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Development of Accurate Chemical Thermodynamic Database for Geochemical Storage of Nuclear Waste. Part I: Models for Predicting Solution Properties and Solid-Liquid Equilibrium in Binary Nitrate Systems of the Type 1-1

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Abstract. In this study we developed very well validated thermodynamic models for solution behavior and solid-liquid equilibrium in 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 T = 25°C. 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. Models are developed on the basis of Pitzer ion interactions approach. 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 $LiNO_3$-H_2O system, are also included in parameterization. To construct models we used different versions of standard molality-based Pitzer approach. It was established that for three of systems under study (HNO_3-H_2O, $LiNO_3$-H_2O, $RbNO_3$-H_2O) application of extended approach with 4 parameters (β^0, β^1, β^2 and C^φ) and variation of a_2 term in fundamental Pitzer equations leads to the lowest values of standard model-experiment deviation. The recommendations on mean activity coefficients ($g_\pm$) given in literature are model-dependent. Therefore, they are not used in parameterization process. However, these data are used to validate the resulting models. The predictions of new developed here models are in excellent agreement with experimental osmotic coefficients data, and with recommendations on activity in binary solutions from low to very high concentration: up to ≈ 29 $mol.kg^{-1}$ in HNO_3-H_2O, and up to 26.8 $mol.kg^{-1}$ in NH_4NO_3-H_2O. The Deliquescence Relative Humidity (DRH), and thermodynamic solubility product (as ln K^o_{sp}) of six solid phases [$LiNO_3.3H_2O(s)$, $NaNO_3(s)$, $KNO_3(s)$, $RbNO_3(s)$, $CsNO_3(s)$, and $NH_4NO_3(s)$] 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.

Key words: Computer chemical and geochemical modeling; Pitzer approach; Binary nitrate systems 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; Solution and solute activity; Solid-liquid phase equilibrium; Geochemical nuclear waste sequestration.

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Used symbols:

β^0, β^1, β^2 and C^φ – Pitzer binary parameters
Θ and Y- Pitzer mixing parameters
a_1 and a_2 - terms in fundamental Pitzer equations
φ - osmotic coefficient
$g_\pm$ - mean activity coefficient
a_w - activity of water
m(sat)- molality of saturated solutions (mol.kg^{-1})
m (max)= maximum molality (mol.kg^{-1}) of experimental activity data
σ = standard deviation of fit of osmotic coefficients
ln K^o_{sp} - logarithm of thermodynamic solubility product
DRH - Deliquescence Relative Humidity
$D_fG^o_m$-standard molar Gibbs free energy of formation
YMTDB- Yucca Mountain Thermodynamic DataBase
THEREDA –THErmodynamic REference DAtabase
UCSD - University California San Diego

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; Andre et al., 2019; Lach et al., 2018; Guignot et al., 2019; Park et al. 2009; Kolev et al., 2013; Lassin et al., 2020; Christov, 1996; 1999; 2000; 2001a; b; 2002a; b; 2003a; b; 2004; 2005; Christov et al., 2012), and from 0° to 290°C (Pabalan & Pitzer, 1987; Lassin et al., 2015; Christov & Moller, 2004a; b; Moller et al, 2006; 2007; Christov, 2007; 2009a; b; 2012a; b).

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 (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. 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. 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. 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. The models presented in our previous studies (Lach et al. 2018; Guignot et al. 2019; Lassin et al., 2020) and in the present work is a step towards this objective. It should be noted that Altmaier et al. (2011) do not include models for nitrate solutions and solids. The models introduced in Sandia National Laboratories (2007), including these for NO_3-systems are restricted up to 6 mol.kg^{-1}.

In this study we developed very well validated accurate thermodynamic models for solution behavior and solid-liquid equilibrium in 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 298.15 K. Models are developed on the basis of Pitzer ion interactions approach.

Material and Methods

FThe 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, 2007; 2009a; 2012b). 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 & Mayorga (1973; 1974) (summarized also in Pitzer, 1991); of Kim & Frederick (1988); Sandia National Laboratories (2007) and Altmaier et al. (2011).

The most widely used are databases of Chemical Modelling Group at UCSD (University California San Diego): at 25°C (Harvie et al., 1984), and T-variation (from 0° to 300°C) (Christov & Moller, 2004a; b; Moller et al., 2006; 2007; Christov, 2009a; b). 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. Some of comprehensive minerals solubilitiy 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 & Mayorga, 1973). Two kinds of interactions are observed: (i) specific Coulomb interaction between 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 & Moller, 2004a; 2004b).

Here only the expression for the activity coefficient of the interaction of cation (M) with other solutes, $\gamma_{(M^+)}$ is given:

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

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,

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

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 & Moller, 2004b).

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

$$B_{MX} = \beta^{(o)}_{MX} + \beta^{(1)}_{MX}\, g(\alpha_1\sqrt{I}) + \qquad (3)$$
$$+\beta^{(2)}_{MX}\, g(\alpha_2\sqrt{I}), \qquad (3A)$$

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,

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

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 $Al(OH)_3{}^{o}(aq)$). 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 & 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 β^0, β^1, and C^{φ} parameters approach (see Eqn. 1) 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 & 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 β^2 term) and α_1 is equal to 2.0. For 2-2 type of electrolytes the model includes the β^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 & Mayorga, 1974; Christov, 1999; 2000; 2003a) and selenate (Ojkova et al., 1998; Christov, 1997; 2003a; Barkov et al., 2001), 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 Gruszkiewicz & Simonson, 2005; Petrenko & Pitzer, 1997; Sterner et al., 1998; Christov, 1996; 1998; 1999; 2000; 2001a; 2004; 2005; Christov et al., 2012; Andre et al., 2019; Lach et al., 2018; Guignot et al., 2019; Lassin et al., 2020), and of 3-2 type (see Reardon, 1988; Christov, 2001; 2002a; b; 2003b) at very high molality using classical 3 parameters (β^0, β^1, and C^{φ}) approach. According to discussion in Christov (2012a), 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), "$CaCl_2(aq)$ type": see Sterner et al. (1998); "$FeCl_2(aq)$ and $FeCl_3(aq)$ type": see Andre et al. (2019), Christov (2004); "$Al_2(SO_4)_3(aq)$ and $Cr_2(SO_4)_3(aq)$ type": see Christov (2001; 2002a; b; 2003b). On next figures (Fig. 1ab) we give a comparison of reference model (Felmy et al., 1994 and Kim & Frederick, 1988a) calculated (lines) osmotic coefficients (φ) of HNO_3 and $LiNO_3$ in binary solutions HNO_3-H_2O (Fig. 1a) and $LiNO_3$-H_2O (Fig. 1b) against molality at T = 298.15 K with recommendations in literature (symbols) (Mikulin, 1968; Hammer &

Wu, 1972). The comparison given on Fig. 1 shows that the 3 parameters (β^0, β^1, and C^φ) model of Felmy et al. (1994) for HNO_3-H_2O (Fig. 1a), included in YMTDB, is in disagreement with the data at high molality. The model of Kim and Frederick (1988a) based on 3 parameters approach (Fig. 1b) is in a very pure agreement with the data at low molality for $LiNO_3$-H_2O solutions. According to the data (see symbols on Fig. 1a and on 3a) the φ vs. molality dependences for HNO_3-H_2O and $LiNO_3$-H_2O solutions have a wide maximum at very high molality.

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 (1996; 1999; 2000; 2005) used a very simple modelling technology: introducing into a model a fourth ion interaction parameter from basic Pitzer theory {$\beta^{(2)}$}, and varying the values of α_1 and α_2 terms. 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 Christov & 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 (Christov, 2005), 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, 1996; 1999; 2000); $FeCl_2$-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, 2001a); $K_2Cr_2O_7$-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, 2001b; 2002a; b; 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 $LiCl.nH_2O(s)$ solubilities from 0°C 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 $\ln K^o_{sp}$ values of precipitated solid phases using solubility approach (Harvie et al., 1984; Christov, 1996; 2012a; 2012b; Christov & Moller, 2004a; b). 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, 2001b, 2002a, 2002b, 2003b). Four parameters (β^0, β^1, β^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, 1996, 1999, 2000). 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; Andre et al., 2019). 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, 2001a), 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°C to 300°C (Christov and Moller, 2004b).

Determination of thermodynamic solubility product (K^o_{sp}) of precipitates

In this study we determine the thermodynamic solubility products (as K^o_{sp}) of solid phases, precipitating from saturated nitrate binary solutions (s.a. anhydrous $NaNO_3(s)$, and hydrate $LiNO_3.3H_2O(s)$ precipitating in $NaNO_3$-H_2O and $LiNO_3$-H_2O). The K^o_{sp} have been determined on the basis of evaluated binary parameters and using experimental m(sat) solubility data, using the following relationships (Christov, 2005, 2009a, 2009,b, 2012a, 2012b):

$$K^o sp\ (NaNO_3) = \gamma_{(\pm)}(sat)^2\ .m(sat)^2$$

$$K^o sp(LiNO_3.3H_2O) = \gamma_{(\pm)}(sat)^2\ .m(sat)^2.a_w(sat)^3 \quad (5)$$

The ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$,and C^φ) evaluations are directly used to determine water activity (a_w(sat)) and mean activity coefficient ($\gamma_{(\pm)}$(sat)) values at saturation. Next, experimentally determined molalities (m(sat) of the saturated binary solutions are used to calculate the thermodynamic solubility product K^o_{sp} . Than, the calculated $K^o sp$ values can be directly used to calculate standard chemical potential ($D_f G^o{}_m$) of nitrate solids (Barkov et al., 2001; Christov, 2000; 2005):

K^o_{sp} vs. standard chemical potential:

$$RTln\ K^o sp\ (LiNO_3.3H_2O) = D_f G^o{}_m(LiNO_3.3H_2O)-D_f G^o{}_m(Li^+) - D_f G^o{}_m(NO_3^-)-3D_f G^o m\ (H_2O) \quad (6)$$

Results and Discussion

Model parameterization and validation of models for binary 1-1 nitrate systems

Validation of reference models for HNO_3-H_2O, $NaNO_3$-H_2O, and KNO_3-H_2O systems

The main goal of this study is to develop Pitzer approach based thermodynamic models for solution behavior and solid-liquid equilibrium in nitrate binary systems 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 at 25°C. Pitzer parameters for all 7 nitrate systems under study are evaluated by many authors. The models of El Guendouzi and Marouani (2003) for $NaNO_3$-H_2O, KNO_3-$H_2O$and NH_4NO_3-H_2O are constructed only using their own low molality experimental data. Pitzer & Mayorga (1973) evaluate binary parameters for all 7 nitrate systems under study. Their standard approach 3 parameters models are valid up to m(max) molality equals to 6 m, and using osmotic coefficients (φ) data from Robinson and Stokes (1965). The m(max) parametrization of Pitzer & Mayorga (1973) is higher than the m(sat) molality of saturation (Silcock, 1979; Mikulin, 1968) for binary nitrate systems KNO_3-H_2O, $RbNO_3$-H_2O, and $CsNO_3$-H_2O (see also Table 1). The sigma value of Pitzer & Mayorga (1973) parameterization for $RbNO_3$-H_2O, and $CsNO_3$-H_2O is 0.001 and 0.002, respectively.

The models of Pitzer & Mayorga (1973) for $LiNO_3$-H_2O, $NaNO_3$-H_2O, and NH_4NO_3-H_2O are valid up to molality, which is much lower than the maximum molality of available experimental osmotic coefficients (φ) data (Hammer & Wu, 1972; Mikulin, 1968) and m(sat) molality of saturation (see Table 1). Their model for HNO_3-H_2O is valid only up to 3 m, while the data are available up to 29.3 m (Hammer & Wu, 1972; Mikulin, 1968). In our previous study (Lach et al., 2018) we present a Pitzer parameterization to predict solution properties and salt solubility in the H-Na-K-Ca-Mg-NO_3-H_2O system. All models for binary sub-systems were parameterized using all available experimental data up to saturation. The models for HNO_3-H_2O and KNO_3-H_2O includes formation of neutral aqueous complexes $HNO_3^o(aq)$ and $KNO_3^o(aq)$. In a previous study of Christov (2005) an extended 4-parameters model for HNO_3-H_2O system is presented. The extended approach with four Pitzer ion interaction binary parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$,and C^φ), accepting α_1 =2, and varying in the values of α_2 term gives an excellent agreement with osmotic coefficients data (σ=0.0043). The model is valid up to m(max) of data, equals to 29.3 m.

On next Figures 2abc we compare reference model calculated (lines) osmotic coefficients (φ) of HNO_3, $NaNO_3$ and KNO_3 in binary solutions HNO_3-H_2O, $NaNO_3$-H_2O and KNO_3- H_2O against molality at T = 25°C with recommendations in literature (symbols). Heavy solid lines represent the predictions of the accepted models of Christov (2005) for HNO_3-H_2O, of Lach et al. (2018) for $NaNO_3$-H_2O, and of Pitzer & Mayorga (1973) for KNO_3- H_2O. Dashed-dotted line represents the predictions of the model of Felmy et al. (1984) for HNO_3-H_2O, of Pitzer & Mayorga (1973) for $NaNO_3$-H_2O, and of Lach et al. (2018) for KNO_3- H_2O. The experimental data on Figs. 2abc are taken from Mikulin (1968) up to saturated solutions (open squares on 2a, and open triangles on 2b and 2c), from Hammer & Wu (1972) (stars on 2a) and El Guendouzi & Marouani (2003) (open squares on 2b and 2c). It should be noted that all three sets of experimental data are in good agreement (see Fig. 2). The vertical lines on 2b and 2c denote the molality of stable crystallization of solid phases $NaNO_3$(cr) and KNO_3(cr), taken from Mikulin (1968). As it is shown the four parameters model of Christov (2005) for HNO_3-H_2O, and the 3 parameters models of Lach et al. (2018) for $NaNO_3$-H_2O, and of Pitzer and Mayorga (1973) for KNO_3- H_2O are in very good agreement with raw experimental data from low to very high concentration. Therefore, these 3 models are accepted in our further calculations. The results given on Fig. 2a and 2b also show that inclusion of neutral species HNO_3^o(aq) and KNO_3^o(aq) into a models for HNO_3-H_2O and KNO_3- H_2O systems is not necessary. The inclusion of complex reactions only complicates, and do not improve the models.

Parametrization of models for $LiNO_3$-H_2O, $RbNO_3$-H_2O, $CsNO_3$-H_2O, and NH_4NO_3-H_2O.

The remaining models developed in this study are those for binary systems $LiNO_3$-H_2O, $RbNO_3$-H_2O, $CsNO_3$-H_2O, and NH_4NO_3-H_2O. New sets of Pitzer ion interaction binary parameters are evaluated using available raw experimental osmotic coefficients (φ) data for whole molality range of solutions. The φ vs. m data for all 4 solutions are given in Hammer and Wu (1972), Mikulin (1968), and Robinson and Stokes (1965). El Guendouzi & Marouani (2003) present the φ data for $LiNO_3$-H_2O and NH_4NO_3-H_2O solutions. All reference φ vs. m data sets are in a good agreement (see also symbols on Fig. 3a,b,e). However, the data of Mikulin (1968) cover the whole molality range of unsaturated and saturated solutions. In case of $LiNO_3$-H_2O Mikulin also reported data for supersaturated solutions (from 12.45 m to 20 m). In this study we parameterize the models using 1) very low molalty (to 0.1 m) data of Hammer and Wu (1972), 2) all data of Mikulin (1968) for whole molalty range of unsaturated solutions from 0.1 m to m(max), 3) the data points at saturation (φ(sat)) (from Mikulin, 1968), and 4) data for supersaturated $LiNO_3$-H_2O solutions (from Mikulin, 1968).

In parameterization process we used the value of Debye-Hückel term ($A^φ$) equals to 0.39147, as given in Christov (2009a; 2009b; 2012a). Following the parameterization scheme described in paragraphs 2.2 and 2.3 the model for all 4 binary nitrate solutions is parameterized using two different approaches: (I) standard for 1-1 electrolytes 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 two α – combinations: (IIa) α_1 =2 and α_2 = 1, and (IIb) α_1 =2 and α_2 = -1 (Christov, 1996; 1999; 2000; 2004; 2005). 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 & Moller (2004b). It was found that similarly to accepted reference binary models for $NaNO_3$-H_2O and KNO_3-H_2O), for 2 of studied systems $CsNO_3$-H_2O and NH_4NO_3-H_2O, the approach with 3 parameters ($\beta^{(0)}$, $\beta^{(1)}$, $C^φ$) give an acceptable agreement with the data, up to much higher molality, than the available parameteri-zations (Pitzer & Mayorga (1973), and El Guendouzi & Marouani (2003). The new model for $CsNO_3$-H_2O fits the osmotic coefficients data with a sigma equals to 0.00052, which is almost four times less than sigma value of parameterization of Pitzer & Mayorga (1973) (σ = 0.002). For these systems introducing into a model of fourth ($\beta^{(2)}$) parameter do not improve considerably the fit of data. The new parameterization for $CsNO_3$-H_2O and NH_4NO_3-H_2O systems is not only concentration-extended up to molality of saturation (m(sat)), but also provide a better fit of data (lowest sigma), than the concentration restricted models presented in literature (Pitzer & Mayorga, 1973; Kim & Frederick (1988) and El Guendouzi & Marouani, 2003). The new NH_4NO_3-H_2O parameterization fits the data up to m(sat) =26.8 m with a sigma equals to 0.0018, which is three times less than sigma value of parameterization of Kim & Frederick (1988) ($\sigma = 0.0054$).

For $LiNO_3$-H_2O system we construct a model on the basis of extended approach (2), and using $\alpha_1 = 2$ and $\alpha_2 = -1$. The resulting model fits the data up to supersaturation zone (m(max) = 20m) with sigma value equals to 0.00137, which is much less than the value of Kim & Frederick (1988) parameterization ($\sigma = 0.0064$). The new model for $RbNO_3$-H_2O also is based on 4 parameters approach and uses $\alpha_1 = 2$ and $\alpha_2 = 1$. The model fits the data with $\sigma = 0.000373$, which is much less than the values of models of Pitzer & Mayorga (1973) ($\sigma = 0.001$), and of Kim & Frederick (1988) ($\sigma = 0.0023$).

On next Figures 3(abcde) we present a comparison of osmotic coefficients in nitrate binary solutions $LiNO_3$-H_2O, $RbNO_3$-H_2O, $CsNO_3$-H_2O, and NH_4NO_3-H_2O calculated by the accepted models developed here (heavy solid lines), models developed by other authors (dashed lines, light solid lines; Pitzer and Mayorga (1973), Kim and Frederick (1988)), and with the recommended values given in literature (symbols) at 25°C. The vertical lines on the figures denote the molality of solutions saturated with corresponding nitrate solid phase (m(sat)), taken from Mikulin (1968). Excellent model – experiment agreement has been obtained for all four systems and from low up to very high molality (see Fig. 3a and 3e). As is shown on Fig. 3b, the new model for $LiNO_3$-H_2O is in excellent agreement not only with the data at high molality, but contrary to the model of Kim & Frederick (1988) (see Fig. 1b) also in low molality range.

The models for all 7 nitrate binary systems under study are also validated by comparison with recommendations given in literature (Hammer & Wu, 1972; Mikulin, 1968) on the mean activity coefficients ($g_\pm$). These recommendations on $g_\pm$ are model-dependent. Therefore, they are not used in parameterization process, and only to validate the resulting models. The comparisons between model predictions and reference recommendations, which are not given here, show an excellent agreement from low to very high concentrations.

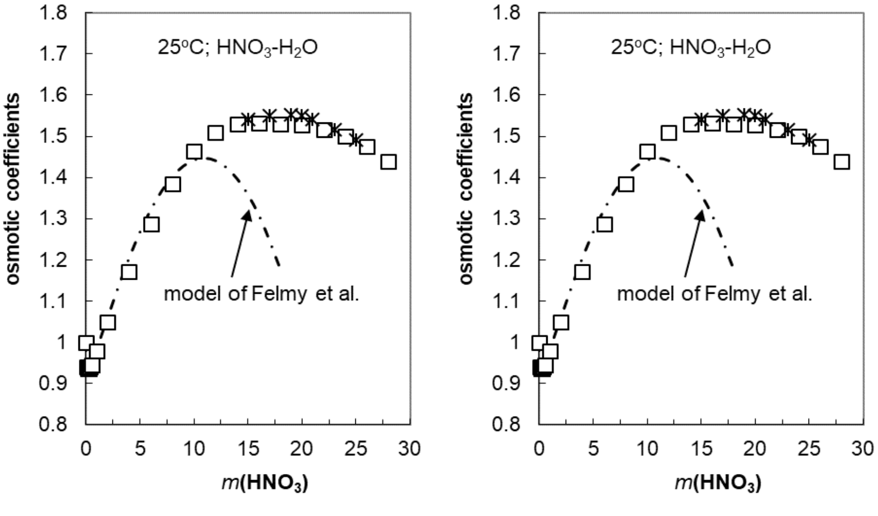
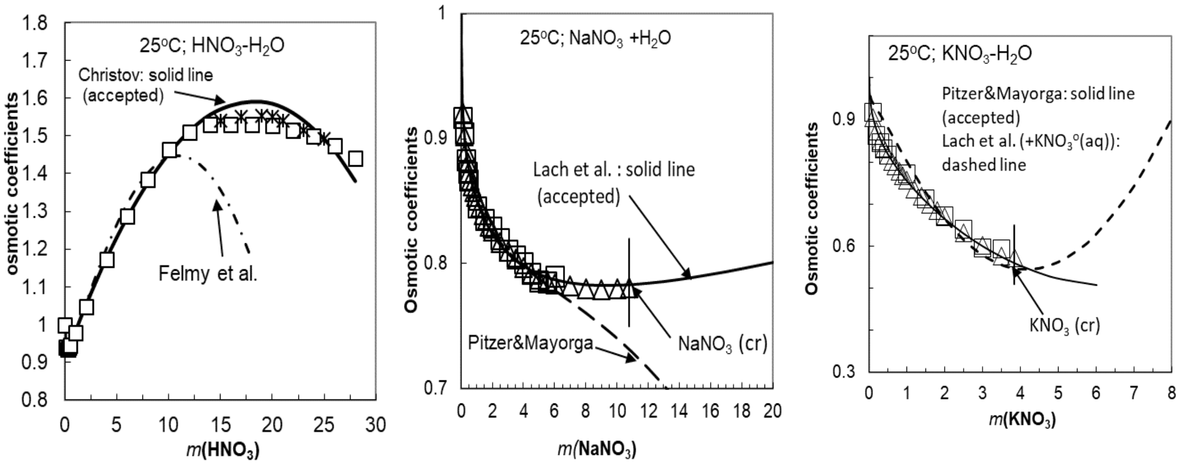
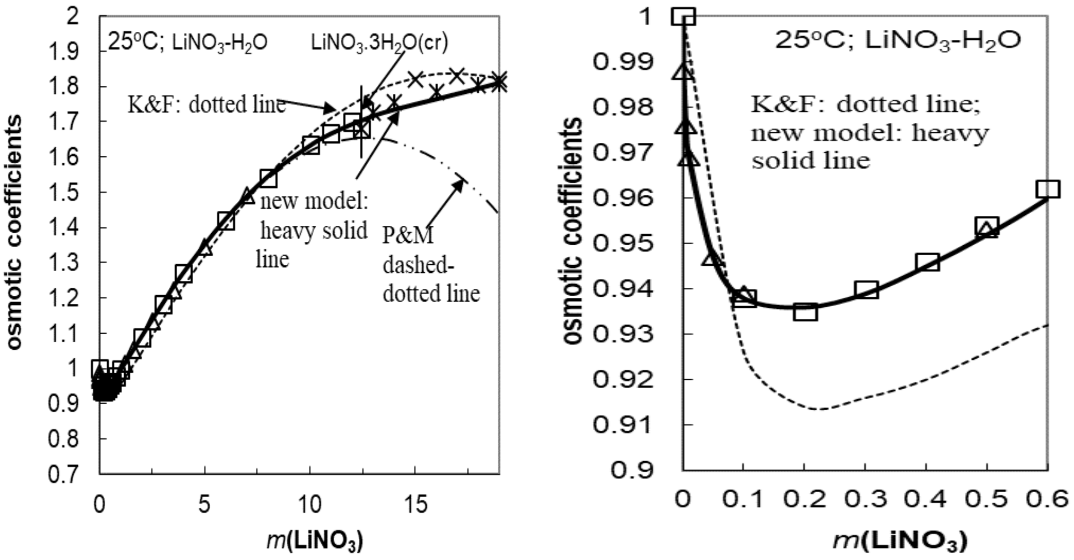


Fig. 1a,b. Comparison of reference model calculated (lines) osmotic coefficients (φ) of HNO_3 (and $LiNO_3$ in binary solutions HNO_3-H_2O (Fig. a) and $LiNO_3$-H_2O (Fig. b) against molality at T = 25°C with recommendations in literature (symbols) (Mikulin, 1968; Hammer & Wu, 1972). The (b) figure is an enlargement of the low molality corner. Dashed-dotted line on (a) represent the predictions of the model of Felmy et al. (1994), and dotted line on (b) are predictions of the model of Kim & Frederick (1988a).

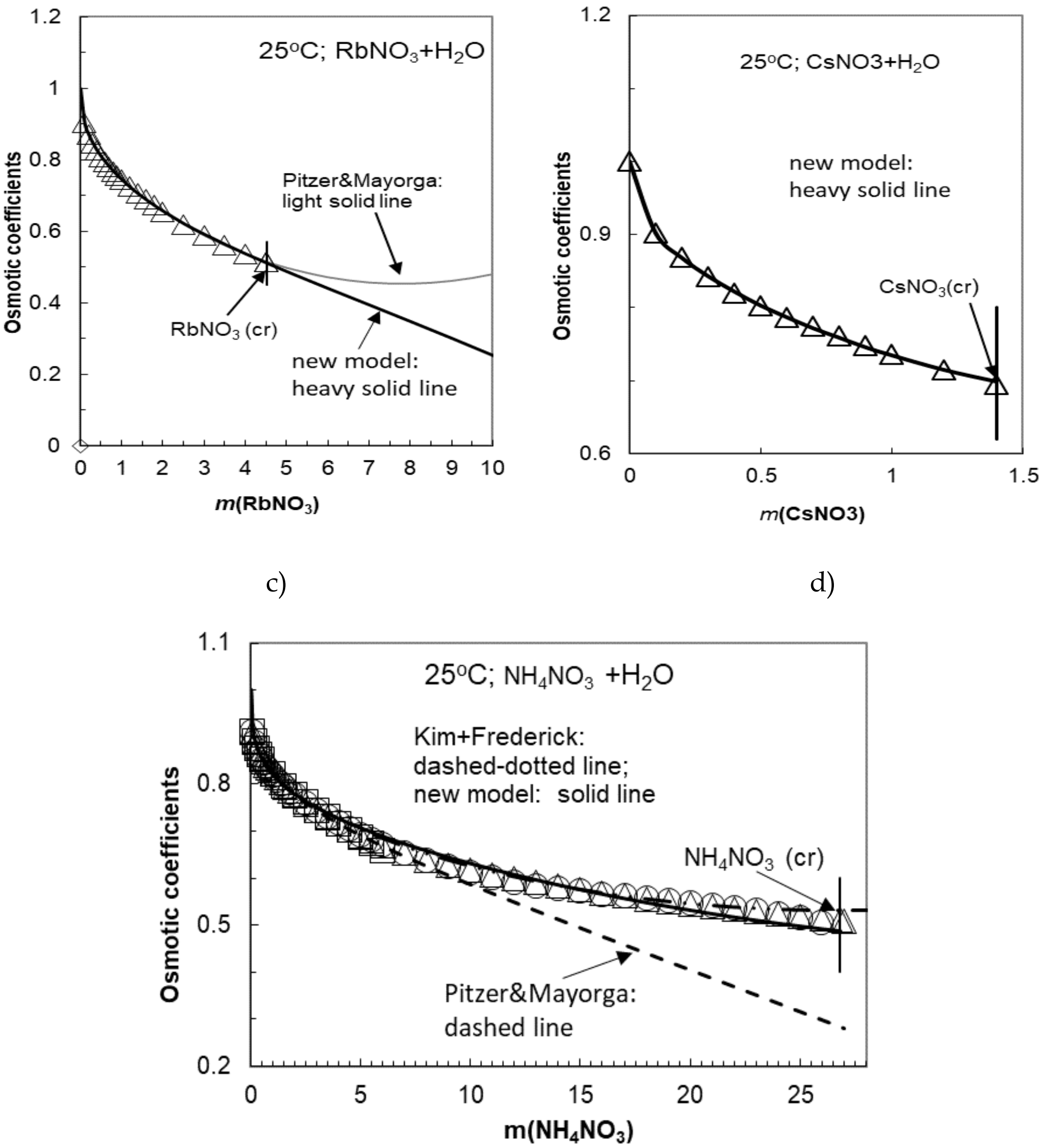


a) b) c)

Fig. 2a,b,c. Comparison of reference model calculated (lines) osmotic coefficients (φ) of HNO_3, $NaNO_3$ and KNO_3 in binary solutions HNO_3-H_2O, $NaNO_3$-H_2O and KNO_3- H_2O against molality at T = 298.15 K with recommendations in literature (symbols). Heavy solid lines represent the predictions of the accepted models of Christov (2005) for HNO_3-H_2O, of Lach et al. (2018) for $NaNO_3$-H_2O, and of Pitzer & Mayorga (1973) for KNO_3- H_2O. Dashed-dotted lines represent the predictions of the model of Felmy et al. (1984) for HNO_3-H_2O, of Pitzer & Mayorga (1973) for $NaNO_3$-H_2O, and of Lach et al. (2018) for KNO_3- H_2O. The model of Lach et al. (2018) includes neutral specie $KNO_3^o(aq)$. The experimental data are taken from Mikulin (1968) up to saturated solutions (open squares on (a), open triangles on (b) and (c)), Hammer & Wu (1972) (stars on (a)), and El Guendouzi & Marouani (2003) (open squares on (b) and (c)). The vertical lines on b and c denote the molality of stable crystallization of solid phases $NaNO_3$(cr) and KNO_3(cr), taken from Mikulin (1968).



a) b)



c) d)

e)

Fig. 3a,b,c,d,e. Comparison of model calculated (lines) osmotic coefficients (φ) of $LiNO_3$(Fig. a and b), $RbNO_3$ (Fig. c), $CsNO_3$ (Fig. d) and NH_4NO_3 (Fig. e) in binary solutions $LiNO_3$-H_2O, $RbNO_3$-H_2O, $CsNO_3$-H_2O and NH_4NO_3-H_2O against molality at T = 298.15 K with recommendations in literature (symbols). The (b) figure is an enlargement of the low molality corner. 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 & Frederick (1988) (Fig. a and b), and of Pitzer & Mayorga (1973) (Fig. c and e). The experimental data are taken from Mikulin (1968) (open squares on 3ab and open triangles on 3cde), Hammer & Wu (1972) (open triangles and stars on 3ab and open circles on 3e), and El Guendouzi & Marouani (2003) (open squares on 3e). The vertical lines denote the molality of stable crystallization of solid nitrate phases.

Conclusions

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 occurs 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 & Brimblecombe, 1995; Christov, 2009a; b; 2012a; b):

$$a_w = P_w / P^o_w = RH/100, \qquad (7)$$

where P_w and P^o_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, 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, 2009a; b; 2012a, 2012b).

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. 7) of solid phases crystallizing from saturated binary nitrate solutions [$LiNO_3.3H_2O(s)$, $NaNO_3(s)$, $KNO_3(s)$, $RbNO_3(s)$, $CsNO_3(s)$, and $NH_4NO_3(s)$]. 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 $LiNO_3.3H_2O(s)$ occurs at lowest relative humidity of environment, although the m(sat)-solubility of $NH_4NO_3(s)$ is more than two times higher.

Table 1. Comparison between model calculated and recommended values of the Deliquescence Relative Humidity [DRH (%) = a_w^s x 100; where a_w^s is activity of water at saturation] and of the logarithm of the thermodynamic solubility product (K^o_{sp}) of nitrate solid phases crystallizing from saturated binary solutions at T = 25°C. *Legend:* [a]Experimental data of Mikulin (1968); [b]Calculated values of Lach et al. (2018).

Salt composition	$m^s/(mol.kg^{-1})^a$	DRH, %		$\ln K^o_{sp}$	
		This study	Reference data	This study	Reference data
$LiNO_3$ $3H_2O$(cr)	12.45	46.9	47.06 [a]	4.9765	-
$NaNO_3$(cr)	10.878	73.72	73.8 [a] 73.76[b]	2.5043	2.502 [b]
KNO_3(cr)	3.84	92.73	92.4 [a] 92.6 [b]	-0.2576	-0.1557 [b]
$RbNO_3$(cr)	4.52	92.02	91.9 [a]	-0.2279	-
$CsNO_3$(cr)	1.4	96.54	96.5 [a]	-1.3275	-
NH_4NO_3(cr)	26.8	62.4	61.1 [a]	2.4731	-

As a next step, using the accepted and new developed parameterizations, and experimentally determined molalities (m(sat) of the saturated binary solutions (Mikulin, 1968) we calculate the logarithm of the thermodynamic solubility product (ln K^{o}_{sp}) of six nitrate solid phases crystallizing from saturated binary nitrate solutions at T = 298.15 K (eqn. (5)). The model calculations are given in Table 1. A good agreement has been obtained for $NaNO_3$(s), and KNO_3(s) with calculations of Lach et al. (2018). The small ln K^{o}_{sp} difference (of 0.1 logarithm units) for KNO_3(s) is mainly due on the different m(sat) values used in calculations (see eqn. (5)). Note that the widely used databases of Pitzer (1991), Pitzer & Mayorga (1973) and Kim & Frederick (1988) do not consider solid phases.

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