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Thermodynamic representation of aqueous sodium nitrate and nitric acid solution with electrolyte NRTL model

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ABSTRACT

Nitric acid solution has been widely used in nuclear waste treatment processes. To support heat and mass balance calculations and process simulation, a comprehensive thermodynamic model is developed for sodium nitrate–water binary, nitric acid–water binary, and nitric-acid–sodium nitrate–water ternary systems. Based on symmetric electrolyte NRTL (eNRTL) activity coefficient model, the present work takes into account complete dissociation of sodium nitrate and partial dissociation of nitric acid in aqueous solution. With up to three temperature coefficients for each eNRTL binary interaction parameter, the model provides an accurate and thermodynamically consistent representation for phase equilibrium properties such as vapor pressure, boiling point, dew point and salt solubility, calorimetric properties such as enthalpy and heat capacity, and speciation properties. The model is validated with data covering temperature up to 473.15 K and sodium nitrate concentration up to saturation for the sodium nitrate–water binary system, temperature up to 379.15 K and nitric acid concentration up to pure acid for the nitric acid–water binary system, and sodium nitrate concentration up to 0.21 mole fraction and nitric acid concentration up to 0.3 mole fraction for the nitric acid–sodium nitrate–water ternary system.

1. Introduction

Nitric acid is widely used as a solvent in reprocessing of spent nuclear fuel and in nuclear waste treatment. For example, the well-known PUREX (plutonium and uranium extraction) process [1] uses hot concentrated nitric acid to dissolve fuel pellets so that the actinides can be recovered by extracting from the resulting aqueous solution with tri-*n*-butyl phosphate (TBP) in an immiscible organic phase. Dilute nitric acid at different concentrations is employed as a scrubbing agent throughout this extraction process, in order to improve partitioning and to backwash fission products that are inevitably co-extracted with plutonium and uranium. Spent solvent is neutralized with sodium carbonate, and produces a large quantity of sodium nitrate waste, approximately 100 kg per tonnes of fuel reprocessed [2].

Accurate thermodynamic models are essential for simulation of chemical processes involving electrolytes [3]. Pitzer's ion interaction model [4] has been extensively used for modeling thermodynamic properties of aqueous electrolyte systems with ionic strength up to approximately 6–10 m. In the classic Pitzer model, the excess Gibbs free energy is assumed to be the sum of two terms, a Debye–Hückel term for long-range ion–ion interaction contributions and a virial expansion expression for short-range interaction contributions. The model requires up to four empirically determined binary cation–anion interaction parameters $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, and C_{MX}^{φ} for aqueous single electrolytes and additional binary ion–ion interaction parameters θ for pairs of ions of like sign and ternary ion–ion–ion interaction parameters ψ for triplets of ions (two of like sign and one of the opposite sign) for aqueous mixed electrolytes. The Pitzer model has been successfully used with aqueous electrolyte systems. As a virial expansion equation, the Pitzer model is subject to all the limitations of a virial model [5]. The model gives no guidance in the temperature dependency of the ion interaction model parameters and up to eight temperature coefficients may be necessary for every Pitzer parameter to cover a temperature interval from 0 to about 200 °C [6].

Based on Pitzer's ion interaction model, several thermodynamic models have been developed for the sodium nitrate–water binary system. As the sodium nitrate solubility in water increases rapidly with temperature reaching around 20.7 m at 373.15 K, Archer [7] proposed an extended Pitzer model by replacing C_{MX}^{φ} with two ionic strength-dependent parameters $C_{MX}^{(0)}$ and $C_{MX}^{(1)}$ to overcome

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the concentration limit of the original Pitzer model. Compared with the classic model, this extended model provided better correlation for osmotic coefficient φ and mean ionic activity coefficient $\gamma_\pm$ for sodium nitrate temperatures from 236 to 425 K, and over the molality range from infinite dilution to near saturation or 25 m [7]. In order to support existing parameter databases based on the Pitzer model, Rard and Wijesinghe [8] derived an analytical method to transform the parameters from Archer's extended model back to parameters in the classic Pitzer model, and showed successful application to aqueous sodium nitrate solutions.

Assuming complete dissociation for nitric acid, Clegg and Brimblecombe [9] applied the Pitzer model together with Henry's law to correlate equilibrium partial pressures of nitric acid in aqueous saline solutions at 298.15 K. The model has been verified for aqueous electrolyte systems of ionic strength up to 6.0 m. To cover the entire concentration range, Clegg and Pitzer [10] later proposed a generalized model for symmetrical electrolytes. The equations, expressed on a mole fraction basis, comprise an extended Debye–Hückel term and a Margules expansion carried out to the four-suffix level. The model requires four adjustable parameters for each electrolyte: one in the extended Debye–Hückel expression, the rest in the Margules expansion. For nitric acid–nitrate salt–water ternary systems, the model requires two additional mixture parameters determined from aqueous nitric acid salt solubility data. Although developed for strong acid–salt–water ternary systems, the model was tested only for salt solubility at 298.15 K. These applications [9–11] of the Pitzer model to aqueous nitric acid solutions are very limited in scope. The assumption of complete dissociation for nitric acid further limits application of the model. For example, the model could not provide calorimetric properties because the solution enthalpy depends on speciation, i.e., how much of the nitric acid exists as an ionic species or molecular species [12].

Taking into account partial dissociation of nitric acid, Sander et al., [13] developed an extended UNIQUAC equation to model nitric acid–calcium/magnesium nitrate–water ternary system. In this extended UNIQUAC model, the excess Gibbs energy is also composed of two terms, a Debye–Hückel term similar to that in the Pitzer model and a UNIQUAC term. For a ternary system like the nitric acid–calcium nitrate–water ternary, two molecular species (H_2O and HNO_3) and four ionic species (H_3O^+, NO_3^-, NO_2^+, and Ca^{2+}) were considered. The model requires unary volume and surface area parameters for each species and temperature dependent binary interaction energy parameters for each molecule–molecule pair, molecule–ion pair, and ion–ion pair including self-interaction. Moreover, additional solvent-specific ion–ion interaction parameters were introduced to address concentration dependency of the interaction parameters for molecule–ion pairs. Although the extended UNIQUAC model accurately represented vapor–liquid equilibrium and the salting-out effect for nitric acid–calcium/magnesium nitrate–water ternary systems at atmospheric pressure, the calorimetric properties, i.e., enthalpy and heat capacity, were not considered. By using a simplified version of the extended UNIQUAC model, Christensen and Thomsen [14] later represented phase behavior and thermal properties of aqueous nitric acid solution and the salting-out effect of $NaNO_3$ upon nitric acid with nitric acid concentration up to 12 m and temperature up to 75 °C.

This work aims to develop an accurate and comprehensive thermodynamic model for the nitric acid–sodium nitrate–water ternary system in order to support heat and mass balance calculations and process simulation. The symmetric electrolyte NRTL (eNRTL) model [15] is chosen as the liquid phase activity coefficient model because it offers a practical and proven thermodynamic framework for both aqueous and mixed solvent electrolyte systems [16]. Available experimental data including mean ionic activity coefficient, osmotic coefficient, water activity, vapor pressure, liquid molar enthalpy, heat capacity, and vapor–liquid equilibrium data are used to quantify eNRTL binary molecule–molecule, molecule–electrolyte, and electrolyte–electrolyte interaction parameters. Solubility data are used to regress the thermodynamic constants for the liquid–solid equilibrium of the sodium nitrate–water binary system.

2. Thermodynamic framework

2.1. Chemical reactions

To develop a comprehensive thermodynamic model for the nitric acid–sodium nitrate–water system, both phase equilibrium and chemical equilibrium should be considered, as shown in Fig. 1. In the liquid phase, sodium nitrate behaves as a strong electrolyte and undergoes complete dissociation. Nitric acid, although treated as a strong electrolyte by some researchers, has been shown to behave as a strong electrolyte at high dilution and a weak electrolyte at high concentration by Raman spectroscopy [17]. The corresponding chemical equilibrium constant K_1 for nitric acid dissociation has been evaluated for various temperature ranges by different approaches [17b,18a,18b,18c]. The solubility of sodium nitrate salt in aqueous solution is treated as a chemical reaction with the solubility product constant, K_{sp}. These reactions are summarized in Eq. (R1)–(R3). Both K_1 and K_{sp} are calculated from the Gibbs free energy relationship in this study.

$$NaNO_3 \rightarrow Na^+ + NO_3^- \tag{R1}$$

$$HNO_3 + H_2O \overset{K_1}{\leftrightarrow} H_3O^+ + NO_3^- \tag{R2}$$

$$NaNO_3(s) \overset{K_{sp}}{\leftrightarrow} Na^+ + NO_3^- \tag{R3}$$

The resulting liquid phase include two molecular species, i.e., nitric acid and water, and three ionic species, i.e., sodium ion, nitrate ion and hydronium ion.

2.2. Vapor–liquid equilibrium

The vapor–liquid equilibrium is described by the equality of component fugacity between the liquid and vapor phases.

$$Py_i\varphi_i = x_i\gamma_i f_i^0 \tag{1}$$

where P is the system pressure, y_i is the vapor phase mole fraction of component i, φ_i is the vapor phase fugacity coefficient calculated from the Redlich–Kwong equation of state, x_i is the liquid phase

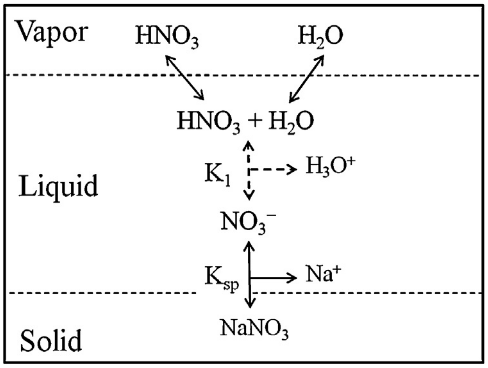

Fig. 1. Solution chemistry and speciation in the nitric acid–sodium nitrate–water system.