

Thermodynamic solid-liquid equilibrium model for mixed systems HF-NaF-H₂O and HF-KF-H₂O up to 2 m HF at T = 25°C

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Abstract: In this study we developed thermodynamic models for solid-liquid equilibrium for mixed systems HF-NaF-H₂O and HF-KF-H₂O up to 2 m HF at T = 25°C. 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-H₂O system. The models for binary systems NaF-H₂O and KF-H₂O are taken from our previous study in the same journal [Donchev et al. ASN (2021) 8(2), 1-15]. To parameterize models for ternary systems we used the available solubility data, i.e. on the basis of solubility approach. The thermodynamic solubility products (as $\ln K_{sp}^{\circ}$) of precipitating in mixed systems double salts [NaF.HF(cr), and KF.HF(cr)] have been determined on the basis of evaluated model ion interaction parameters and using experimental $m(\text{sat})$ solubility data. The model is in a good agreement with experimental solubility data in the systems HF-NaF-H₂O and HF-NaF-H₂O up to maximum HF molality of 2 mol·kg⁻¹. At higher acid molality the model predicts much higher solubility of double salts (NaF.HF(cr) and KF.HF(cr) for both mixed systems. It was concluded that not a correct raw data for binary HF-H₂O system used in parameterization are the main reason for concentration restriction of mixed HF models presented here.

Keywords: Computer chemical modeling; Pitzer approach; Solid-liquid phase equilibrium; HF-NaF-H₂O and HF-KF-H₂O systems

Introduction

During the 70thies Kenneth Pitzer suggested a method allowing the calculation of the activity coefficient in unsaturated solutions of electrolytes with an accuracy of 2 to 6% (Pitzer 1973, 1991). Harvie et al. (1984) and Filippov et al. (1980) were the first to use the Pitzer model under the conditions of chemical and phase equilibrium for prediction of the phase diagrams of multicomponent water-salt systems in which phases with constant stoichiometric compositions (simple and double salts) crystallize. The applicability of Pitzer equations to the simulation of solutions where solid solutions crystallize was also demonstrated (Christov 1996, 1997, 2003, 2005). In many papers the ion-interaction model is utilized for simulation of electrolyte solutions at temperatures and pressures differing from the standard (Christov and Moller, 2004; Christov 2005, 2007, 2009a, 2009b, 2012). The small number of parameters taking into account the ion interactions even in highly concentrated multicomponent solutions and the not complicated fundamental equations allowing relatively easy computerization have contributed to the model becoming a real hit in the scientific literature. Pitzer model is used successfully for the solution of various theoretical (Christov et al. 2012; Harvie et al., 1984; Christov and Moller, 2004a; Christov, 2019, 2020) and practical (Park et al., 2009; Lach et al., 2018; Guignot et al. 2019; Lassin et al. 2015, 2020; Trendafelov et al. 1995a, 1995b; Christov 2009a, 2009b) tasks.

The thermodynamic properties of the alkali fluoride aqueous solutions are of great interest for the knowledge and better understanding of the physical-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 (El Guendouzi and Faridi, 2020, 2021). 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. Models for high soluble solid fluorides (s.a. $\text{KF} \cdot 2\text{H}_2\text{O}(\text{cr})$, $\text{KF} \cdot \text{HF}(\text{cr})$) are of interest in development of strategies and programs for nuclear waste sequestration (Donchev et al., 2021). During the phosphoric acid production process, the fluorine is partially released within the gas streams in the form of HF and SiF_4 and is partitioned between the other phases, phosphogypsum and the phosphoric acid product, depending on the used process and the quality of phosphate. In the atmospheric environment, the release of hydrogen fluoride (HF) can produce toxic and corrosive mist when mixed with moist air. (El Guendouzi et al., 2019).

In this study we developed solid-liquid equilibrium thermodynamic models for mixed systems HF-NaF-H₂O and HF-KF-H₂O up to 2 m HF at T = 25°C. Models are developed on the basis of Pitzer ion interactions methodology (Pitzer 1973, 1991). Pitzer mixing parameters (θ and ψ) for the ternary systems in which stoichiometric compounds crystallize, were determined from experimental data on the

compositions of the saturated ternary solutions, i.e. on the basis of solubility approach (Harvie et al., 1984; Christov and Moller, 2004; Barkov et al. 2001; Christov 1994, 1999, 2000, 2001, 2002ab, 2004). The main purpose of the thermodynamic simulation was: (a), plotting the theoretical solubility isotherms, and (b), determining the thermodynamic characteristics of the solid phases crystallizing from the saturated ternary solutions.

Methodology

The solutions were investigated according to the following scheme: determination of Pitzer binary parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, C^ϕ) which take into account the interionic interactions of two ions and three ions; determination of Pitzer ternary parameters (θ and ψ) characterizing the interaction between two different ions of the same sign and the interaction between three ions, respectively; calculation of the solubility isotherms of the three-component systems (Christov, 2004, 2005, 2019).

Binary systems

Since calculation of the compositions of saturated ternary solutions is the main purpose of the simulation, the applicability of the binary parameters to high concentrations of the binary solutions up to saturation at the lowest value of the standard deviation (σ) is a very important criterion for the choice of the binary parameters.

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, 1974). 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). The Pitzer's equations are described and widely discussed in the literature (Harvie et al., 1984; Christov and Moller, 2004; Christov, 2005, 2019; Donchev et al., 2021). Therefore, these equations are not given here. According to the basic Pitzer equations, at constant temperature and pressure, the solution model parameters to be evaluated for mixed ternary system 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 (Christov, 2003, 2005; Donchev et al., 2021; Park et al., 2009).

Pitzer and Mayorga (1973) did not present analysis for any 2-2 (e.g. $\text{MgSO}_4\text{-H}_2\text{O}$) or higher {e.g. 3-2: $\text{Al}_2(\text{SO}_4)_3\text{-H}_2\text{O}$ } electrolytes. In their next study Pitzer and Mayorga (1974) modify the original equations for the description of 2-2 binary solutions: parameter $\beta^{(2)}$ (M,X), and an associated α_2 term are added to the original expression. 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, Na₂SO₄, or MgCl₂), 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 & Mayorga, 1974; Christov, 1999, 2000) and selenate (Christov, 1997; Barkov et al., 2001; Ojkova et al. 1999) electrolytes, giving excellent representation of activity data covering the entire concentration range from low molality up to saturation and beyond.

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 (1994, 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 (see Christov, 1994, 2005, 2019; Guignot et al. 2019). According to previous studies of Christov an approach with 4 ion interaction parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^ϕ), and varying in α_1 and 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 HNO₃-H₂O (Christov, 2005) and LiCl-H₂O (Lassin et al., 2015)}, 2-1 {such as NiCl₂-H₂O, CuCl₂-H₂O, MnCl₂-H₂O, CoCl₂-H₂O: (Christov, 1994, 1999, 2000); Ca(NO₃)₂-H₂O: (Lach et al., 2018); UO₂(NO₃)₂-H₂O: (Lassin et al., 2020), 1-2 {such as K₂Cr₂O₇-H₂O and Na₂Cr₂O₇-H₂O: (Christov, 2001)}, 3-1 {such as FeCl₃-H₂O: (Christov, 2004; Andre et al. 2013, 2019), and 3-2 {such as Al₂(SO₄)₃-H₂O, Cr₂(SO₄)₃-H₂O (Christov, 2002ab, 2003, 2019, 2020), and Fe₂(SO₄)₃-H₂O: (Christov, 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 $\{m(\text{sat})\}$, and in case of data availability: up to supersaturation.

As a next step, using the accepted new developed parameterizations, and experimentally determined molalities ($m(\text{sat})$) of the saturated binary solutions (Mikulin, 1968) we calculate the logarithm of the thermodynamic solubility product ($\ln K^\circ_{\text{sp}}$) of solid phases crystallizing from saturated binary solutions, according to:

$$\begin{aligned} K^\circ_{\text{sp}}(\text{NaF}) &= \gamma_{(\pm)}(\text{sat})^2 \cdot m(\text{sat})^2 \\ K^\circ_{\text{sp}}(\text{KF} \cdot 2\text{H}_2\text{O}) &= \gamma_{(\pm)}(\text{sat})^2 \cdot m(\text{sat})^2 \cdot a_w(\text{sat})^2 \end{aligned} \quad (1)$$

Ternary systems

Pitzer parameters (θ and ψ) for the ternary systems in which stoichiometric compounds crystallize, were determined from experimental data on the compositions of the saturated ternary solutions (see Christov, 1999, 2001, 2005, 2009a, 2009b; Christov and Moller, 2004, 2004b; Andre et al., 2019; Balarew et al., 1998, 1999; Park et al., 2009).

The choice of the parameters is based on the minimum deviation of the logarithm of the solubility product ($\ln K_{sp}^o$) for the whole crystallization curve of the component from its value for the binary solution. In addition, the $\ln K_{sp}^o$ value for the double salts crystallizing in the solutions has to be constant along the whole crystallization branch of the double salt. The solutions containing the same cations (e. g. LiCl-MgCl₂-H₂O and LiBr-MgBr₂-H₂O) or the same anions (e.g. NaCl-Na₂CrO₄-H₂O and KCl-K₂CrO₄-H₂O) have been simulated simultaneously in order to preserve the same value of the θ parameter. In this case we have varied the ψ values only.

The solubility isotherms of the ternary system at 25°C are calculated on the basis of the thermodynamic functions obtained. At phase and chemical equilibria of a given salt ($l_1A_1.l_2A_2.l_3A_3$) with its saturated solution, the following equation is applied:

$$\ln\{K_{sp}^o(l_1, l_2, l_3)\} = l_1 \ln a_1 + l_2 \ln a_2 + l_3 \ln a_3 = \text{constant}, \quad (2)$$

where a_1 , a_2 , and a_3 are the activities of the components A_1 , A_2 , and A_3 =H₂O in the saturated solution, and l_1 , l_2 , and l_3 denote the stoichiometric numbers in the salt. Then the solubility isotherm may be calculated as a geometric locus of points meeting condition (2). The eutonic of the ternary system is a point that satisfies two equations which describe the solubility isotherms of two solid phases, respectively. This eutonic represents the solution of

$$\ln\{K_{sp}^o(l_1, l_2, l_3; m_1, m_2)\} = \text{constant}' \quad (3)$$

$$\ln\{K_{sp}^o(l'_1, l'_2, l'_3; m_1, m_2)\} = \text{constant}''$$

Results and Discussions

Models for binary subsystems HF-H₂O, NaF-H₂O, and KF-H₂O

For HF-H₂O solutions the only available mean activity ($\gamma_{\pm}$) and osmotic (ϕ) coefficients data are those of Hammer and Wu (1972). Our preliminary modeling 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, in this study the model for HF-H₂O solutions have been parameterized on the basis of activity coefficients ($\gamma_{\pm}$) data of Hammer and Wu. To construct the model, we used different versions of standard molality-based Pitzer approach. It was established that for HF-H₂O solutions application of extended approach with 4 parameters (β^0 , β^1 , β^2 and C^ϕ) and variation of both (α_2 and α_2) terms (see paragraph 2) leads to the lowest values of standard model-experiment deviation up to 20 mol. kg⁻¹ in HF-H₂O (Christov, 2005, 2019). The resulting parameterization is given in Table 1. The extremely low β^1 value can be explained with the very low activity coefficients recommendations of Hammer and Wu (1972) even at low molality of HF-H₂O solutions. On Figure 1 we present a comparison of model calculated (heavy solid lines) mean activity coefficients (Fig. 1a) and osmotic coefficients (ϕ) (Fig. 1b) of HF in binary solutions HF-H₂O against molality at T = 25°C with osmotic (ϕ) coefficients data, and activity coefficients ($\gamma_{\pm}$) recommendations in

literature (symbols: Hammer and Wu (1972). Dashed-dotted lines represent the predictions of the reference model of Kim and Frederick (1988). A very good present model – experiment agreement has been obtained for activity coefficients ($\gamma_{\pm}$) up to 20 mol. kg⁻¹ HF-H₂O (Fig. 1a). According to $\gamma_{\pm}$ data and our model predictions the activity coefficients very sharply decrease with molality and at 1 mol. kg⁻¹ $\gamma_{\pm} = 0.0249$, at 5 mol. kg⁻¹ $\gamma_{\pm} = 0.0211$, and at 20 mol. kg⁻¹ $\gamma_{\pm} = 0.00275$. The reference model of Kim and Frederick (1988) predicts much higher activity coefficients than the data of Hammer and Wu (1972) for whole concentration range of data. Therefore, the model of Kim and Frederick cannot be used for solubility predictions in mixed HF systems.

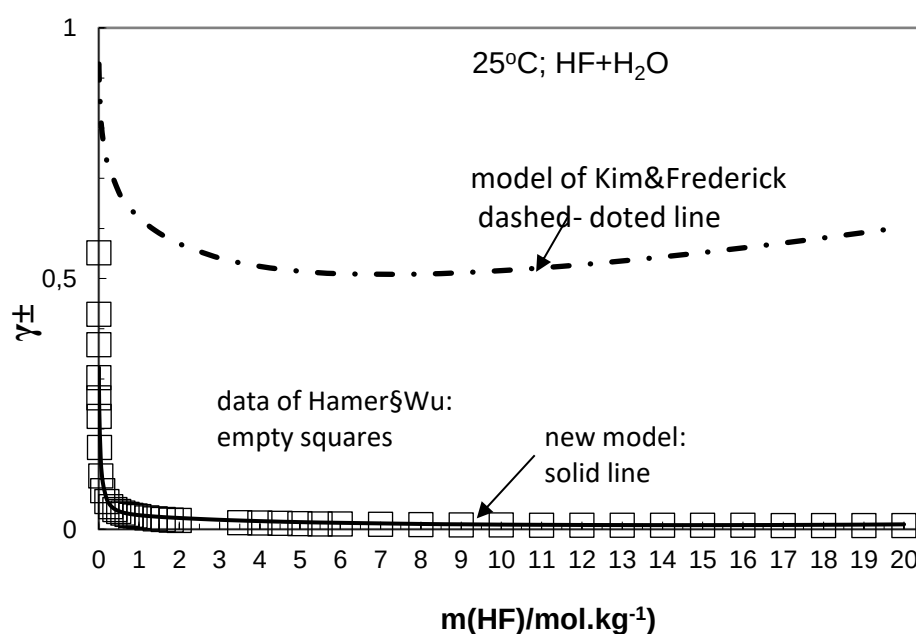
Table 1. Pitzer binary parameters for HF-H₂O at T = 25°C where σ is the standard deviation of the osmotic coefficients, and m(max) is the highest solution's molality of the experimental activity data used in parameterization

System	Ref. Models /This study/	α_1	α_2	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	$\beta^{(2)}$	σ	m (max)/ (mol.kg ⁻¹)	Activity data source
HF (aq)	K&F ^a	2	-	0.02212	0.40156	-0.00018	-	0.00305	20.0	Hamer&Wu (1972)
	this study	30	4.2	-0.060273	-471.901	0.003238	-14.34236	0.01178	20.0	Hamer&Wu (1972)

^aKim and Frederick (1988)

According to comparison presented on Fig. 1b the present model predicts lower osmotic coefficients values in the molality range from 0.4 mol.kg⁻¹ to 0.8 mol. kg⁻¹, and from 7 mol.kg⁻¹ to 17 mol.kg⁻¹, and higher from 0.9 mol.kg⁻¹ to 5.5 mol.kg⁻¹. The maximum ϕ difference between the model and experiment is approximately 0.1. It can be concluded that the main reason for the good $\gamma_{\pm}$ model – experiment agreement (Fig. 1a) and the pure ϕ model –experiment agreement (Fig. 1b) is mainly due on some inconsistency between ϕ data and $\gamma_{\pm}$ recommendations for HF-H₂O solutions, presented by Hammer and Wu (1972).

a)



b)

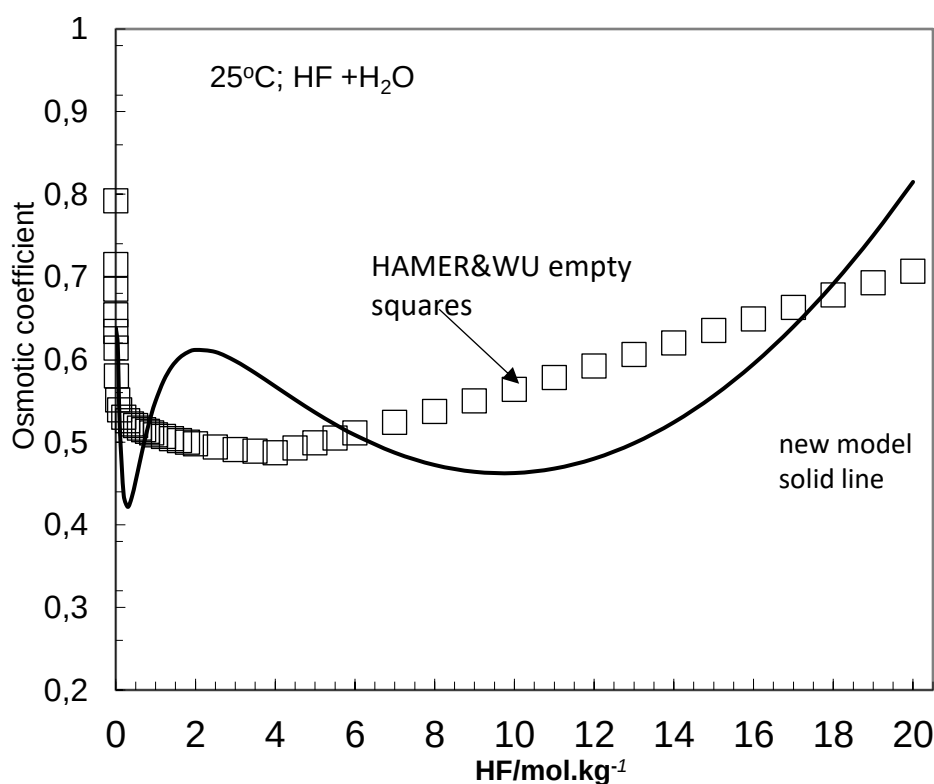


Figure 1. A comparison of model calculated (heavy solid lines) mean activity coefficients (Fig. 1a) and osmotic coefficients (ϕ) (Fig. 1b) of HF in binary solutions HF-H₂O against molality at $T = 25^\circ\text{C}$ with osmotic (ϕ) coefficients data, and activity coefficients ($\gamma_{\pm}$) recommendations in literature (symbols: Hammer and Wu (1972). Dashed-dotted line (Fig. 1a) represents the predictions of the reference model of Kim and Frederick (1988)

In previous study in ASN (Donchev et al., 2021) we developed well validated thermodynamic models for solution behavior and solid-liquid equilibrium for NaF-H₂O, and KF-H₂O systems from low to very high concentration (up to 17.5 mol.kg⁻¹ in KF-H₂O). Models are developed on the basis of Pitzer ion interactions approach. To parameterize models, we used all available raw experimental osmotic coefficients data (ϕ) for whole concentration range of solutions, and up to saturation point. To construct the models for NaF-H₂O, and KF-H₂O we applied extended approach with 4 parameters (β^0 , β^1 , β^2 and C^ϕ), with variation of α_2 term, and keeping $\alpha_1=2$ in fundamental Pitzer equations (see Christov, 1994, 1999, 2001; Donchev et al., 2021; Lassin et al., 2020 and paragraph 2). The predictions of developed models are in excellent agreement with experimental osmotic coefficients data, and with recommendations on activity coefficients in binary solutions. Thermodynamic solubility products (as $\ln K_{sp}^0$) of solid phases [NaF(cr), and KF.2H₂O(cr)] have been determined on the basis of evaluated model parameters and using experimental $m(\text{sat})$ solubility data (see Eqn. 3). The $\ln K_{sp}^0$ values for simple fluoride salts used in parameterization of mixed solutions are presented in Table 2.

Table 2. Model calculated values of logarithm of the thermodynamic solubility product, K_{sp}^0 , for fluoride solid phases crystallizing from saturated mixed solutions HF-NaF-H₂O and HF-KF-H₂O at $T = 25^\circ\text{C}$; $m(\text{sat})$ is the molality of saturated binary solutions NaF-H₂O and KF-H₂O

Formula	$m(\text{sat})/(\text{mol.kg}^{-1})$		$\ln K_{sp}^0$
	Calculated	Experimental	
NaF(cr)	1.00	1.00 ^a	-1.115
KF.2H ₂ O (cr)	17.5	17.5 ^a (16.68 ^b)	5.84 (6.1051 ^b)
KF.HF(cr)			-1.006
NaF.HF(cr); Model 1			-8.73
NaF.HF(cr); Model 2			-8.0

^a Mikulin, 1968; ^bEl Guendouzi&Faridi, 2020

Models for ternary systems HF-NaF-H₂O and HF-KF-H₂O

Pitzer parameters (θ and ψ) for the ternary systems in which stoichiometric compounds crystallize HF-NaF-H₂O and HF-KF-H₂O were determined from experimental data on the compositions of the saturated ternary solutions (see paragraph 2), i.e. on the basis of solubility approach. According to experimental solubility data, summarized in Zdanovskii et al. (2003) only solid phases with constant stoichiometric composition (simple and double salts) precipitate from saturated mixed solutions under study. The data for HF-NaF-H₂O system are given by Clark (1919) at 25°C, by Jehu and Hudleston (1924) at 20°C, and by Tananaev (1941) at 20°C. According to the data presented two solid phases precipitate in

ternary HF-NaF-H₂O system: NaF (cr) and NaF.HF(cr) at 20°C and 25°C. The composition of invariant point NaF (cr) + NaF.HF(cr) have been determined by Jehu and Hudleston (1924) and by Tananaev (1941).

The experimental data for HF-KF-H₂O system used in parameterization are from Clark (1919) at 25°C, and from Tananaev (1938a, 1938b) at 20°C (look also Zdanovskii (2003). According to the data presented two solid phases precipitate in this ternary system (KF.2H₂O (cr) and KF.HF(cr)) at 20°C and 25°C and up to high acid molality. The authors did not determine the composition of invariant point. Both sets of solubility data are close to each other at low acid concentration. Harvie et al. (1984) develop a standard temperature model for corresponding chloride (HCl-NaCl-H₂O, and HCl-KCl-H₂O) and sulfate (H₂SO₄-Na₂SO₄-H₂O and H₂SO₄-K₂SO₄-H₂O) systems with the same cations. Christov and Moller (2004) develop a T-variation (0-250°C) model for the same four chloride and sulfate H-Na and H-K ternary systems. We develop 2 models for HF-NaF-H₂O system. In model 1 we used a value for $\theta(\text{Na,H})$ from T-variable model of Christov and Moller (2004) adapted to 25°C and varied the $\psi(\text{Na,H,F})$ value only. In model 2 we used a value for $\theta(\text{Na,H})$ from 25°C model of Harvie et al. (1984) and varied the $\psi(\text{Na,H,F})$ value only. The model for HF-KF-H₂O system has been constructed using a value for $\theta(\text{K,H})$ from 25°C model of Harvie et al. (1984) and varied the $\psi(\text{K,H,F})$ value only. To evaluate $\psi(\text{Na,H,F})$ and $\psi(\text{K,H,F})$, to determine the logarithm of the solubility product ($\ln K_{sp}^o$) of precipitating from mixed solutions double salts (NaF.HF(cr) and KF.HF(cr)) and to build the theoretical phase diagrams we used the solubility approach described in paragraph 2. The calculated $\ln K_{sp}^o$ values for double salts are given in Table 2. The resulting mixing parameterization for HF-NaF-H₂O and HF-KF-H₂O systems is presented in Table 3.

Table 3. Pitzer mixing parameters $\theta(\text{MN})$ and $\psi(\text{MNX})$ for ternary fluoride systems HF-NaF-H₂O and HF-KF-H₂O at T = 25°C

System	$\theta(\text{MN})$	$\psi(\text{MNX})$
KF-HF-H ₂ O	0.005 [HMW]	-0.015
NaF-HF-H ₂ O; Model 1	0.03454 [C&M]	-0.012
NaF-HF-H ₂ O; Model 2	0.036 [HMW]	-0.012

^aHMW = Harvie et al. (1984); ^bC&M = Christov and Moller (2004a)

In Table 4 we compare model calculated (25°C) and experimental (20°C) composition of invariant points in ternary systems HF-NaF-H₂O and HF-KF-H₂O.

Table 4. Comparison between model calculated (25°C) and experimental (20°C: Jehu and Hudleston (1924), Tananaev (1941), Zdanovskii et al. (2003) composition ($\text{mol}\cdot\text{kg}^{-1}$) of invariant points in ternary systems HF-NaF-H₂O and HF-KF-H₂O

	m_{KF}	m_{NaF}	m_{HF}	Solid Phases
Calculated (25°C)	12.03-		0.46-	KF.2H ₂ O +KF.HF
Calculated (25°C): Model 1		0.951	0.357	NaF+NaF.HF
Calculated (25°C): Model 2		0.868	0.787	
Experimental (20°C) ^a		1.08	0.28	
Experimental (20°C) ^b		0.99	0.50	

^aJehu and Hudleston (1924); ^bTananaev (1941)

On Figures 2 and 3 we compare calculated (25°C; lines) and experimental (20°C, 25°C; symbols) solubility in the systems HF–NaF–H₂O and HF–NaF–H₂O up to maximum HF molality equals to 2 $\text{mol}\cdot\text{kg}^{-1}$. At higher acid molality the model predicts much higher solubility of double salts (NaF.HF(cr) and KF.HF(cr) for both mixed systems. According to the model - experiment comparison for binary system HF–H₂O given on Fig. 1 the main reason is the inconsistency between low and high molality osmotic coefficients data of Hammer and Wu (1972).

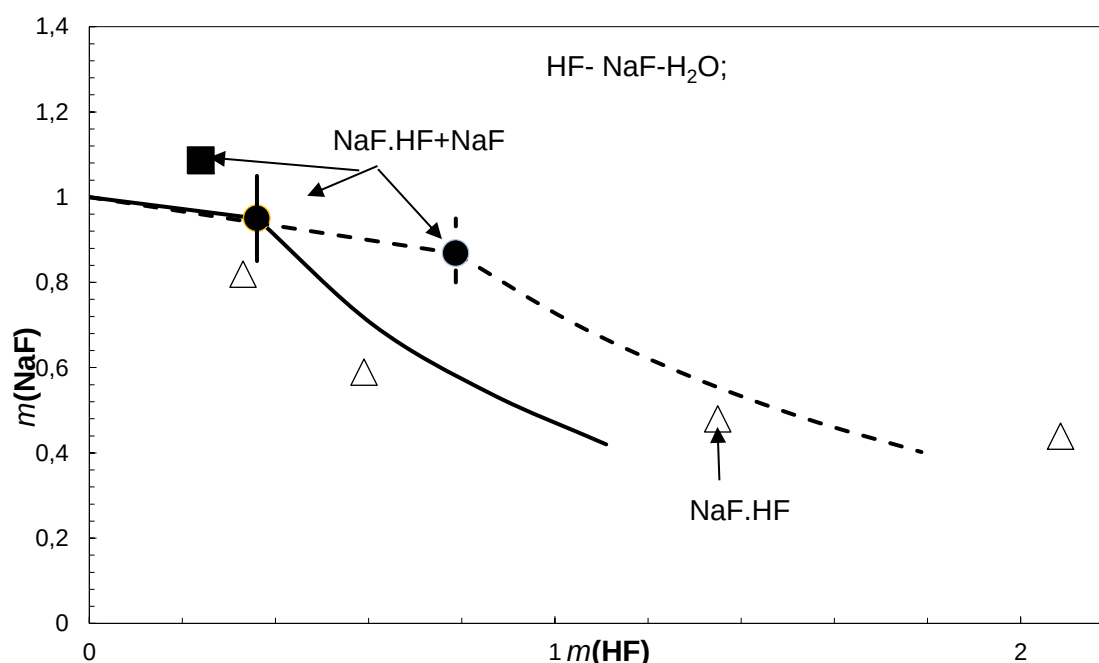


Figure 2. Calculated (25°C; solid line-Model 1; dashed line-Model 2) and experimental (20°C – symbols) solubility in the system HF –NaF–H₂O. Symbols: NaF.HF(cr) –open triangles. The experimental data are from Jehu and Hudleston (1924) at 20 °C (look also Zdanovskii (2003)). The closed circles represent the model calculated invariant point NaF(cr)+ NaF.HF(cr). The closed square represents the experimental invariant point NaF(cr)+ NaF.HF(cr) (Jehu and Hudleston, 1924)

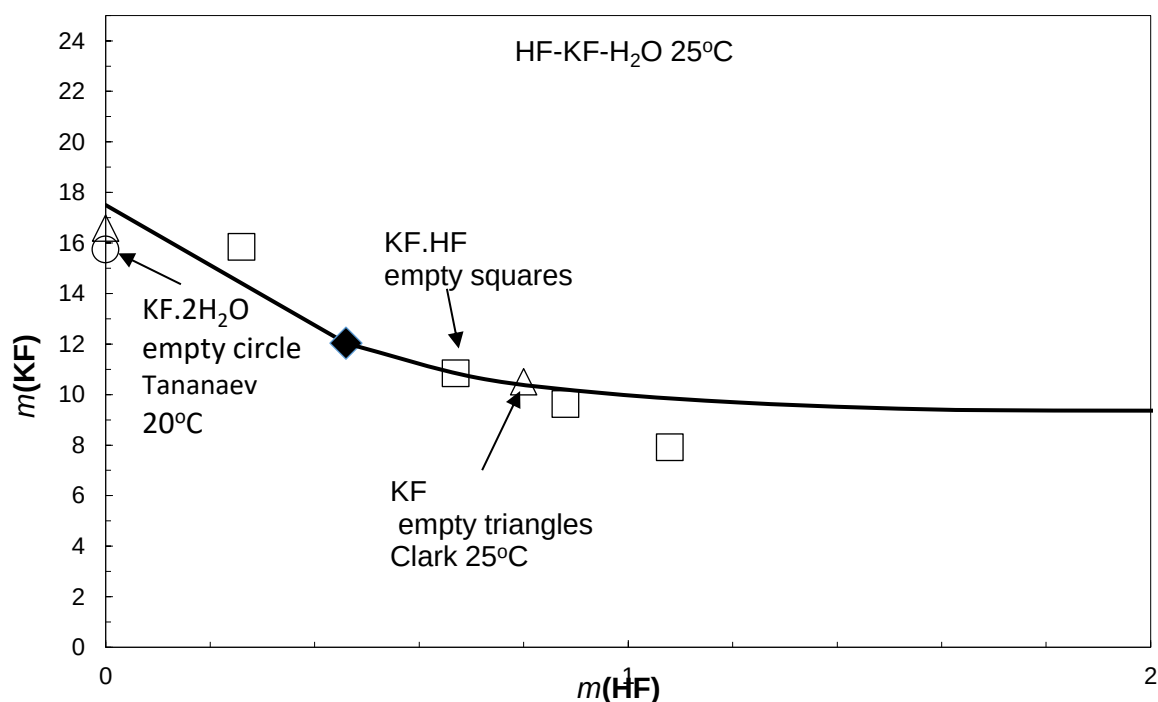


Figure 3. Calculated (25°C –solid line) and experimental (20°C, 25°C – symbols) solubility in the system HF –KF–H₂O. Symbols: KF.HF(cr) – open squares, KF.2H₂O(cr) – open circle and KF(cr) – open triangles. The experimental data are from Clark (1919) at 25°C, and from Tananaev (1938) at 20°C (look also Zdanovskii (2003)). The closed diamond represents the the model calculated invariant point KF.2H₂O(cr)+ KF.HF(cr)

These not a correct raw data for binary HF–H₂O system obviously are the main reason for concentration restriction of mixed HF models presented here. In the meantime, El Guendouzi et al. (2019) and Elmaazouzi et al. (2022) reported a new set of data for binary HF–H₂O solutions. In our next study we will use these data to develop a new HF–H₂O model, and consequently construct not HF –high molality restricted model for quaternary system HF–NaF–KF–H₂O.

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