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Development of accurate chemical thermodynamic database for geochemical storage of nuclear waste. Part II: Models for predicting solution properties and solid-liquid equilibrium in binary nitrate systems

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Abstract

The main purpose of this study is to develop new thermodynamic models for solution behavior and solid-liquid equilibrium in 10 nitrate binary systems of the type 2–1 ($Mg(NO_3)_2$-H_2O, $Ca(NO_3)_2$-H_2O, $Ba(NO_3)_2$-H_2O, $Sr(NO_3)_2$-H_2O, and $UO_2(NO_3)_2$-H_2O), 3–1 ($Cr(NO_3)_3$-H_2O, $Al(NO_3)_3$-H_2O, $La(NO_3)_3$-H_2O, $Lu(NO_3)_3$-H_2O), and 4–1 ($Th(NO_3)_4$-H_2O) from low to very high concentration at 25 °C. To construct models, we used different versions of standard molality-based Pitzer approach. To parameterize models, we used all available raw experimental osmotic coefficients data (φ) for whole concentration range of solutions, and up to supersaturation zone. The predictions of developed models are in excellent agreement with φ-data, and with recommendations on activity coefficients ($\gamma_{\pm}$) in binary solutions from low to very high concentration. The Deliquescence Relative Humidity (DRH), and thermodynamic solubility product (as ln K°_{sp}) of 12 nitrate solid phases, precipitating from saturated binary solutions have been calculated. The concentration-independent models for nitrate systems described in this study are of high importance for development of strategies and programs for nuclear waste geochemical storage.

Keywords

Nuclear waste sequestration, Chemical modelling,Pitzer approach, DRH and K°_{sp} of $Mg(NO_3)_2.6H_2O(s)$, $Ca(NO_3)_2.4H_2O(s)$, $Ca(NO_3)_2.3H_2O(s)$, $Ba(NO_3)_2(s)$, $Sr(NO_3)_2(s)$, $UO_2(NO_3)_2.6H_2O(s)$, $Al(NO_3)_3.9H_2O(s)$, $Cr(NO_3)_3(s)$, $La(NO_3)_3.6H_2O$ (s), $La(NO_3)_3(s)$, $Lu(NO_3)_3.5H_2O(s)$ and $Th(NO_3)_4.6H_2O(s)$

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Introduction

Computer models that predict solution behavior and solid-liquid-gas equilibria close to experimental accuracy have wide applicability. They can simulate the complex changes that occur in nature and can replicate conditions that are difficult or expensive to duplicate in the laboratory. Such models can be powerful predictive and interpretive tools to study the geochemistry of natural waters and mineral deposits, solve environmental problems and optimize industrial processes. However, development of comprehensive models for natural systems, with their complexity and sensitivity, is a very difficult, time consuming and challenging task. The specific interaction approach for describing electrolyte solutions to high concentration introduced by Pitzer (1973, 1991) represents a significant advance in physical chemistry that has facilitated the construction of accurate computer thermodynamic models. It was showed that this approach could be expanded to accurately calculate solubilities in complex brines, and to predict the behavior of natural and industrial fluids from very low to very high concentration at standard temperature of 25 °C (Harvie et al. 1984; Trendafelov et al. 1995a, 1995b; Christov 1996a, 1998, 1999, 2001, 2002a, 2002b, 2003a, 2003b, 2003c, 2004, 2005; Christov et al. 1998; Ojkova et al. 1999; Park et al. 2009; Kolev et al. 2013; Lach et al. 2018; Guignot et al. 2019; Donchev and Christov 2020; Lassin et al. 2020; Donchev et al. 2021; Tsenov et al. 2021), and from 0 to 290 °C (Petrenko and Pitzer 1997; Christov and Moller 2004ab; Moller et al. 2006, 2007; Lassin et al. 2015; Christov 1995, 1996b, 2005, 2007, 2009, 2012, 2020).

A long term safety assessment of a repository for radioactive waste requires evidence, that all relevant processes are known and understood, which might have a significant positive or negative impact on its safety. It has to be demonstrated, that the initiated chemical reactions don't lead to an un-due release of radionuclides into the environmental geo-, hydro-, and bio-sphere. One key parameter to assess the propagation of a radionuclide is its solubility in solutions interacting with the waste. Solubility estimations can either be based on experimental data determined at conditions close to those in the repository or on thermodynamic calculations. A so called "thermodynamic database" created from experimental data is the basis for thermodynamic model calculations. Since the disposal of radioactive waste is a task encompassing decades, the database is projected to operate on a long-term basis. Chemical models that predict equilibrium involving mineral, gas and aqueous phases over a broad range of solution compositions and temperatures are useful for studying the interactions between used nuclear fuel waste and its surroundings. The reliability of such predictions depends largely on the thermodynamic database. Waters of high salinity are not a typical of many geochemical environments which may be chosen as future nuclear waste repository sites. This suggests that an accurate description of highly saline waters should be required for modeling of chemical interactions in and around nuclear repositories. Currently, the most accurate description of saline waters uses the Pitzer ion interaction model. Extensive thermodynamic databases, which are based on the Pitzer ion interaction model was developed within the Yucca Mountain Project (YMTDB: data0.ypf.r2) (Sandia National Laboratories 2007), and Thereda project (THermodynamic REference DAtabase, THEREDA-Final Report) (Altmaier et al. 2011). Unfortunately,

many of introduced in YMTDB and in THEREDA databases Pitzer models are concentration restricted and cannot describe correctly the solid-liquid equilibrium in geochemical and industrial systems of interest for nuclear waste programs.

Nitrates are expected to play a significant role in the context of the underground geochemical repository of nuclear waste (Lach et al. 2018; Guignot et al. 2019; Donchev and Christov 2020; Lassin et al. 2020). More precisely, long-lived, intermediate-level radioactive wastes that are planned to be stored in deep clay formations are composed of dried sludge from effluent treatments that contain significant quantities of nitrate amongst other elements. They are enclosed in specific containers which are placed in underground cavities dug in a very low-permeable argillite host rock. "The storage safety analyses show that, despite the protection of the concrete or stainless steel-made external layers of the containers, the formation water of the host rock is likely to migrate and reach the waste during the disposal period" (Donchev and Christov 2020; Lassin et al. 2020). This would result in the potential dissolution of large amounts of nitrate and other elements, resulting in a highly saline, corrosive and oxidative media with a high reactivity towards the containment materials and their surroundings, including the host rock. Several options for the management of radioactive waste involve their preliminary leaching using nitric acid or nitrate salts to recover U and Pu, followed by the incorporation of the leaching residues into concrete or metal packages, which are then stored underground. For safety analysis purpose, the scenarios envisaged for these options assume that formation water returns to the storage compartments sometime after the end of the operating period Dossier ANDRA (2005). With a natural pH value slightly above 7 in clayey formations, pore water has to flow through basic concrete materials before being in contact with the acidic nuclear waste. A large range of pH leading to various chemical behaviors can thus be expected in the vicinity of the waste. At near-neutral to basic pH values, reactions of hydrolysis, complexation, and formation of solid phases can take place and control the fate of radionuclides (Wang et al. 2006; Lassin et al. 2020). Therefore, this reactivity must be characterized by development of not concentration restricted thermodynamic models, which accurately describe not only solution behavior at low molality, but also low and high molality solid-liquid phase equilibrium in nitrate systems (Donchev and Christov 2020). The experimental data presented in Rard et al. (1977, 2004), Rard and Spedding (1981), Maliutin et al. (2020), El Guendouzi and Marouani (2003), and accurate models reported in previous studies (Wang et al. 2006; Lach et al. 2018; Guignot et al. 2019; Donchev and Christov 2020; Lassin et al. 2020), and in the present work is a step towards this objective. It should be noted that THEREDA (Altmaier et al. 2011) do not include models for nitrate solutions and solids. The models introduced in YMTDB (Sandia National Laboratories 2007), including these for NO_3-systems are restricted up to 6 mol.kg^{-1}.

In our previous study (Donchev and Christov 2020) we reported very well validated accurate thermodynamic models based on Pitzer ion interactions approach for 7 nitrate binary systems of the type 1–1 (HNO_3-H_2O, $LiNO_3$-H_2O, $NaNO_3$-H_2O, KNO_3-H_2O, $RbNO_3$-H_2O, $CsNO_3$-H_2O, and NH_4NO_3-H_2O) from low to very high concentration at 25 °C. In this study we developed very well validated not concentration restricted thermodynamic models for solution behavior and solid-liquid equi-

librium in 10 nitrate binary systems of the type 2–1 ($Mg(NO_3)_2$-H_2O, $Ca(NO_3)_2$-H_2O, $Ba(NO_3)_2$-H_2O, $Sr(NO_3)_2$-H_2O, and $UO_2(NO_3)_2$-H_2O), 3–1 ($Cr(NO_3)_3$-H_2O, $Al(NO_3)_3$-H_2O, $La(NO_3)_3$-H_2O, $Lu(NO_3)_3$-H_2O), and 4–1 ($Th(NO_3)_4$-H_2O) from low to very high concentration at 25 °C. Models are developed on the basis of Pitzer ion interactions approach. The models for nitrate systems described in this study are of high importance, especially in development of strategies and programs for nuclear waste geochemical storage. These models are also of interest for industrial application, such as production and purification of nitrate compounds.

Methodology

The models for nitrate binary systems have been developed on the basis of Pitzer's semi-empirical equations (Pitzer 1973, 1991). Since the Pitzer's representation of the aqueous phase is based on the excess free energy, all the activity expressions are consistent, allowing different kinds of data (e.g., osmotic, emf, and solubility measurements) to be used in the parameter evaluations and other thermodynamic functions to be calculated (Christov and Moller 2004a, Christov and Moller 2004b; Christov 2007, 2009, 2012). Pitzer approach has found extensive use in the modeling of the thermodynamic properties of aqueous electrolyte solutions. Several extensive parameter databases have been reported. These include: 25 °C database of Pitzer and Mayorga (1973, 1974) (summarized also in Pitzer 1991); of Kim and Frederick (1988); YMTDB (Sandia National Laboratories 2007), and THEREDA (Altmaier et al. 2011). However, some of the models in all of these databases are concentration restricted, and do not include all minerals precipitating from saturated and supersaturated binary and mixed systems. The most widely used are databases of Chemical Modelling Group at UCSD (University California San Diego): at 25 °C (Harvie et al. 1984; Park et al. 2009), and T-variation (from 0 to 300 °C) (Christov and Moller 2004a, Christov and Moller 2004b; Moller et al. 2006, 2007; Christov 2009). Some of comprehensive minerals solubilitiy YMTDB (Sandia National Laboratories 2007), and THEREDA (Altmaier et al. 2011) databases also contain concentration restricted models for some low-, or high- concentration binary and mixed sub-systems with strong association reactions in unsaturated solutions. The concentration restricted sub-models are developed using experimental activity data in binary solutions, and solubility data in binary and high order systems up to maximum concentration (m(max)), which is much lower than concentration of saturated or supersaturated binary and mixed solutions (m(sat)). Such a restricted models predict minerals solubility, which is in pure agreement with experimental data.

The Pitzer's equations

According to Pitzer theory electrolytes are completely dissociated and in the solution there are only ions interacting with one to another (Pitzer 1973; Pitzer and Mayorga 1973). Two kinds of interactions are observed: (i) specific Coulomb interaction be-

tween distant ions of different signs, and (ii) nonspecific short-range interaction between two and three ions. The first kind of interaction is described by an equation of the type of the Debye-Hueckel equations. Short-range interactions in a binary system (MX(aq)) are determined by Pitzer using the binary parameters of ionic interactions ($\beta^{(0)}$,$\beta^{(1)}$, C^{φ}, and $\beta^{(2)}$). The Pitzer's equations (1 to 4) are described and widely discussed in the literature (Harvie et al. 1984; Moller et al. 2006, 2007; Christov and Moller 2004a, Christov and Moller 2004b; Christov 2005). Here only the expression for the activity coefficient of the interaction of cation (M) with other solutes, $\gamma_{(M^+)}$ is given:

$$\ln \gamma_M = z_M^2 F + \sum_a m_a \left(2B_{Ma}(I) + ZC_{Ma}\right) + \sum_c m_c \left(2\Phi_{Mc} + \sum_a m_a \psi_{Mca}\right) + \sum_a \sum_{a<a'} m_a m_a \psi_{Mka'} + |z_M| \sum_c \sum_a m_c m_a C_{ca}$$
$$+ \sum_n m_n \left(2\lambda_{nM}\right) + \sum_n \sum_a m_n m_a \zeta_{naM} \quad (1)$$

Equation (1) is symmetric for anions. The subscripts c and a in eqn 1 refer to cations and anions, and *m* is their molality; z is the charge of the M^+ ion. B and Φ represent measurable combinations of the second virial coefficients; C and ψ represent measurable combinations of third virial coefficients. B and C are parameterized from single electrolyte data, and Φ and ψ are parameterized from mixed solution data. The function F is the sum of the Debye-Hueckel term,

$$-A^{\varphi} [\sqrt{I} / (1 + b\sqrt{I}) + (2/b) (\ln(1 + b\sqrt{I})], \quad (2)$$

and terms with the derivatives of the second virial coefficients with respect to ionic strength (see Harvie et al. 1984). In Eq. (2), b is a universal empirical constant assigned to be equal to 1.2. A^{φ} (Debye-Hückel limiting law slope for the osmotic coefficient) is a function of temperature, density and the dielectric constant of water (Christov and Moller 2004b).

For the interaction of any cation M and any anion X in a binary system MX-H_2O, Pitzer assumes that in Eq. (1) B has the ionic strength dependent form:

$$B_{MX} = \beta^{(o)}_{MX} + \beta^{(1)}_{MX}\, g(\alpha_1\sqrt{I}) + \quad (3)$$

$$+\beta^{(2)}_{MX}\, g(\alpha_2\sqrt{I}), \quad (3A)$$

where $g(x) = 2[1 - (1 + x)e^{-x}] / x^2$ with $x = \alpha_1\sqrt{I}$ or $\alpha_2\sqrt{I}$. α terms are function of electrolyte type and does not vary with concentration or temperature.

In Eq. 1, the Φ terms account for interactions between two ions i and j of like charges. In the expression for Φ,

$$\Phi_{ij} = \theta_{ij} + {}^{E}\theta_{ij}\,(I), \quad (4)$$

θ_{ij} is the only adjustable parameter. The ${}^{E}\theta_{ij}$ (I) term accounts for electrostatic unsymmetric mixing effects that depend only on the charges of ions i and j and the total ionic

strength. The ψ_{ijk} parameters are used for each triple ion interaction where the ions are not all of the same sign. Their inclusion is generally important for describing solubilities in concentrated multicomponent systems. Therefore, according to the basic Pitzer equations, at constant temperature and pressure, the solution model parameters to be evaluated are: 1) pure electrolyte $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} for each cation-anion pair; 2) mixing θ for each unlike cation-cation or anion-anion pair; 3) mixing ψ for each triple ion interaction where the ions are all not of the same sign.

Fluids commonly encountered in natural systems include dissolved neutral species (such as carbon dioxide ($CO_{2(aq)}$, $SiO_{2(aq)}$, and $Al(OH)_3^{\circ}(aq)$). To account neutral specie interactions in aqueous solutions the UCSD Chemical Modelling Group included in their models additional terms to Pitzer equations, denoted as $\lambda_{N,X}$ or $\lambda_{N,A}$, and $\zeta_{N, A,X.}$ (Eq. (1)) (Harvie et al. 1984; Moller et al. 2006, 2007).

The $\beta^{(2)}$ parameter (Eqn. 3A) for 2–2 type of electrolytes

Pitzer and Mayorga (1973) did not present analysis for any 2–2 (e.g. $MgSO_4$-H_2O) or higher {e.g. 3–2: $Al_2(SO_4)_3$-H_2O} electrolytes. Indeed, they found that three $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} parameters approach (see Eqns. 1 and 3) could not accurately fit the activity data for these types of solutions. For these electrolytes mean activity ($\gamma_{\pm}$) and osmotic (φ) coefficients drop very sharply in dilute solutions, while showing a very gradual increase, with a very wide minimum at intermediate concentration. Pitzer concluded that this behaviour is due to ion association reactions and that the standard approach with three evaluated solution parameters cannot reproduce this behaviour. This lead to a further (Pitzer and Mayorga 1974) modification to the original equations for the description of binary solutions: parameter $\beta^2(M,X)$, and an associated $\alpha_2\sqrt{I}$ term are added to the B_{MX} expression (see Eqn. (3A). Pitzer presented these parameterizations assuming that the form of the functions (i.e. 3 or 4 β and C^{φ} values, as well as the values of the α terms) vary with electrolyte type. For binary electrolyte solutions in which either the cationic or anionic species are univalent (e.g. NaCl, Na_2SO_4, or $MgCl_2$), the standard Pitzer approach use 3 parameters (i.e. omit the $\beta^{(2)}$ term) and α_1 is equal to 2.0. For 2–2 type of electrolytes the model includes the $\beta^{(2)}$ parameter and α_1 equals to 1.4 and α_2 equals to 12. This approach provides accurate models for many 2–2 binary sulfate (Pitzer and Mayorga 1974; Christov 1999, 2003a) and selenate (Christov 2003a; Christov et al. 1998) electrolytes, giving excellent representation of activity data covering the entire concentration range from low molality up to saturation and beyond.

Inclusion of "standard Pitzer approach" $\beta^{(2)}$ parameter into a models for 1–1, 2–1, 3–1, 4–1, 1–2, 1–3, and 3–2 type of electrolytes

Some authors found that there are some restrictions limited the potential of the model to describe correctly activity and solubility properties in some binary electrolyte systems with minimum one univalent ion (see Petrenko and Pitzer 1997, 2012; Gruszkiewicz and Simonson 2005; Lach et al. 2018; Guignot et al. 2019; Lassin et al. 2020),

and of 3–2 type (see Christov, 2002ab, 2003b) at very high molality using classical 3 parameters ($\beta^{(0)}$, $\beta^{(1)}$, and C^{φ}) approach. According to discussion in Christov (2004, 2005, 2012) and in Lassin et al. (2015), there is one major factor which determined these restrictions: type of φ (osmotic coefficient) vs. m, or $\gamma_{\pm}$ (activity coefficient) vs. m dependences at high concentration. For all these systems φ vs. m, or $\gamma_{\pm}$ vs. m curves have a wide maximum at molality approaching molality of saturation: "LiCl(aq) type": see Lassin et al. (2015), "$FeCl_2$(aq) and $FeCl_3$(aq) type": see Christov (2003c, 2004); "HNO_3(aq) type": see Donchev and Christov (2020);"$Al_2(SO_4)_3$(aq), $Cr_2(SO_4)_3$(aq) type": see Christov (2002a, 2002b, 2003b).

To describe the high concentration solution behaviour of systems showing a "smooth" maximum on $\gamma_{\pm}$ vs. m dependence, and to account strong association reactions at high molality, Christov (1996a, 1998, 1999, 2001, 2005) used a very simple modelling technology: introducing into a model a fourth ion interaction parameter from basic Pitzer theory {$\beta^{(2)}$ in Eqn. (3A)}, and varying the values of α_1 and α_2 terms in Eqs. (3 and 3A))). The author also found that by variation of the values of α_1 and α_2 terms it is possible to vary the concentration range of binary solutions at which association reactions become more important and should be account by introducing $\beta^{(2)}$ parameter. According to Christov (2005), model which uses α_1 = 1.4 and α_2 = 12 accounts association only at low molality solutions (see also Christov and Moller (2004b) for $Ca(OH)_2$-H_2O model). According to previous studies of one of the authors (Christov) an approach with 4 ion interaction parameters ($\beta^{(0)}$,$\beta^{(1)}$, $\beta^{(2)}$,and C^{φ}), and accepting α_1 = 2, and varying in α_2 values can be used for solutions for which ion association occurs in high molality region. This approach was used for binary electrolyte systems of different type: 1–1 type {such as HNO_3-H_2O, $LiNO_3$-H_2O (Donchev and Christov 2020), CsF -H_2O (Tsenov et al. 2021), and LiCl-H_2O (Lassin et al. 2015)}, 2–1 {such as $NiCl_2$-H_2O, $CuCl_2$-H_2O, $MnCl_2$-H_2O, $CoCl_2$-H_2O: (Christov 1996a, 1999); $FeCl_2$-H_2O: (Christov 2004); $Ca(NO_3)_2$-H_2O: (Lach et al. 2018); $UO_2(NO_3)_2$-H2O (Lassin et al. 2020)}, 1–2 {such as $Na_2Cr_2O_7$-H_2O: (Christov 2001); $K_2Cr_2O_7$-H_2O: (Christov 1998)}, 3–1 {such as $FeCl_3$-H_2O: (Christov 2004); $Ln(NO_3)_3$(aq): (Guignot et al. 2019)}, and 3–2 {such as $Al_2(SO_4)_3$-H_2O, $Cr_2(SO_4)_3$-H_2O, and $Fe_2(SO_4)_3$-H_2O: (Christov 2001, 2002a, 2003b, 2004, 2005)}. The resulting models reduce the sigma values of fit of experimental activity data, and extend the application range of models for binary systems to the highest molality, close or equal to molality of saturation {m(sat)}, and in case of data availability: up to supersaturation. For example, aqueous complexes free 4 parameters model for LiCl-H_2O system predicts LiCl.nH2O(s) solubilities from 0 to 200°C and up to 40 mol.kg^{-1} (Lassin et al. 2015). The resulting accurate 4 - parameters solution models are used directly to determine $\ln K^{\circ}_{sp}$ values of precipitated solid phases using solubility approach (Harvie et al. 1984; Christov 1995, Christov 1996a, Christov 1996b, Christov 2005, Christov 2012; Christov and Moller 2004a, Christov and Moller 2004b). Therefore, the developed not high molality restricted parameterization, were used without any changes for development of solid-liquid equilibrium models for high order systems. Thus, models for $Al_2(SO_4)_3$(aq) and $Cr_2(SO_4)_3$(aq) are used without additional adjustments to construct a model for multi-

component ($Na+K+NH_4+Mg+Al+Cr+SO_4+H_2O$) system (Christov, 2002ab, 2003b). Four parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^{φ}) models for $NiCl_2$(aq), $CuCl_2$(aq), $MnCl_2$(aq), and $CoCl_2$(aq) are used for construction of Na-K-Rb-Cs-Ni-Co-Cu-Mn-Cl-H_2O model (Christov 1996a, 1999). Four parameters models for $FeCl_2$(aq)and $FeCl_3$(aq) are directly used in development of high accuracy minerals solubility model for ($Na+K+Mg+Fe(II)+Fe(III)+Cl+SO_4+H_2O$) system (Christov 2004). A model for binary systems $Na_2Cr_2O_7$(aq), $K_2Cr_2O_7$(aq) was used without any changes to develop a comprehensive model for: ($Na+K+Cl+SO_4+Cr_2O_7+H_2O$) system (Christov 1998, 2001), and $Ca(OH)_2$(aq) model is used as s strong base for $H+Na+K+Ca+OH+Cl+SO_4+H_2O$ model from from 0 to 300°C (Christov and Moller, 2004b).

Results and discussions

Model parameterization and validation of models for binary 2–1, 3–1, and 4–1 type nitrate systems

In this study we developed new thermodynamic models for solution behavior and solid-liquid equilibrium in 10 nitrate binary systems of the type 2–1 ($Mg(NO_3)_2$-H_2O, $Ca(NO_3)_2$-H_2O, $Ba(NO_3)_2$-H_2O, $Sr(NO_3)_2$-H_2O, and $UO_2(NO_3)_2$-H_2O), 3–1 ($Cr(NO_3)_3$-H_2O, $Al(NO_3)_3$-H_2O, $La(NO_3)_3$-H_2O, $Lu(NO_3)_3$-H_2O), and 4–1 ($Th(NO_3)_4$-H_2O) from low to very high concentration at 298.15 K. New sets of Pitzer ion interaction binary parameters are evaluated using available raw experimental osmotic coefficients (φ) data for whole molality range of solutions. Rard and co-authors (1977, 1981) reported an extensive experimental activity database for rare earth nitrate systems. Data of Rard and Spedding (1981) are used to parametrize the model for $Lu(NO_3)_3$-H_2O system. The φ vs. m data for remaining 9 nitrate solutions under study are given in Mikulin (1968), and Robinson and Stokes (1959). Reference φ vs. m data sets of Mikulin (1968), and Robinson and Stokes (1959) are in a good agreement. Data of Mikulin (1968) for $La(NO_3)_3$-H_2O are also in good agreement with the data of Rard (1987). However, the data of Mikulin (1968) cover the whole molality range of unsaturated and saturated solutions. In case of $Ca(NO_3)_2$-H_2O, $UO_2(NO_3)_2$-H_2O, and $Th(NO_3)_4$-H_2O systems, Mikulin also reported data for supersaturated solutions. In this study we parameterize the models using 1) all data of Mikulin (1968) for whole molalty range of unsaturated solutions from 0.1 m to m(max), 2) the data points at saturation (φ(sat)) (from Mikulin 1968), and 3) data for supersaturated $Ca(NO_3)_2$-H_2O, $UO_2(NO_3)_2$-H_2O, and $Th(NO_3)_4$-H_2O solutions (from Mikulin 1968), and 4) all experimental and recommended data of Rard and Spedding (1981) for $Lu(NO_3)_3$-H_2O system.

In parameterization we used the value of Debye-Hückel term (A^{φ}) equals to 0.39147 (Christov 2007, 2009, 2012). Following the parameterization scheme described in previous paragraph the model for all 10 binary nitrate solutions is parameterized using two different approaches: (I) standard for N-1 electrolytes (N = 2, 3, 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 α_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) α_1 = 2 and α_2 = 1, and (IIb) α_1 = 2 and α_2 = -1 (Christov 1996a, 1998, 1999, 2004, 2005) and (IIc) α_1 = 2 and α_2 = 0.3 (Guignot et al. 2019; Donchev and Christov 2020; Donchev et al. 2021). 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. For definition of sigma (σ) see Christov and Moller (2004b), and Christov (2007, 2009, 2012). It was found that for 2 of studied systems $Ba(NO_3)_2$-H_2O, and $Sr(NO_3)_2$-H_2O, 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: for $Lu(NO_3)_3$-H_2O system. 1) α_1 = 2 and α_2 = 0.3 (approach IIc), and 2) α_1 = 2 and α_2 = 1 (approach IIa), and 3) α_1 = 2 and α_2 = -1 (approach IIb). The resulting models fits the data up to supersaturation zone (m(max) = 14.77 m in $Ca(NO_3)_2$-H_2O) with sigma values, which is much less than the sigma values of models of Pitzer and Mayorga (1973), and of Kim and Frederick (1988).

On next Figure 1 we present a comparison of osmotic coefficients in nitrate binary solutions 2–1 ($Mg(NO_3)_2$-H_2O, $Ca(NO_3)_2$-H_2O, $Ba(NO_3)_2$-H_2O, $Sr(NO_3)_2$-H_2O, and $UO_2(NO_3)_2$-H_2O), 3–1 ($Cr(NO_3)_3$-H_2O, $Al(NO_3)_3$-H_2O, $La(NO_3)_3$-H_2O, $Lu(NO_3)_3$-H_2O), and 4–1 ($Th(NO_3)_4$-H_2O) calculated by the accepted models developed here (heavy solid lines), and models developed by other authors (dashed lines and light solid lines: Pitzer and Mayorga (1973), Kim and Frederick (1988), Rard and Spedding (1981) (for $Lu(NO_3)_3$-H_2O system only), Rard et al. (2004) (for $Mg(NO_3)_2$-H_2O system only), and Wijesinghe and Rard (2005) (for $Ca(NO_3)_2$-H_2O system only). The recommended osmotic coefficients values given in literature at 25 °C are given on Fig. 1 by symbols. The vertical lines on the figures denote the molality of solutions saturated with corresponding nitrate solid phase (m(sat)), taken from Mikulin (1968). Excellent accepted new model (heavy solid line) – experiment (symbols) agreement has been obtained for all 10 systems and from low (see figures for $Mg(NO_3)_2$-H_2O, $Ca(NO_3)_2$-H_2O systems) and up to very high molality. As is shown Fig. 1, the new model for $Ca(NO_3)_2$-H_2O is in excellent agreement not only with the data at high molality ((m(max) = 14.77 m), but contrary to the models of Kim and Frederick (1988) and Wijesinghe and Rard (2005) also in low molality range. It should be noted that all reference models presented on Fig. 1 by dashed, dashed-dotted, and light solid lines (Kim and Frederick (1988), Pitzer and Mayorga (1973), Rard et al. (2004), Wijesinghe and Rard (2005), and Rard and Spedding (1981)) have been constructed on the basis of standard Pitzer approach with 3 interaction parameters. Therefore, these models

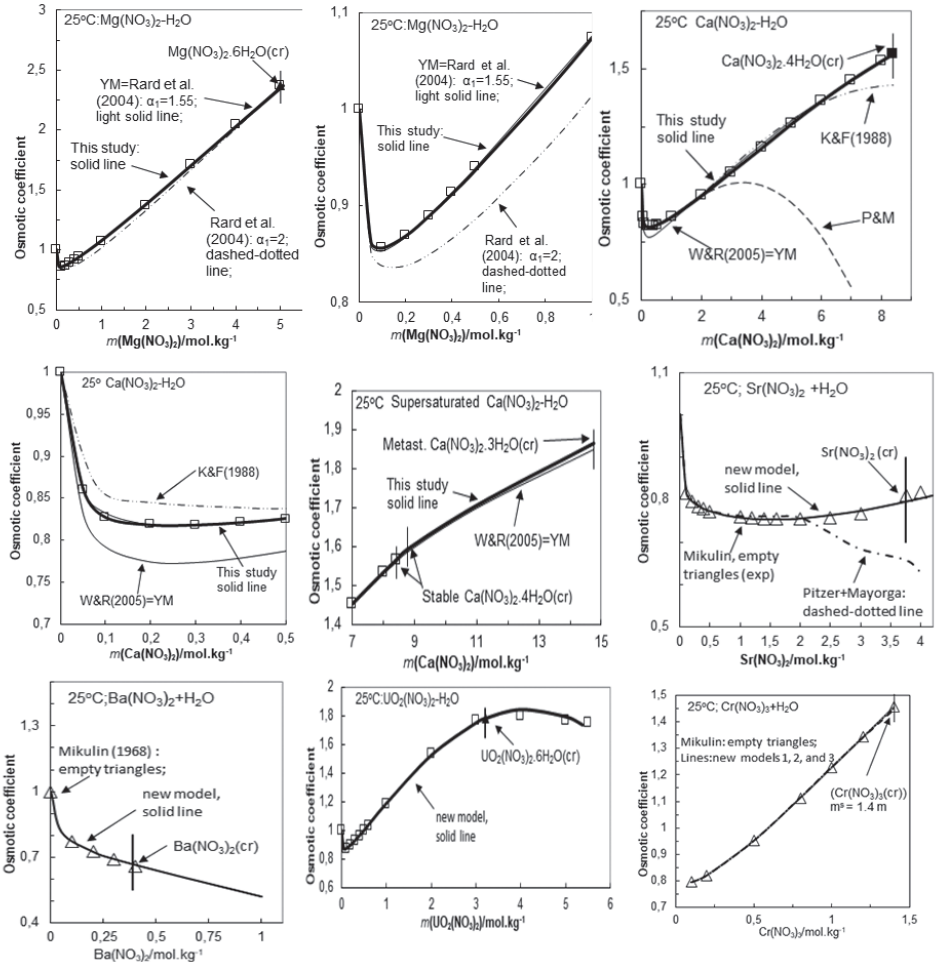

Figure 1. Comparison of model calculated (lines) osmotic coefficients (φ) of $Mg(NO_3)_2$ $Ca(NO_3)_2$, $Ba(NO_3)_2$, $Sr(NO_3)_2$, $UO_2(NO_3)_2$, $Cr(NO_3)_3$, $Al(NO_3)_3$, $La(NO_3)_3$, $Lu(NO_3)_3$, and $Th(NO_3)_4$ in binary solutions 2–1 ($Mg(NO_3)_2$-H_2O, $Ca(NO_3)_2$-H_2O, $Ba(NO_3)_2$-H_2O, $Sr(NO_3)_2$-H_2O, and $UO_2(NO_3)_2$-H_2O), 3–1 ($Cr(NO_3)_3$-H_2O, $Al(NO_3)_3$-H_2O, $La(NO_3)_3$-H_2O, $Lu(NO_3)_3$-H_2O), and 4–1 ($Th(NO_3)_4$-H_2O) against molality at T = 298.15 K, with recommendations in literature (symbols). For $Mg(NO_3)_2$-H_2O and $Ca(NO_3)_2$-H_2O systems an enlargement of the low molality corner is also given. Heavy solid lines represent the predictions of the developed in this study and accepted models. Dashed-dotted, dashed and light solid lines represent the predictions of the reference models of Kim and Frederick (1988), of Pitzer and Mayorga (1973), of Rard et al. 2004 (for $Mg(NO_3)_2$-H_2O), of Wijesinghe and Rard (2005) (for $Ca(NO_3)_2$-H_2O), and of Rard and Spedding (1981) (for $Lu(NO_3)_3$-H_2O). On Figures YM denotes YMTDB (Sandia National Laboratories 2007). For $Lu(NO_3)_3$-H_2O the experimental data and recommended data are taken from Rard et al. (1977) (open squares), and Rard and Spedding (1981) (crosses), respectively. For all other systems the experimental data of Mikulin (1968) are used (open squares and open triangles). The molality of stable and metastable (for $Ca(NO_3)_2$-H_2O) crystallization of solid nitrate phases (m(sat)) is given on all figures by vertical lines (see Table 1).

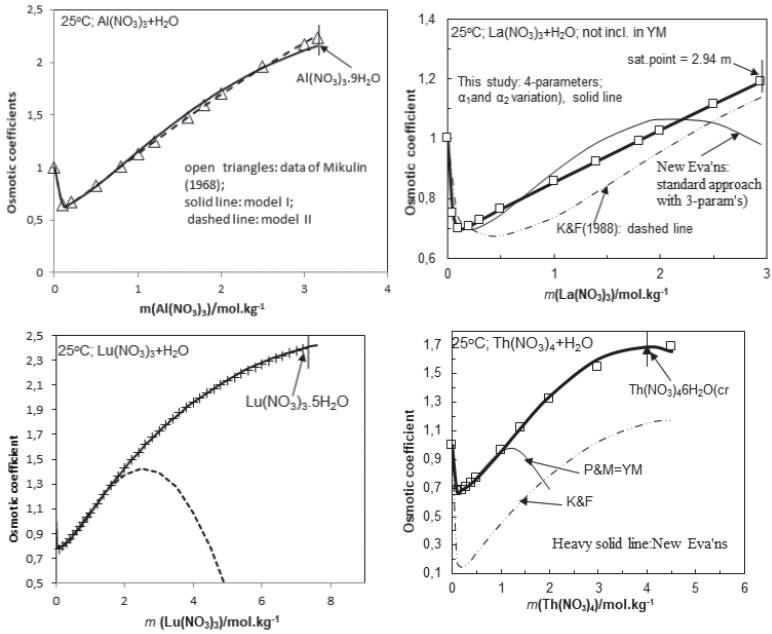

Figure 1. Continue.

cannot reproduce well the experimental data (Fig. 1). To illustrate this conclusion on Fig. 1 we give the predictions of two new models for $La(NO_3)_3$-H_2O system. As it is shown the 3 parameters model (light solid line) is in pure agreement with the data.

The models for all nitrate binary systems under study are also validated by comparison with recommendations given in literature (Rard and Spedding (1981) for $Lu(NO_3)_3$-H_2O); and Mikulin (1968)) (for all other 9 systems under study) on the mean activity coefficients ($\gamma_{\pm}$). These recommendations on $\gamma_{\pm}$ are model-dependent. Therefore, they are not used in parameterization process, and only to validate the resulting models. The comparisons between predictions of new developed models and reference recommendations, which are not given here, show an excellent agreement from low to very high concentrations.

Deliquescence relative humidity (DRH) calculations

Deliquescence of single inorganic salt or their mixture is a process of spontaneous solid-liquid phase change. It is a process in which a soluble solid substance sorbs water vapor from the air to form a thermodynamically stable saturated aqueous solution on the surface of the particle. It is occurring when relative humidity (RH) in the gas-phase environment is at, or above deliquescence relative humidity (DRH) of the salt, or mutual deliquescence relative humidity (MDRH) of a salt mixture. Within the solid-

liquid equilibrium model, relative humidity is related to water activity(a_w) (Clegg et al. 1998; Christov 2009, 2012; Donchev and Christov 2020) according to Eqn. (5):

$$a_w = P_w / P^\circ_w = RH/100, \quad (5)$$

where P_w and P°_w are the vapor pressure of the saturation solution and pure water, respectively, at given temperature. As a result, both DRH and MDRH of saturated surface solutions depend of temperature, the salt stoichiometry, and the solution composition. This process is of interest in many areas, such as heterogeneous chemistry of inorganic salts, corrosion of metals in wet atmosphere, in studies of chemistry of sea-type aerosol atmospheric system (Kolev et al. 2013), and especially in development of strategies and programs for nuclear waste geochemical storage. Because of very high complicity of experiments, the relative humidity DRH experimental data are sparse. Therefore, different sophisticated thermodynamic models have been proposed and developed to describe the deliquescence behavior of inorganic salts at wet conditions. In our previous studies it was showed that calculations based on not high concentration restricted Pitzer models can be used for accurate determinations of both DRH and MDRH of saturated solutions in a wide range of temperatures, and compositions (Christov 2009, 2012; Donchev and Christov 2020). On the basis of evaluated binary parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$,and C^φ) in this study we also determine water activity (a_w) and Deliquescence Relative Humidity (DRH (%)) (eqn. 5) of 12 solid phases crystallizing from saturated binary nitrate solutions [$Mg(NO_3)_2.6H_2O$(s), $Ca(NO_3)_2.4H_2O$(s), $Ca(NO_3)_2.3H_2O$(s), $Ba(NO_3)_2$(s), $Sr(NO_3)_2$(s), $UO_2(NO_3)_2.6H_2O$(s), $Al(NO_3)_3.9H_2O$(s), $Cr(NO_3)_3$(s), $La(NO_3)_3.6H_2O$(s), $La(NO_3)_3$(s) $Lu(NO_3)_3.5H_2O$(s) and $Th(NO_3)_4.6H_2O$(s)]. Note that the widely used databases of Pitzer (1991), Pitzer and Mayorga (1973), Pitzer and Kim (1974) and Kim and Frederick (1988) do not consider solid phases. The results of calculations are given in Table 1. The model DRH predictions are in excellent agreement with the experimental data determined using isopiestic method, and given in Mikulin (1968). According to model calculations the solid-liquid phase change of $Ca(NO_3)_2.3H_2O$(s), and $Lu(NO_3)_3.5H_2O$(s) occurs at lowest relative humidity of environment. It can be concluded that the solid-liquid phase change of solid nitrates of Lanthanide metals is more activated in the presence of calcium in the nuclear storage environment.

Determination of thermodynamic solubility product (K°_{sp}) of precipitates

In this study we determine the thermodynamic solubility products (as K°_{sp}) of solid phases, precipitating from saturated nitrate binary solutions, s.a. anhydrous $Ba(NO_3)_2$(s) and hydrate $Ca(NO_3)_2.3H_2O$(s), precipitating in $Ba(NO_3)_2$-H_2O and $Ca(NO_3)_2$-H_2O. The K°_{sp} have been determined on the basis of evaluated binary parameters and using experimental m(sat) solubility data, and using the following relationships (Christov 2005, 2007, 2009, 2012):

$$K^\circ sp\,(Ba(NO_3)_2) = 4 \cdot \gamma_{(\pm)}(sat)^3 \cdot m(sat)^3$$
$$K^\circ sp(Ca(NO_3)_2.3H_2O) = 4 \cdot \gamma_{(\pm)}(sat)^3 \cdot m(sat)^3 \cdot a_w(sat)^3 \quad (6)$$

Table 1. Comparison between model calculated and recommended values of the Deliquescence Relative Humidity [DRH (%) = a_w(sat) . 100; where a_w(sat) is activity of water at saturation] and of the logarithm of the thermodynamic solubility product (as $\ln K°_{sp}$) of nitrate solid phases crystallizing from saturated binary solutions at T = 25° C.

Salt composition	*m*(sat) (exp) (*mol.kg*$^{-1}$)	$\ln K°_{sp}$		DRH(%)	
		This work calculated	Reference data	This work calculated	Reference data[a]
$Mg(NO_3)_2.6H_2O$(cr)	5.06[a]	7.0098	7.02[b]	52.32	52.90
$Ca(NO_3)_2.4H_2O$(cr) (stable solid)	8.41[a]	4.4362	4.53[b]	49.07	49.10
$Ca(NO_3)_2.3H_2O$(cr) (metastable solid)	14.77[a]	6.6449	5.34[b] (m(sat) = 15.0 m)	22.52	-
$Ba(NO_3)_2$(cr)	0.39[a]	-5.125	-	98.61	98.60
$Sr(NO_3)_2.4H_2O$ (cr)	3.76[a]	0.0327	-	84.83	84.80
$UO_2(NO_3)_2.6H_2O$(cr)	3.21[a]	5.3022	5.251[c]	73.44	73.60
$Al(NO_3)_3.9H_2O$ (cr)	3.16[a]	4.3081	-	59.88	60.20
$Cr(NO_3)_3$ (cr)[e]	1.4[e]	1.2097	-	86.38	-
$La(NO_3)_3.6H_2O$ (cr)[d]	4.615[d]	2.1599	2.97[d]	62.38	-
$La(NO_3)_3$ (cr)[a]	2.94[a]	1.4704	-	77.73	77.60
$Lu(NO_3)_3 5H_2O$ (cr)	6.815[d]	10.7681	10.67	31.27	-
$Th(NO_3)_4.6H_2O$(cr)	4.00[a]	4.4886	4.71[c] (as $Th(NO_3)_4.5H_2O$)	54.46	55.0

Experimental data of Mikulin (1968); [b]Calculated values of Lach et al. (2018) [c]Calculated values of Lassin et al. (2020); [d] Values from Guignot et al. (2019); [e] Accepted m(sat) molality and stoichiometry of solid phase.

As a next step, using the accepted new developed parameterizations, and experimentally determined molalities (m(sat) of the saturated binary solutions (Mikulin 1968; Guignot et al. 2019; Lassin et al. 2020)) we calculate the logarithm of the thermodynamic solubility product ($\ln K°_{sp}$) of twelve nitrate solid phases crystallizing from saturated binary nitrate solutions at 25 °C (Eqn. (6)). The model calculations are given in Table 1. With only 2 exceptions (for $Ca(NO_3)_2.3H_2O$(s) and $La(NO_3)_3.6H_2O$(s)) a good agreement has been obtained with calculations of Lach et al. (2018), Lassin et al. (2020), and Guignot et al. (2019) for all nitrate solids. The $\ln K°_{sp}$ differences are mainly due on the 1) different m(sat) values used in calculations (see Eqn. (6)), and 2) different experimental data source with different m(max) values used in parameterization.

Summary and conclusions

In this study we developed new thermodynamic models for solution behavior and solid-liquid equilibrium in 10 nitrate binary systems of the type 2–1 ($Mg(NO_3)_2$-H_2O, $Ca(NO_3)_2$-H_2O, $Ba(NO_3)_2$-H_2O, $Sr(NO_3)_2$-H_2O, and $UO_2(NO_3)_2$-H_2O), 3–1 ($Cr(NO_3)_3$-H_2O, $Al(NO_3)_3$-H_2O, $La(NO_3)_3$-H_2O, $Lu(NO_3)_3$-H_2O), and 4–1 ($Th(NO_3)_4$-H_2O) from low to very high concentration at 25 °C. To parameterize models for binary systems we used all available raw experimental osmotic coefficients data (φ) for whole concentration range of solutions, and up to saturation point. Data for supersaturation zone, available for $Ca(NO_3)_2$-H_2O, $UO_2(NO_3)_2$-H_2O, and $Th(NO_3)_4$-H_2O systems, are also included in parameterization. To construct models, we used different versions of standard molality-based Pitzer approach. It was established that with only 2 exceptions ($Ba(NO_3)_2$-H_2O, and $UO_2(NO_3)_2$-H_2O) application of extended approach

with 4 parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$,and C^{φ}) and variation of α_2 term in fundamental Pitzer equations leads to the lowest values of standard model-experiment deviation. The predictions of new developed here models are in excellent agreement with experimental osmotic coefficients data (see Fig. 1), and with recommendations on activity coefficients (not given here) in binary solutions from low to very high concentration: up to 14.77 mol. kg^{-1} in $Ca(NO_3)_2$-H_2O. The Deliquescence Relative Humidity (DRH), and thermodynamic solubility product (as ln K°_{sp}) of of 12 solid phases crystallizing from saturated binary nitrate solutions [$Mg(NO_3)_2.6H_2O(s)$, $Ca(NO_3)_2.4H_2O(s)$, $Ca(NO_3)_2.3H_2O(s)$, $Ba(NO_3)_2(s)$, $Sr(NO_3)_2(s)$, $UO_2(NO_3)_2.6H_2O(s)$, $Al(NO_3)_3.9H_2O(s)$, $Cr(NO_3)_3(s)$, $La(NO_3)_3.6H_2O(s)$, $La(NO_3)_3(s)$ $Lu(NO_3)_3.5H_2O(s)$ and $Th(NO_3)_4.6H_2O(s)$] have been determined on the basis of evaluated binary parameters and using experimental m(sat) solubility data. Model predictions are in good agreement with available reference data. The accurate solid-liquid equilibrium models for nitrate systems described in this study are of high importance for development of strategies and programs for nuclear waste geochemical storage.

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