ϕ) for whole concentration range of solutions (Hamer, Wu (1972), Robinson, Stokes R. (1959), Mikulin (1968)), and up to saturation point (Mikulin, 1968). Data for supersaturation zone, available for $\text{LiNO}_3\text{-H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$ and $\text{Lu}(\text{NO}_3)_3\text{-H}_2\text{O}$ systems, are also included in parameterization.

The models for all nitrate binary systems under study are also validated by comparison with recommendations given in literature (Hamer, Wu (1972), Mikulin, (1968)) on the mean activity coefficients (γ_{\pm}). These recommendations on γ_{\pm} are model-dependent. Therefore, they are not used in parameterization process, and only to validate the resulting models.

In parameterization process we used the value of Debye-Hückel term (A^ϕ) equals to 0.39147, as given in Christov (2005). Following the parameterization scheme described in previous studies the model for all binary nitrate solutions is parameterized using two different approaches: (I) standard for N-1 electrolytes ($N=2, 3, \text{ or } 4$) approach with 3 ion interaction binary parameters ($\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ) and setting α_1 term equals to 2, and $\alpha_2 = 0.0$, and (II) an extended approach with four Pitzer ion interaction binary parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^ϕ) and varying in the values of α_1 and α_2 terms. As a first step in parameterization we used classical 3 parameters approach (I) and evaluate binary parameters using all available raw ϕ data for whole molality range of solutions. As a next step, using the same ϕ data we re-parameterize the models on the basis of extended approach (II), and using three α -combinations: (IIa) $\alpha_1 = 2$ and $\alpha_2 = 1$, and (IIb) $\alpha_1 = 2$ and $\alpha_2 = -1$ (Christov, 2005) and (IIc) $\alpha_1 = 2$ and $\alpha_2 = 0.3$ (Lach et al, 2018). It was found that more combinations in "alfa" values do not improve the fit of data used in parameterization. The main criterion in the choice of established parameterization was the value of standard deviation (σ) of fit of used ϕ data, i.e. parameterization with the lowest sigma value is accepted. It was found that for some of studied systems (s.a. $\text{NaNO}_3\text{-H}_2\text{O}$, $\text{KNO}_3\text{-H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2\text{-H}_2\text{O}$, and $\text{Sr}(\text{NO}_3)_2\text{-H}_2\text{O}$) the approach (I) with 3 parameters ($\beta^{(0)}$, $\beta^{(1)}$, C^ϕ) give an acceptable agreement with the data. For these systems introducing into a model of fourth ($\beta^{(2)}$) parameter do not improve considerably the fit of data. For all other nitrate systems under study we construct a model on the basis of extended approach (II), and using different combinations of "alfa" values. The resulting models fits the data up to supersaturation zone ($m(\text{max}) = 14.77 \text{ m}$ in $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$) with sigma values, which is much less than the sigma values of models of P&M (1973), and of K&F (1988). The comparisons between predictions of new developed model with experimental osmotic coefficients data and reference γ_{\pm} recommendations, show an excellent agreement from low to very high concentrations ($m(\text{max}) \approx 30 \text{ m}$ in $\text{HNO}_3\text{-H}_2\text{O}$)

RESULTS

On next figures with the experimental data we compare predictions of the models developed here (solid line), reference models (dashed or dotted lines) with experimental osmotic coefficients data and reference γ_{\pm} recommendations (symbols). On the figures the vertical lines denote the molality of saturated solutions. Figure 1 presents the results of three different models for the $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$ system, along with the experimental data. Each of these models has its own limitations in predicting the osmotic coefficient as a function of concentration. A good fit was achieved by Pitzer and Mayorga (1973) at low concentrations, but the model breaks down above 2 m. Pitzer and Mayorga (1973) tabulated $\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ values for 227 pure aqueous electrolyte systems (most of them were compiled in Pitzer, 1991). Their parameterization was focused on a good representation of activity properties (osmotic coefficient) of low molality up to 6m in unsaturated solutions, with the maximum allowable deviation in osmotic coefficient of 1%. Kim and Frederick (1988) extended the concentration to 6 m by sacrificing at low concentrations. Wijesinghe and Rard (2005) were able to predict the saturation of $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$, but the fit was the worse at low concentrations. The Deliquescence Relative Humidity (DRH), thermodynamic solubility product (as $\ln K_{sp}^\circ$), and standard molar Gibbs free energy of formation ($\Delta_f G_m^\circ$) of 18 nitrate solid phases [$\text{LiNO}_3\cdot 3\text{H}_2\text{O}(\text{s})$, $\text{NaNO}_3(\text{s})$, $\text{KNO}_3(\text{s})$, $\text{RbNO}_3(\text{s})$, $\text{CsNO}_3(\text{s})$, $\text{NH}_4\text{NO}_3(\text{s})$, $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}(\text{s})$, $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}(\text{s})$, $\text{Ca}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}(\text{s})$, $\text{Ba}(\text{NO}_3)_2(\text{s})$, $\text{Sr}(\text{NO}_3)_2(\text{s})$, $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}(\text{s})$, $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}(\text{s})$, $\text{Cr}(\text{NO}_3)_3(\text{s})$, $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}(\text{s})$, $\text{La}(\text{NO}_3)_3(\text{s})$, $\text{Lu}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}(\text{s})$ and $\text{Th}(\text{NO}_3)_4\cdot 6\text{H}_2\text{O}(\text{s})$] have been determined on the basis of evaluated binary parameters and using $m(\text{sat})$ solubility data. Model predictions are in good agreement with available reference data.

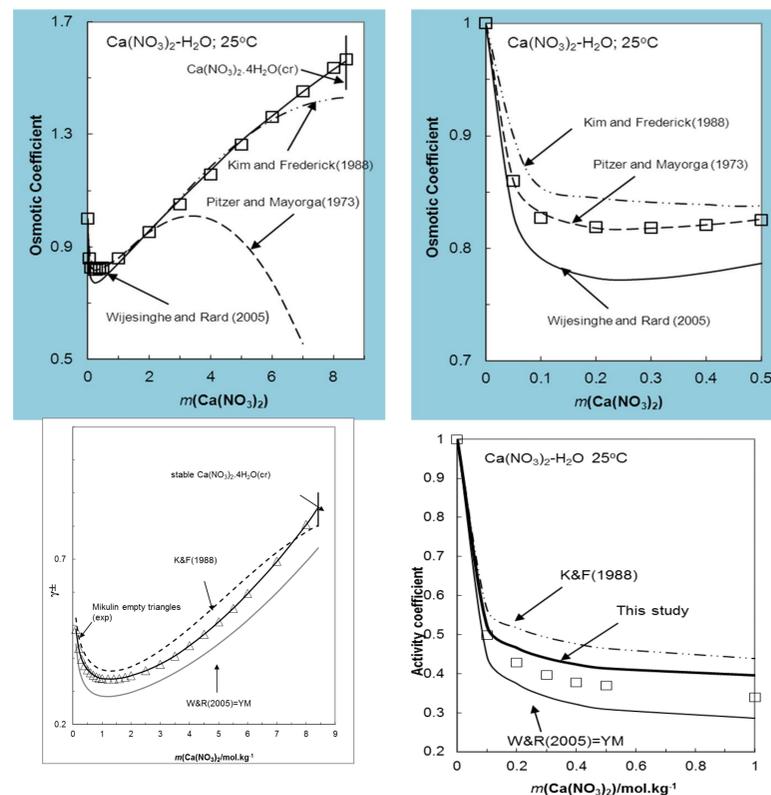


Figure 1: Osmotic and activity coefficient vs. molality for the $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$ system at 25°C . (left) Entire molality range; (right) Low concentration. Solid line – present model; Dotted line - prediction using Pitzer and Mayorga (1973); Dashed line - prediction using Kim and Frederick (1988a); Symbols - experimental data from Mikulin (1968).

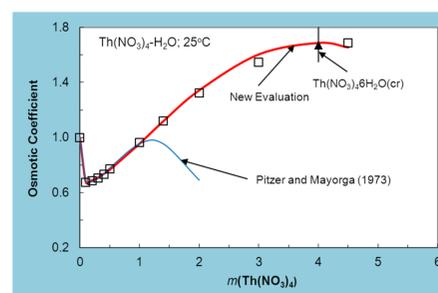


Figure 2: Osmotic coefficient vs. molality for the $\text{Th}(\text{NO}_3)_4\text{-H}_2\text{O}$ system at 25°C . Red line - new evaluation; Blue line - model prediction of Pitzer and Mayorga (1973); Open squares - experimental data from Mikulin (1968).

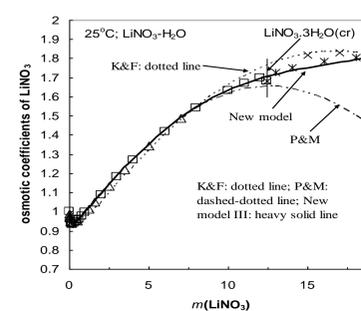


Figure 3: Osmotic coefficient vs. molality for the $\text{LiNO}_3\text{-H}_2\text{O}$ system at 25°C . Solid line – present model; Dotted line -prediction using Kim and Frederick (1988), Dashed line -prediction using Pitzer and Mayorga (1973); Symbols - experimental data from Mikulin (1968) and Hamer and Wu (1972).

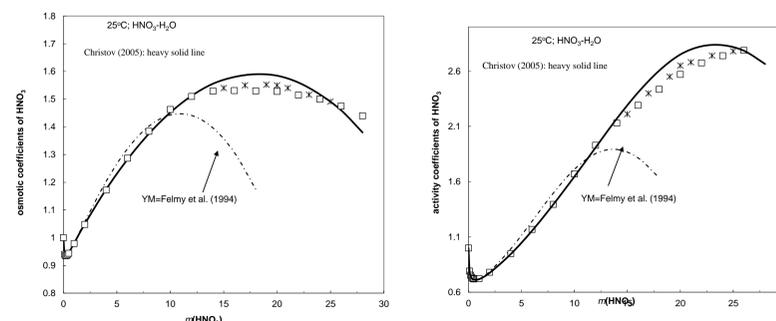


Figure 4: Osmotic (left) and activity (right) coefficient vs. molality for the $\text{HNO}_3\text{-H}_2\text{O}$ system at 25°C . Solid line - model prediction using Christov (2005); Dashed line-model prediction using Felmy et al. Symbols= - experimental data.

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