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Computer models for predicting solution properties and solid-liquid equilibrium in binary fluoride systems

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Abstract. The thermodynamic properties of the alkali fluoride aqueous solutions are of great interest for the knowledge and better understanding of the physico-chemical processes governing industrial and environmental processes. The study of behavior of solid fluorides and hydrogen fluorides in aqueous solutions play an important role in industrial applications. Thus, the solid potassium fluoride is widely used in the metallurgy, glass fiber optics industry and ceramic manufacturing processes. In the agriculture, KF(s) has been employed in a range of applications, including pesticides, herbicides, and insecticides. The solution and solid-liquid equilibrium models for fluoride systems are also of high importance in development of technology for production of fluoride compounds needed in pharmaceutical industry.

In this study we developed very well validated thermodynamic models for solution behavior and solid-liquid equilibrium for all fluoride binary systems, for which activity data are available. The subject of modeling study are 5 fluoride systems of the type 1-1 (HF-H_2O, NaF-H_2O, KF-H_2O, RbF-H_2O, and CsF-H_2O) from low to very high concentration at 298.15 K. Models are developed on the basis of Pitzer ion interactions approach. The recommendations on mean activity coefficients ($\gamma_{\pm}$) have been used to construct the model for HF-H_2O system. To parameterize models for all other 4 binary systems we used all available raw experimental osmotic coefficients data (φ) for whole concentration range of solutions, and up to saturation point. The predictions of new developed here models are in excellent agreement with experimental osmotic coefficients data, and with recommendations on activity coefficients in binary solutions from low to very high concentration: up to 20 $mol.kg^{-1}$ in HF-H_2O, and up to $\approx$ 36 $mol.kg^{-1}$ in CsF-H_2O. The thermodynamic solubility products (as $\ln K^o_{sp}$) of 4 solid phases [$NaF(s)$, $KF.2H_2O(s)$, $RbF(s)$, and $CsF(s)$] have been determined on the basis of evaluated model parameters and using experimental m(sat) solubility data

Keywords: Computer chemical modeling; Pitzer approach; Binary fluoride systems (HF-H_2O, NaF-H_2O, KF-H_2O, RbF-H_2O, and CsF-H_2O); Solution activity; Solid-liquid phase equilibrium.

1   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 not low-, and high- concentration restricted models 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, 1998, 1999, 2000, 2001a, 2001b, 2002a, 2002b, 2003a, 2003b, 2005), and from 0° to 290°C (Lassin et al., 2015; Christov & Moller, 2004a, 2004b; Moller et al, 2006; Christov, 2007, 2009a, 2009b, 2012).

The thermodynamic properties of the alkali fluoride aqueous solutions are of great interest for the knowledge and better understanding of the physico-chemical processes governing industrial and environmental processes. The study of behavior of solid fluorides and hydrogen fluorides in aqueous solutions play an important role in industrial applications. Thus, the solid potassium fluoride is widely used in the metallurgy, glass fiber optics industry and ceramic manufacturing processes. In the agriculture, KF(s) has been employed in a range of applications, including pesticides, herbicides, and insecticides. The solution and solid-liquid equilibrium models for fluoride systems are also of high importance in development of technology for production of fluoride compounds needed in pharmaceutical industry.

In this study we developed well validated thermodynamic models for solution behavior and solid-liquid equilibrium for all fluoride binary systems, for which activity data are available. The subject of modeling study are 5 fluoride systems of the type 1-1 (HF-H_2O, NaF-H_2O, KF-H_2O, RbF-H_2O, and CsF-H_2O) from low to very high concentration at 298.15 K. Models are developed on the basis of Pitzer ion interactions approach (Pitzer (1973, 1991)).

2   Methodology

2.1. Pitzer's equations

The Pitzer's equations (1 to 4) are described and widely discussed in the literature (Harvie et al., 1984; Moller et al., 2006; Christov and Moller, 2004a, 2004b).

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

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

$$+ \sum_n m_n (2\lambda_{nM}) + \sum_n \sum_a m_n m_a \varsigma_{naM} \tag{1}$$

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,

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

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:

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

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

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,

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

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.

2.2. 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 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 (Christov, 2003a) electrolytes, giving excellent representation of activity data covering the entire concentration range from low molality up to saturation and beyond.

2.3. 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

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 $\alpha_1 = 1.4$ and $\alpha_2 = 12$ accounts association only at low molality solutions (see 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 $\alpha_1 = 2$, 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); $Ca(NO_3)_2$-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: (Andre et al., 2019); $Ln(NO_3)_3(aq)$: (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, 2002b, 2003b, 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.

3. Results and discussions. Model parameterization and validation of models for binary 1-1 fluoride systems

The activity data for fluoride systems are presented by Mikulin (1968) (for NaF-H_2O, KF-H_2O, RbF-H_2O, and CsF-H_2O solutions), by Hammer and Wu (1972) (for all 5 systems under study HF-H_2O, NaF-H_2O, KF-H_2O, RbF-H_2O, and CsF-H_2O solutions), by El Guendouzi and Faridi (2020) (for KF-H_2O only), and by Robinson and Stokes (1959) (for NaF-H_2O, and KF-H_2O). The data of Mikulin (1968) and Hammer and Wu (1972) are in excellent agreement for NaF-H_2O, KF-H_2O, RbF-H_2O, and CsF-H_2O systems. The low molality data of Robinson and Stokes (1959) are also in excellent agreement with the data of Mikulin and Hammer and Wu. Mikulin reported data not only for unsaturated solutions, but also at saturation point. El Guendouzi and Faridi (2020) reported a little higher values for the osmotic coefficients data at high molality in KF-H_2O solutions, compare to the data of Mikulin (1968), and Hammer and Wu (1972) (max diff. of 0.04). For HF-H_2O solutions the only available mean activity ($\gamma_{\pm}$) and osmotic (φ) coefficients data are those of Hammer and Wu (1972). However, our preliminary test shows that there is some inconsistency between the φ data at low molality ($< 1m$), obtained on the basis of E.M.F. experiments, and the φ data at higher molality, obtained using isopiestic experiments. Therefore, the model for HF-H_2O solutions have been parameterized on the basis of activity coefficients ($\gamma_{\pm}$) data of Hammer and Wu. For the remaining 4 fluoride systems the osmotic (φ) coefficients data for unsaturated, saturated and super-saturated (for KF-H_2O system) solutions from Mikulin (1968) are used to construct the models.

In parameterization process we used the value of Debye-Hückel term (A^{φ}) equals to 0.39147 at 25°C, as given in Christov (2009a, 2009b, 2012). To construct the models we used different versions of standard molality-based Pitzer approach. It was established that for all 5 systems under study application of extended approach with 4 parameters (β^0, β^1, β^2 and C^{φ}) and variation of α_2 term in fundamental Pitzer equations leads to the lowest values of standard model-experiment deviation (see paragraph 2.3).

On next figures (A,B,C,D,E and F) we compare model calculated (lines) mean activity coefficients (Fig. A) and osmotic coefficients (φ) (Fig. B,C,D,E and F) of HF (Fig. A), NaF (Fig. B), KF (Fig. C), RbF (Fig. D) and CsF (Fig. E and F) in binary solutions HF-H_2O, NaF-H_2O, KF-H_2O, RbF-H_2O, and CsF-H_2O) against molality at T = 298.15 K with osmotic (φ) coefficients data, and activity coefficients ($\gamma_{\pm}$) recommendations in literature (symbols). The (E) 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, and dashed lines represent the predictions of the reference models of Kim and Frederick (1988) (Fig. A), of Pitzer and Mayorga (1973) (Fig. B, C, D, E and F), and of El Guendouzi and Faridi (2020) (Fig. C). The experimental data are taken from Mikulin (1968) (open triangles on all figures and open squares on Fig. E and F), Hammer and Wu (1972) (open squares on Fig. A, B, C and D), and El Guendouzi and Faridi (2020) (crosses on Fig. C). The vertical lines on figures denote the molality of stable crystallization of solid fluoride phases (from Mikulin (1968)).
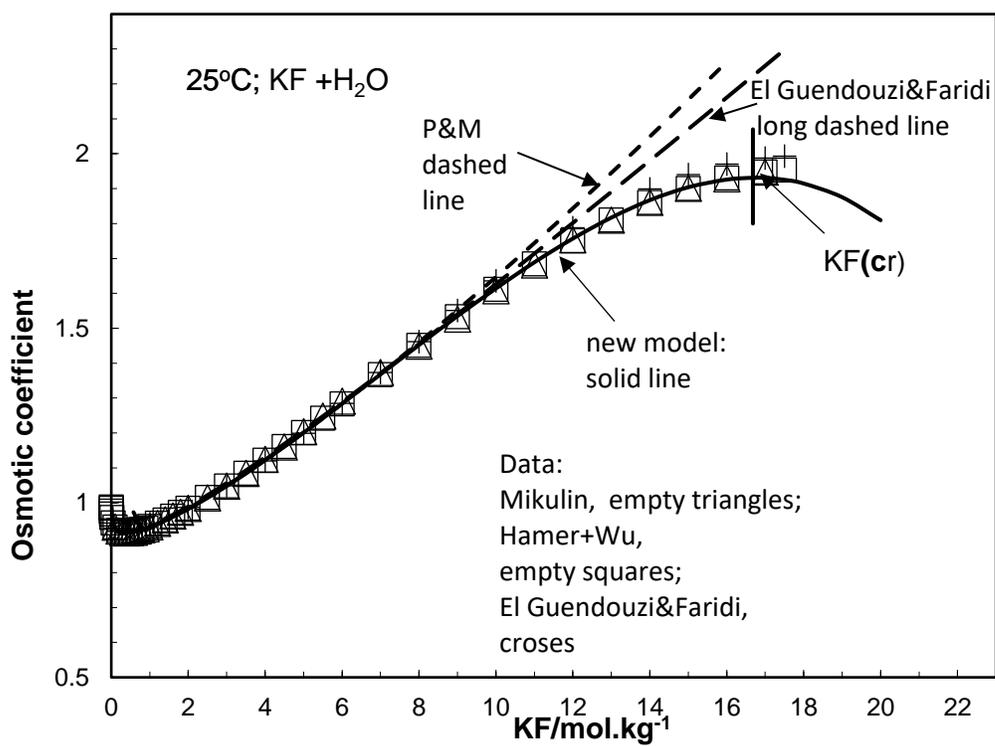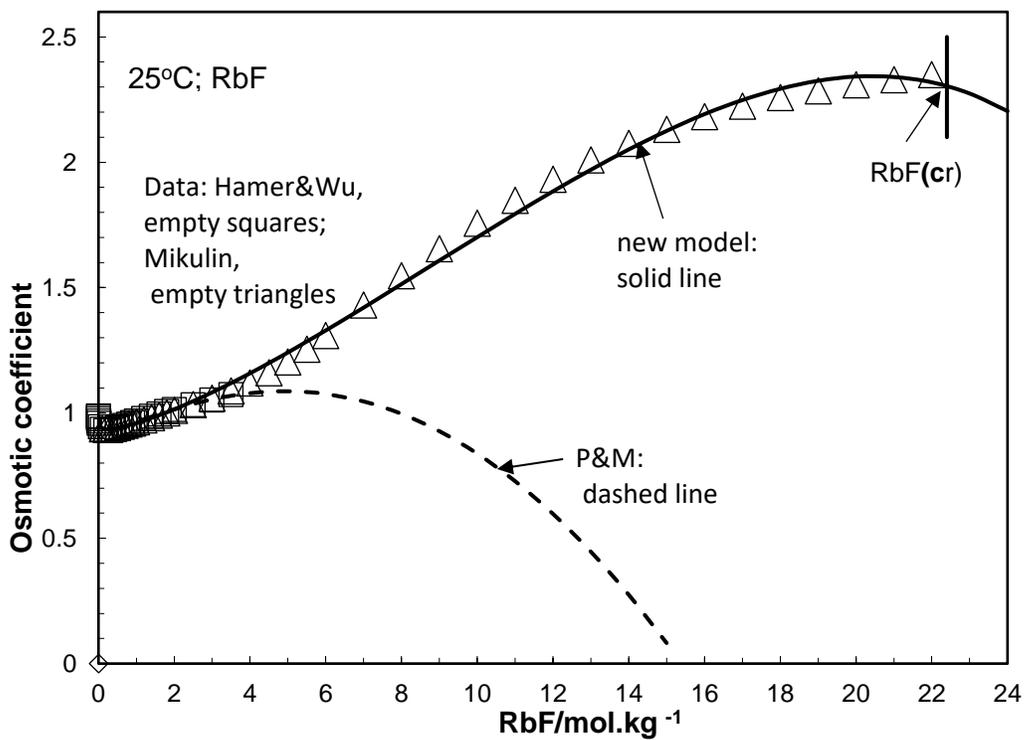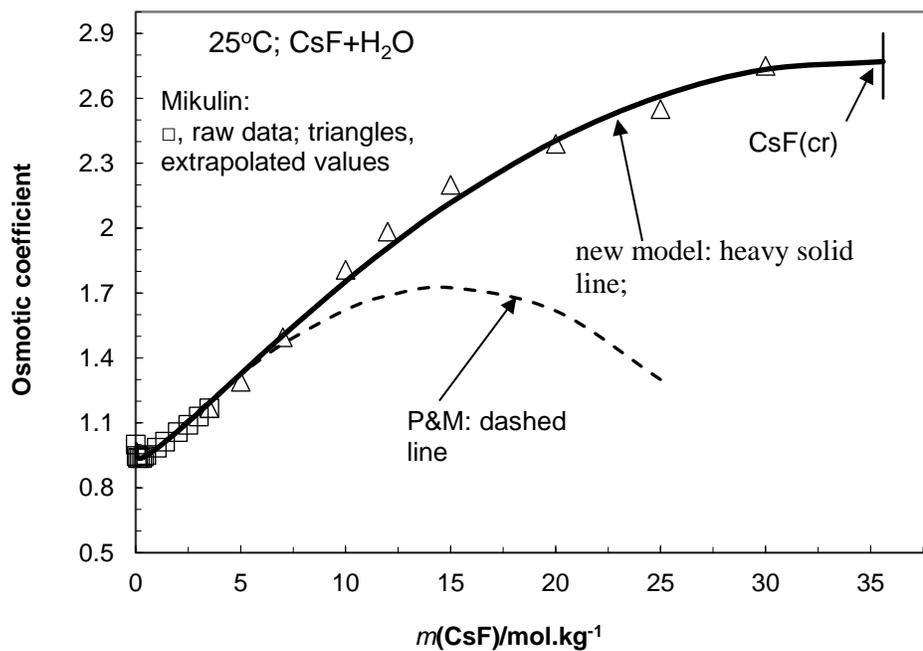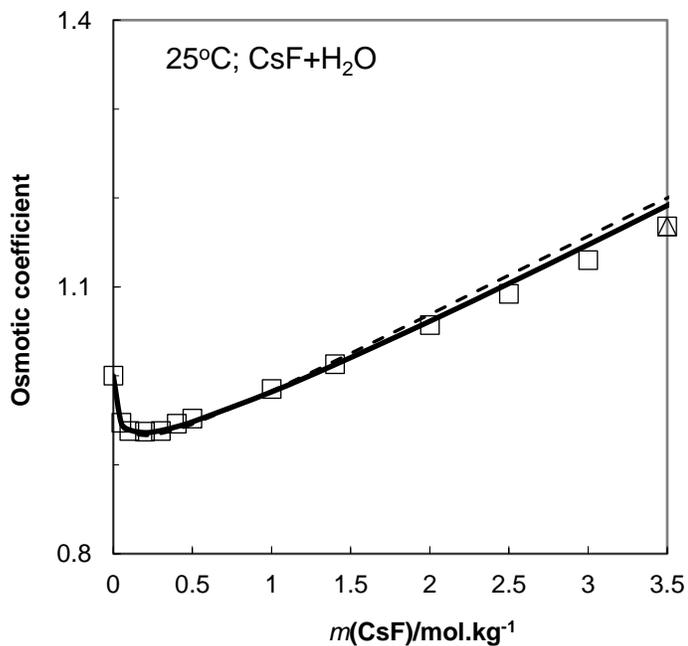
A)
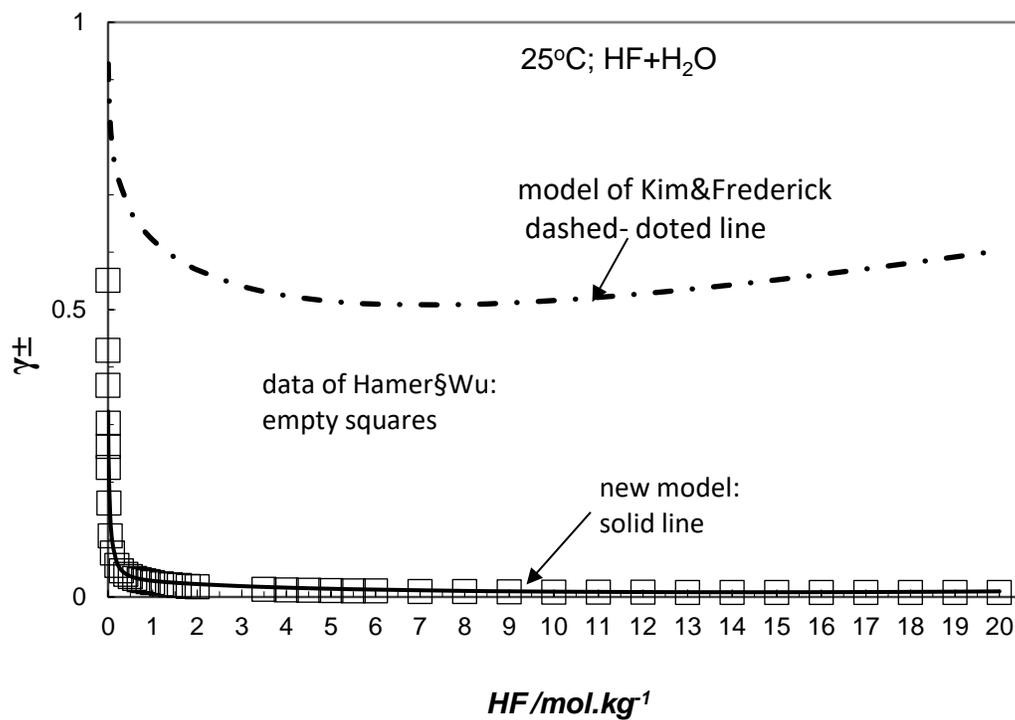
B)
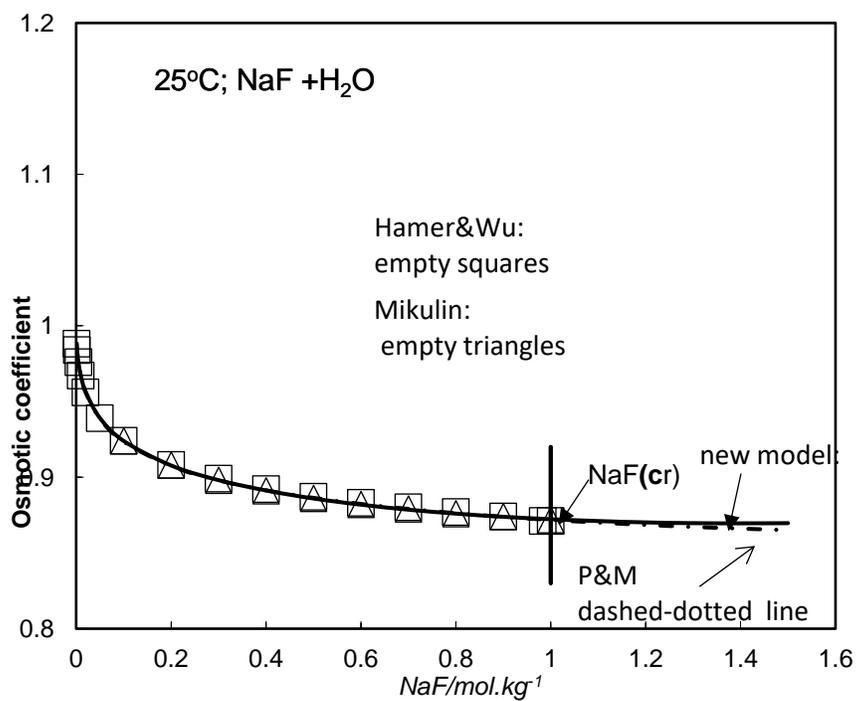
C)

D)

E)

F)

As shown on figures above the predictions of new developed here models are in excellent agreement with experimental osmotic coefficients data, and with recommendations on activity

coefficients in binary solutions from low (see Fig. F) to very high concentration:up to 20 mol.kg^{-1} in HF-H$_2$O, up to 17.5 mol.kg^{-1} in KF-H$_2$O, up to 22.4 mol.kg^{-1} in RbF-H$_2$O and up to 35.6 mol. kg^{-1} in CsF-H$_2$O. With only one exception (for NaF-H$_2$O), the models developed here are in a pure agreement with models reported in literature. For NaF-H$_2$O system our model is in very good agreement with the low molality model of Pitzer and Mayorga (1973), and the data. The model of Kim&Frederick (1988) predicts much higher activity coefficients for whole concentration range (up to 20 m) for HF-H$_2$O solutions, compare to the data and our new model. For KF-H$_2$O solutions the predictions of the models of Pitzer and Mayorga (1973) and of El Guendouzi and Faridi (2020) are in good agreement with data and our model only up to ≈ 10 m. At higher molality these models predict higher values of osmotic coefficients. The comparison on Fig. (D) and (E) shows that for RbF-H$_2$O and CsF-H$_2$O systems the model of Pitzer and Mayorga (1973) reproduced well the data only at low molality (up to ≈ 3.0 m for RbF-H$_2$O, and up to ≈ 7 m for CsF-H$_2$O). Therefore, it can be concluded that with only one exception (the model of Pitzer and Mayorga for NaF-H$_2$O) all other models given in literature are concentration restricted and can not be used for solubility calculations and correct determination of properties of crystallizing solid phases.

On the basis of evaluated in this study binary parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$,and C$^{\varphi}$) we also determine water activity (a_w) and Deliquescence Relative Humidity (DRH (%)) (see eqn. 5) of solid phases crystallizing from saturated binary fluoride solutions [NaF(s), KF.2H$_2$O(s), RbF(s), and CsF(s)].

Within the solid-liquid equilibrium model, relative humidity is related to water activity, a_w (Clegg and Brimblecombe, 1995; Christov, 2009a,b; 2012):

$$a_w = P_w/ P^o_w = RH/100, \tag{5}$$

where P$_w$ and P^o_w are the vapor pressure of the saturation solution and pure water, respectively, at given temperature. 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 CsF(s) occurs at lowest relative humidity (RH) of environment (≈ 2.5 %).

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 4 solid phases crystallizing from saturated binary fluoride solutions at T = 298.15 K (eqn. (6)).

$$K^o sp \text{ (NaF)} = \gamma_{(\pm)}(sat)^2 .m(sat)^2$$
$$K^o sp(KF.2H_2O) = \gamma_{(\pm)}(sat)^2 .m(sat)^2 .a_w(sat)^2 \tag{6}$$

The model calculations are given in Table 1. The small ln K$^o_{sp}$ difference (of 0.26 logarithm units) for KF.2H$_2$O (s) compare to calculations of El Guendouzi and Faridi (2020) is mainly due on the different m(sat) values used in calculations (see eqn. (6) and Table 1). Note that the widely used databases of Pitzer (1991), Pitzer and Mayorga (1973, 1974), and Kim and Frederick (1988) do not consider solid phases.

TABLE 1. Comparison between model calculated and recommended values of t hermodynamic properties for fluoride solid phases crystallizing from saturated binary solutions at T = 298.15 K: 1) Deliquescence Relative Humidity [DRH (%) = a_w^s x 100; where a_w^s is activity of water at saturation], and 2) logarithm of the thermodynamic solubility product, K^o_{sp},

Salt composition	m(sat) (exp)[a]	DRH (%)		lnK^o_{sp}	
	$(mol.kg^{-1})$	Calculated	Ref. data[a]	Calculated	El Guendouzi and Faridi [b]
NaF(cr)	1.0	96.91	96.90	-1.115	
KF.2H₂O(cr)	16.68	31.33	31.10	5.84	6.1051 (m(sat)=17.5)
RbF(cr)	22.4	15.20	14.50	10.801	
CsF(cr)	35.6	2.46	4.00	14.74	

[a]from Mikulin (1968)
[b]from El Guendouzi and Faridi (2020)

Acknowledgement

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