

Shumen University “ Episkop Konstantin Preslavski”

Faculty of Natural Sciences

Dept. Chemistry

Tsvetan Vasilev Tsenov

Title of Dissertation: ”Thermodynamics of electrolyte solutions.
Experimental and modeling studies”

ABSTRACT OF PhD DISSERTATION

Scientific area: 4. Natural Sciences, Mathematics and Informatics

Professional sub-area: 4.2. Chemical Sciences

Professional direction: Inorganic Chemistry

Scientific Advisors: Prof. Christomir Christov, D.Sci.

Assoc. Prof. Romyana Yankova-Avramova, PhD

SHUMEN

2024

The dissertation has been discussed on 08.02.2024 on the meeting of Chemistry department, Fac. Nat. Sci, Shumen University, and directed to the public defense in front of scientific Jury. The public defense of dissertation will be held at 14h. on 29.04.2024 in the 309 auditorium, hall 1 of Shumen University.

The dissertation contains 127 standard pages, incl. 23 Tables, and 45 figures. The reference list includes 105 references. All materials are deposited in room 107, hall 1 of Shumen University.

Members of Scientific JURY:

- 1) Prof. Stoyan Karakashev, PhD- Shumen University “Episkop Konstantin Preslavski”
- 2) Prof. Tsvetoslava Ignatova-Ivanova, PhD- Shumen University “Episkop Konstantin Preslavski”
- 3) Prof. Panteley Denev, D.Sci. - University of Food Technology-Plovdiv
- 4) Assoc. Prof. Blagovesta Midyurova, PhD- Burgas University "Prof. Dr. Assen Zlatarov"
- 5) Assoc. Prof. Aleksandar Dimitrov, PhD- Burgas University "Prof. Dr. Assen Zlatarov"

Acknowledgement

The work of my scientific advisor Prof. Christomir Christov on dissertation was supported by the European Regional Development Fund within the Operational Programme “Science and Education for Smart Growth 2014-2020” under the Project CoE “Universities for Science, Informatics and Technologies in e-Society (UNITe) BG05M2OP001-1.001-0004”. The work on dissertation was also partially supported by the Shumen University Research Fund (projects RD 21-244 /28.02.2019, Project No. RD 08-124/03.02.2020, Project No. RD 08-131/04.02.2021, and Project № RD -08-160/04.03.2022).

The main purpose of research activity summarized in dissertation is to develop Pitzer formalism-based concentration well validated ThermoDynamic DataBase (TDDB), which accurately describe solution properties and stable and metastable phase equilibrium in binary and mixed systems. The models, developed here are not concentration restricted. The developed TDDB consider all experimentally identified solid phases, which precipitate from saturated and supersaturated solutions.

The **major tasks** of dissertation are as follow:

1. Development, validation and application of new thermodynamic models for solution behavior and solid-liquid equilibrium for 24 binary systems at 25°C:
 - 1a. For 8 binary acetate systems of the type 1-1: $\text{LiCH}_3\text{COO-H}_2\text{O}$, $\text{NaCH}_3\text{COO-H}_2\text{O}$, $\text{KCH}_3\text{COO-H}_2\text{O}$, $\text{RbCH}_3\text{COO-H}_2\text{O}$, $\text{CsCH}_3\text{COO-H}_2\text{O}$ и $\text{TlCH}_3\text{COO-H}_2\text{O}$, and of the type 2-1: $\text{Ba}(\text{CH}_3\text{COO})_2\text{-H}_2\text{O}$ и $\text{Mg}(\text{CH}_3\text{COO})_2\text{-H}_2\text{O}$;
 - 1b. For binary rubidium systems $\text{RbCl-H}_2\text{O}$, $\text{RbBr-H}_2\text{O}$; and $\text{Rb}_2\text{SO}_4\text{-H}_2\text{O}$;
 - 1c. For binary cesium systems $\text{CsCl-H}_2\text{O}$, $\text{CsBr-H}_2\text{O}$ and $\text{Cs}_2\text{SO}_4\text{-H}_2\text{O}$;
 - 1d. For 10 binary selenate systems of the type 1-2: $\text{Li}_2\text{SeO}_4\text{-H}_2\text{O}$, $\text{Na}_2\text{SeO}_4\text{-H}_2\text{O}$, $(\text{NH}_4)_2\text{SeO}_4\text{-H}_2\text{O}$, $\text{K}_2\text{SeO}_4\text{-H}_2\text{O}$, $\text{Rb}_2\text{SeO}_4\text{-H}_2\text{O}$, $\text{Cs}_2\text{SeO}_4\text{-H}_2\text{O}$; and of the type 2-2: $\text{MgSeO}_4\text{-H}_2\text{O}$, $\text{CoSeO}_4\text{-H}_2\text{O}$, $\text{NiSeO}_4\text{-H}_2\text{O}$, $\text{ZnSeO}_4\text{-H}_2\text{O}$;
 - 1e. Determination of important thermodynamic characteristics (the thermodynamic solubility products ($\ln K^{\circ}_{\text{sp}}$), the Deliquescence Relative Humidity (DRH), and standard molar Gibbs Energy of formation ($\Delta_f G^{\circ}_m$)) of solid phases, precipitating from saturated binary solutions.
2. Development, validation and application of new thermodynamic models for solution behavior and solid-liquid equilibrium for 10 mixed systems at 25°C:
 - 2a. For 3 rubidium systems of the type 1-1+2-1 $\text{RbCl-MgCl}_2\text{-H}_2\text{O}$, $\text{RbBr-MgBr}_2\text{-H}_2\text{O}$ and of the type 1-2+2-2 $\text{Rb}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$;
 - 2b. For 3 cesium systems of the type 1-1+2-1 $\text{CsCl-MgCl}_2\text{-H}_2\text{O}$, $\text{CsBr-MgBr}_2\text{-H}_2\text{O}$, and of the type 1-2+2-2 $\text{Cs}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$;
 - 2c. For 4 selenate mixed systems of the type 1-2+2-2 $\text{Na}_2\text{SeO}_4\text{-CdSeO}_4\text{-H}_2\text{O}$, $\text{Na}_2\text{SeO}_4\text{-FeSeO}_4\text{-H}_2\text{O}$, $(\text{NH}_4)_2\text{SeO}_4\text{-FeSeO}_4\text{-H}_2\text{O}$ и $\text{K}_2\text{SeO}_4\text{-FeSeO}_4\text{-H}_2\text{O}$;
 - 2d. Determination of important thermodynamic characteristics (the thermodynamic solubility products ($\ln K^{\circ}_{\text{sp}}$), standard molar Gibbs Energy of synthesis reaction from simple

salts ($\Delta_r G^{\circ}_m$), and standard molar Gibbs Energy of formation ($\Delta_f G^{\circ}_m$) of double salts, precipitating from saturated ternary solutions.

3. Experimental laboratory studies include:

3a. Determination of solubilities in the mixed system LiBr-CaBr₂-H₂O at 35°C and 50°C.

3b. Synthesis and characterization of selenate solid phases Na₂SeO₄·H₂SeO₃ and Na₂Cd(SeO₄)₂·2H₂O

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) 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. 1995ab, Lach et al., 2018; Guignot et al., 2019; Lassin et al., 2020; Park et al. 2009; Kolev et al., 2013; Ojkova et al., 1999; Donchev and Christov, 2020; Donchev et al., 2021; Christov, 1996a, 1998, 1999, 2001, 2002ab, 2003abc, 2004, 2005; Christov et al., 1998), 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).

Methodology

The models for binary and mixed systems described here have been developed and tested on the basis of Pitzer's semi-empirical equations (Pitzer, 1973). The specific interaction approach for describing electrolyte solutions to high concentration introduced by Pitzer (1973) represents a significant advance in physical chemistry that has facilitated the construction of accurate computer thermodynamic models. Pitzer approach has found extensive use in the modeling of

the thermodynamic properties of aqueous electrolyte solutions. It was showed that this approach could be expanded to accurately calculate solubilities in binary and complex systems , 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; Lach et al., 2018; Park et al. 2009; Christov, 1998, 1999, 2003ab, 2005), and from 0° to 290°C (Christov and Moller, 2004; Moller et al, 2006; Christov, 1995a, 1996a, 2005, 2007, 2009, 2012, 2020). Several extensive parameter databases have been reported. These include: 25°C database of Pitzer & Mayorga (P&M) (1973, 1974), of Kim & Frederick (K&F) (1988), the most widely used database 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 & Moller, 2004; Moller et al., 2006; Christov, 2009ab).

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 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 ($\beta^{(0)}, \beta^{(1)}, C^\varphi$). The Pitzer's equations are described and widely discussed in the literature (Harvie et al., 1984; Moller et al., 2006; Christov and Moller, 2004a; Christov, 2005). 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, 2003a,b, 2005).

Models for binary systems

Pitzer and Mayorga (1973) did not present analysis for any 2-2 (e.g. MgSO₄-H₂O) or higher {e.g. 3-2: Al₂(SO₄)₃-H₂O} electrolytes. In their next study (Pitzer & 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, 2003a) and selenate (Christov, 2003a; Christov et al., 1998; Barkov et al., 2001) 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 γ_{\pm} vs. m dependence, and to account strong association reactions at high molality, Christov (1996b, 1998ab, 1999, 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. According to previous studies of 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 $\text{HNO}_3\text{-H}_2\text{O}$, $\text{LiNO}_3\text{-H}_2\text{O}$ (Donchev and Christov, 2020), and $\text{LiCl-H}_2\text{O}$ (Lassin et al., 2015)}, 2-1 {such as $\text{NiCl}_2\text{-H}_2\text{O}$, $\text{CuCl}_2\text{-H}_2\text{O}$, $\text{MnCl}_2\text{-H}_2\text{O}$, $\text{CoCl}_2\text{-H}_2\text{O}$: (Christov and Petrenko, 1996; Christov, 1996b, 1999); $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$: (Lach et al., 2018); 1-2 {such as $\text{Na}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{O}$ and $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{O}$: (Christov, 1998, 2001)}, 3-1 {such as $\text{FeCl}_3\text{-H}_2\text{O}$: (Christov, 2005), and 3-2 {such as $\text{Al}_2(\text{SO}_4)_3\text{-H}_2\text{O}$, $\text{Cr}_2(\text{SO}_4)_3\text{-H}_2\text{O}$, and $\text{Fe}_2(\text{SO}_4)_3\text{-H}_2\text{O}$: (Christov, 2001, 2002, 2003, 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.

Models for mixed systems

In this study we developed a model for 10 mixed systems. Models for mixed systems are developed on the basis of solubility approach (Harvie et al., 1984; Christov 2009ab; Park et al., 2009). The Pitzer mixing ion interaction parameters (θ and ψ) for the systems have been evaluated on the basis of the experimental data on the compositions of the saturated ternary solutions, i.e. using “solubility approach”(Harvie et al., 1984; Christov, 1995a, 1996ab, 1998, 1999, 2005, 2012). The developed and validated here parameterization for binary selenate, rubidium and cesium systems have been used without adjustment to develop a model for mixed systems. The choice of the mixing 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 selenate, rubidium and cesium double salts crystallizing from the saturated ternary solutions has to be constant along the whole crystallization branch of the double salt.

Results and discussion

Model parameterization and validation of models for binary systems

In this study we developed new thermodynamic models for solution behavior and solid-liquid equilibrium in 8 binary acetate systems from low to very high concentration at 25°C. 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 acetate solutions under study are given in Hammer and Wu (1972) (for 1-1 systems), Mikulin (1968), and Robinson and Stokes (1965). Reference ϕ vs. m data sets of Mikulin (1968), and Robinson and Stokes (1965) are in a good agreement. However, the data of Mikulin (1968) cover the whole molality range of unsaturated and saturated solutions. In this study we parameterize the models using 1) all data of Mikulin (1968) for whole molality range of unsaturated solutions from 0.1 m to $m(\max)$, 2) the data points at saturation ($\phi(\text{sat})$) (from Mikulin, 1968), and 3) low molality experimental and recommended data of Hammer and Wu (1972) (for 1-1 acetate systems). In parameterization process we used the value of Debye-Hückel term (A^ϕ) from Christov (2007,2009,2012) (A^ϕ) = 0.39147). Following the parameterization scheme described above the model for all acetate solutions is parameterized using two different approaches: (I) standard for N-1 electrolytes (N=1, 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 $\alpha_2 = 0.0$, 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. 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 all acetate systems under study we construct a model on the basis of extended approach (II), and using different combinations of "alfa" values (see the table below)

Table 1. A comparison of Pitzer ion interaction parameters for binary acetate systems Li(CH₃COO) (aq), Na(CH₃COO) (aq), K(CH₃COO) (aq), Cs(CH₃COO) (aq), Rb(CH₃COO) (aq), Tl(CH₃COO) (aq), Ba(CH₃COO)₂ (aq), Mg(CH₃COO)₂ (aq), calculated in this study and those given in literature. $m(\max)$ = maximum molality of experimental data used in parametrization (mol.kg⁻¹); σ = standard deviation of experimental data for osmotic coefficients; n = number of experimental data-points used in parametrization, given in branches.

System	Ref. Models /This study/model No.	α_1	α_2	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	$\beta^{(2)}$	σ	m (max)/ (mol.kg ⁻¹)	Activity data (ϕ) Source
1-1 Systems										
Li(CH ₃ COO) (aq)	K&F ^a	2	-	0.11215	0.20243	-0.00519	-	0.00117	4	Hamer&Wu (1972)
	P&M ^b	2	-	0.1124	0.2483	-0.00525	-	0.001	4	Robinson&Stokes (1965)
	This study (accepted)	2	-1	0.1101621	0.2526717	-0.005976593	0.0006792136	0.0003974	9	Mikulin (1968) (n=24)
Na(CH ₃ COO) (aq)	K&F ^a	2	-	0.13723	0.34195	-0.00474	-	0.00096	3.5	Hamer&Wu (1972)
	P&M ^b	2	-	0.1426	0.3237	-0.00629	-	0.001	3.5	Robinson&Stokes (1965)
	This study (accepted)	2	1	0.1145735	0.1737538	-0.003332250	0.1261344	0.0003667	8	Mikulin (1968) (n=24)
K(CH ₃ COO) (aq)	K&F ^a	2	-	0.15283	0.35513	-0.00432	-	0.00087	3.5	Hamer&Wu (1972)
	P&M ^b	2	-	0.1587	0.3251	-0.00660	-	0.001	3.5	Robinson&Stokes (1965)
	This study (accepted)	2	-1	0.1568094	0.3276846	-0.007273526	0.0004604949	0.00259	25	Mikulin (1968) (n=41)
Rb(CH ₃ COO) (aq)	K&F ^a	2	-	0.16296	0.32918	-0.00561	-	0.00062	3.5	Hamer&Wu (1972)
	P&M ^b	2	-	0.1622	0.3353	-0.00551	-	0.001	3.5	Robinson&Stokes (1965)
	This study (accepted)	2.62	0.02	-2.247348	0.2646586	0.002146084	2.478809	0.0016081	40	Mikulin (1968) (n=48)
Cs(CH ₃ COO) (aq)	K&F ^a	2	-	0.17144	0.32896	-0.00793	-	0.00063	3.5	Hamer&Wu (1972)
	P&M ^b	2	-	0.1628	0.3605	-0.00555	-	0.001	3.5	Robinson&Stokes (1965)
	This study (accepted)	-0.8	1	0.1121867	0.0001087	-0.002520496	0.2873556	0.0043650	53	Mikulin (1968) (n=47)
	K&F ^a	2	-	0.00878	-0.04105	-0.00153	-	0.00215	6	Hamer&Wu (1972)

Tl(CH ₃ COO) (aq)	P&M ^b	2	-	0.0082	0.0131	-0.00127	-	0.001	6	Robinson&Stokes (1965)
	This study(accepted)	2	1	0.02670215	0.1311124	-0.003260541	-0.09122355	0.0002064	6	Mikulín (1968) (n=23)
Mg(CH ₃ COO) ₂ (aq)	K&F ^a	2	-	0.22930	2.04167	-0.01460	-	0.00370	4	Robinson&Stokes (1959)
	This study (accepted)	2	1	0.111212	-0.279428	0.000802	0.714664	0.002513	6	Mikulín (1968) (n=21)
Ba(CH ₃ COO) ₂ (aq)	K&F ^a	2	-	0.28725	2.87507	-0.04539	-	0.00663	3.5	Robinson&Stokes (1959)
	This study (accepted)	2	1	-0.013209	-1.441129	0.005192	1.634772	0.002005	5	Mikulín (1968) (n=18)

a- Kim and Frederlck, 1988.

b- Pitzer and Mayorga, 1973

The resulting models fits the data up to extremely high concentration: up to 40 m in RbCH₃COO-H₂O, and up to 53 m in CsCH₃COO-H₂O) with sigma values, which is less than the sigma values of models of Pitzer and Mayorga (1973), and of Kim and Frederick (1988). Excellent new/accepted models (heavy solid line) – experiment (symbols) agreement has been obtained for all binary systems and from low and up to very high molality (see Fig. 1). It should be noted that reference models presented on Fig. 1 by dashed, and dashed-dotted li (Kim and Frederick (1988), Pitzer and Mayorga (1973) have been constructed on the basis of standard Pitzer approach with 3 interaction parameters. Therefore, these models cannot reproduce well the experimental data (Fig. 1). The models for acetate binary systems under study are also validated by comparison with recommendations given in literature on the mean activity coefficients (γ_{\pm}). These recommendations on γ_{\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, show an excellent agreement from low to very high concentrations (Fig.1).

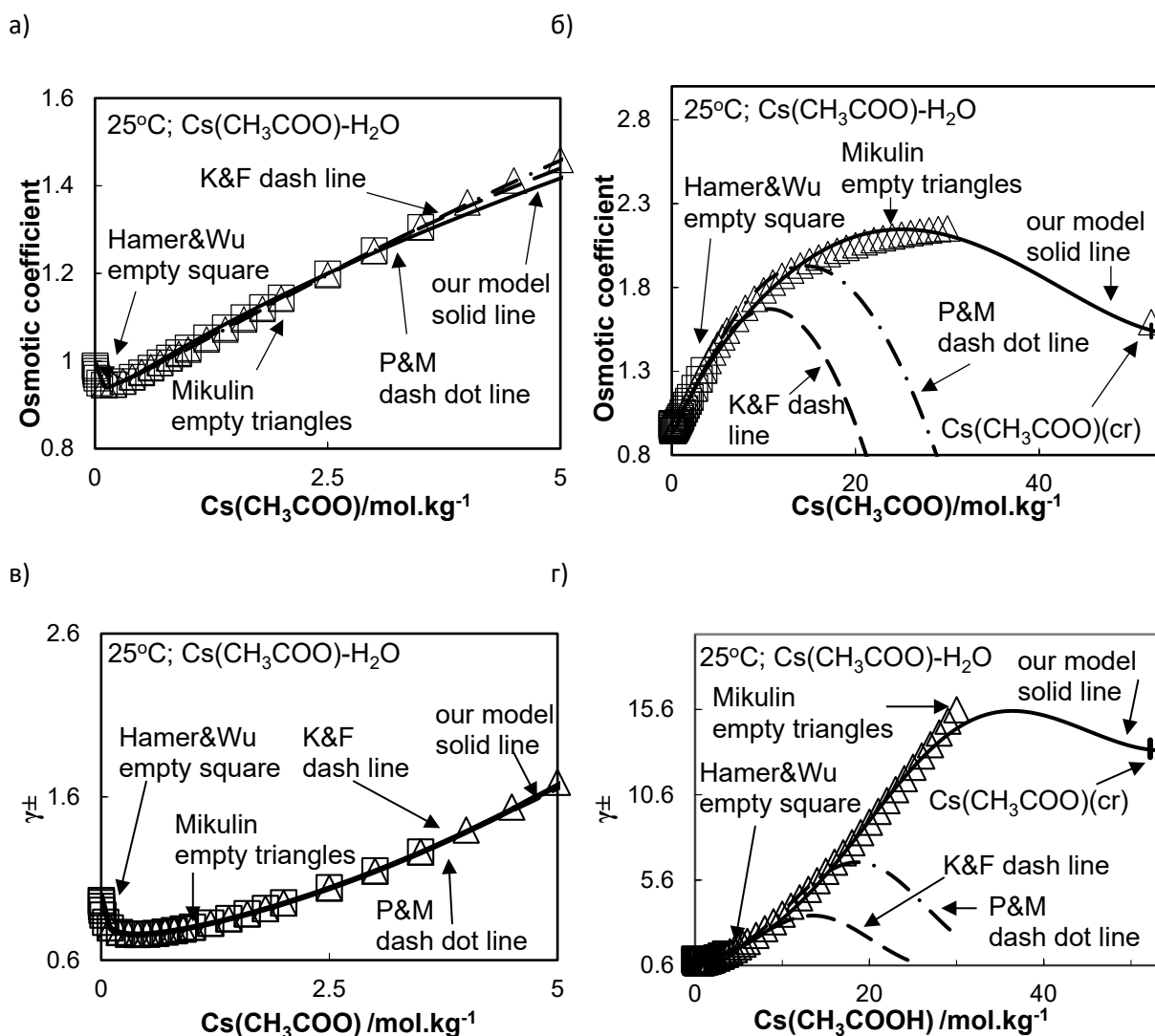


Fig. 1. Comparison of model calculated (lines) osmotic coefficients (ϕ) of $\text{CsCH}_3\text{COO-H}_2\text{O}$ and mean activity coefficients at $T = 25^\circ\text{C}$, with recommendations in literature (symbols). An enlargement of the low molality corner is also given. Heavy solid lines represent the predictions of the developed in this study and accepted model. Dashed-dotted, dashed and light solid lines represent the predictions of the reference models of Kim and Frederick (K&F) (1988), of Pitzer and Mayorga (P&M) (1973). The molality of stable crystallization of solid phases ($m(\text{sat})$) is given on figures by vertical lines.

In this study we also validated the previously developed models for 3 binary rubidium systems $\text{RbCl-H}_2\text{O}$, $\text{RbBr-H}_2\text{O}$; and $\text{Rb}_2\text{SO}_4\text{-H}_2\text{O}$, for 3 binary cesium systems $\text{CsCl-H}_2\text{O}$, $\text{CsBr-H}_2\text{O}$ and $\text{Cs}_2\text{SO}_4\text{-H}_2\text{O}$ and for 10 binary selenate systems $\text{Li}_2\text{SeO}_4\text{-H}_2\text{O}$, $\text{Na}_2\text{SeO}_4\text{-H}_2\text{O}$, $(\text{NH}_4)_2\text{SeO}_4\text{-H}_2\text{O}$, $\text{K}_2\text{SeO}_4\text{-H}_2\text{O}$, $\text{Rb}_2\text{SeO}_4\text{-H}_2\text{O}$, $\text{Cs}_2\text{SeO}_4\text{-H}_2\text{O}$, $\text{BaSeO}_4\text{-H}_2\text{O}$, $\text{SrSeO}_4\text{-H}_2\text{O}$, $\text{CaSeO}_4\text{-H}_2\text{O}$, and $\text{MgSeO}_4\text{-H}_2\text{O}$.

H₂O, K₂SeO₄-H₂O, Rb₂SeO₄-H₂O, Cs₂SeO₄-H₂O; MgSeO₄-H₂O, CoSeO₄-H₂O, NiSeO₄-H₂O, ZnSeO₄-H₂O. The models of Balarew et al. (1993) for RbCl-H₂O, RbBr-H₂O, CsCl-H₂O, CsBr-H₂O, of Palmer et al. (2002) for Rb₂SO₄-H₂O and Cs₂SO₄-H₂O, of Ojkova et al. (1998) for Li₂SeO₄-H₂O, of Christov et al. (1998) for Na₂SeO₄-H₂O, of Ojkova et al. (1999) for (NH₄)₂SeO₄-H₂O, K₂SeO₄-H₂O, of Barkov et al (2003) for Rb₂SeO₄-H₂O, of Barkov et al (2001) for Cs₂SeO₄-H₂O, and of Christov (1997) for MgSeO₄-H₂O, CoSeO₄-H₂O, NiSeO₄-H₂O, and ZnSeO₄-H₂O are in excellent agreement with experimental data on osmotic coefficients (ϕ) and on mean activity coefficients for whole concentration range of solutions up to saturation.

In this study we determine the thermodynamic solubility products ($\ln K_{sp}^{\circ}$), the Deliquescence Relative Humidity (DRH), and standard molar Gibbs Energy of formation ($\Delta_f G_m^{\circ}$) of 24 solid acetate, rubidium, cesium and selenate phases, precipitating from saturated binary solutions. These thermodynamic properties have been determined on the basis of evaluated binary parameters and using experimental $m(\text{sat})$ solubility data. The calculated DRH and $\Delta_f G_m^{\circ}$ values are compared with recommendations given in literature. The model calculations for acetate solids are given in Table 2.

Solid phase	$m^s(\text{mol.kg}^{-1})$		$\ln K_{sp}^{\circ}$	DRH(%)		$\Delta_f G_m^{\circ} / (\text{kJ.mol}^{-1})$		
	Exp. ^a	Calc.	Calc.	Calc.	Mikulin ^a (1968)	Calc. ^c	Wagman et al ^b (1982)	Mikulin ^a (1968)
Li(CH ₃ COO).2H ₂ O(cr)	6.79	6.79	3.4669	72.81	72.70	-1128.28	-	- 1135.16
Na(CH ₃ COO).3H ₂ O(cr)	6.1	6.1	3.4977	73.46	73.5	-1333.93	-1328.6	- 1340.34
K(CH ₃ COO).1.5H ₂ O(cr)	23.8	23.8	7.7063	21.84	22.5	-989.17	-	- 997.26
Rb(CH ₃ COO)(cr)	39.2	39.2	11.9479	9.77	~ 10	- 623.67	-	- 622.12
Cs(CH ₃ COO)(cr)	52.2	52.2	13.0764	5.48	~ 5	-628.916	-	-
Mg(CH ₃ COO) ₂ .4H ₂ O(cr)	4.62	4.62	2.5138	72.47	72.9	-2135.704	-	- 2149.40
Ba(CH ₃ COO) ₂ .H ₂ O(cr)	3	3	0.6006	87.33	87.4	-1535.03	-	- 1546.82

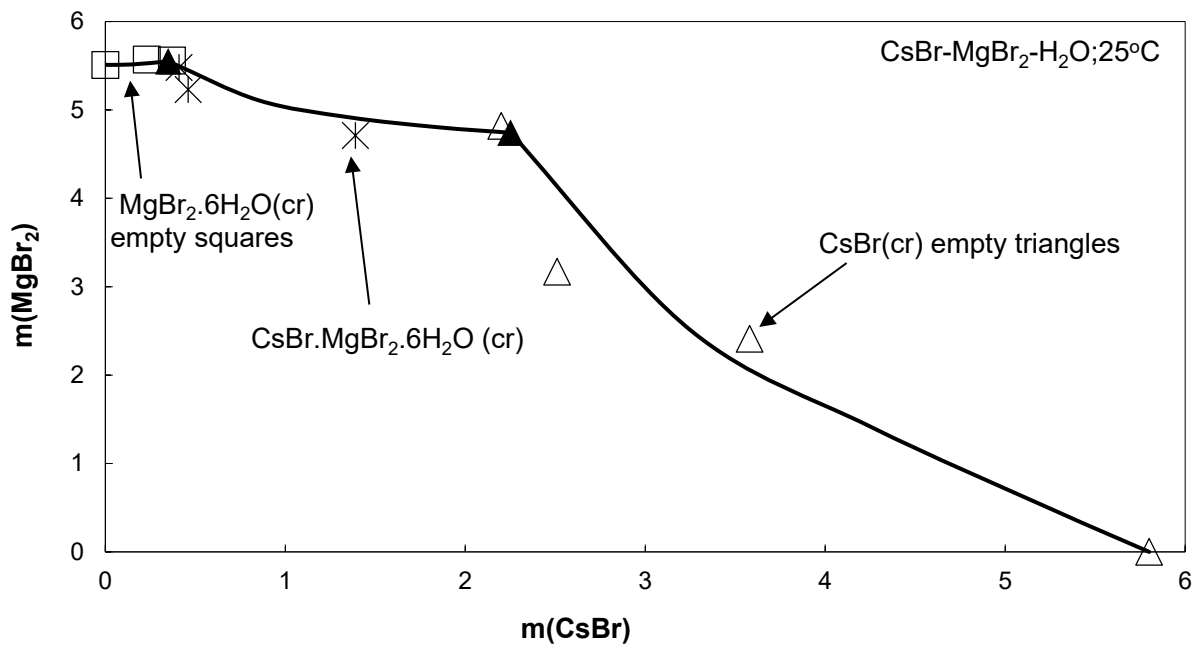
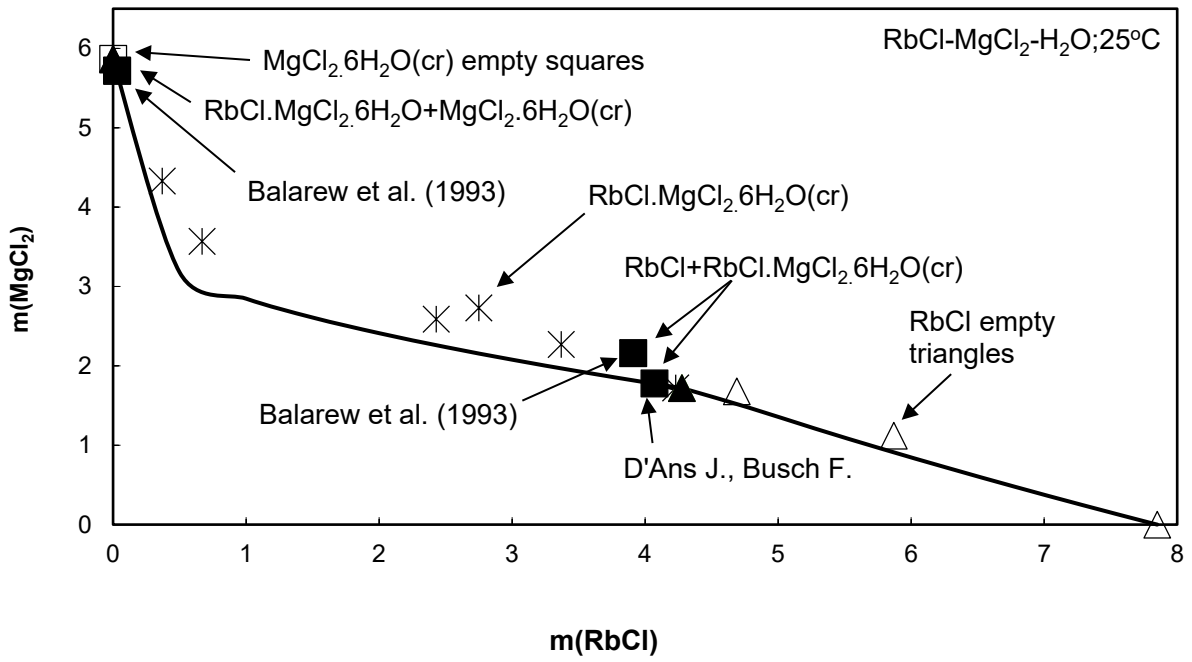
a- Mikulin G., 1968.

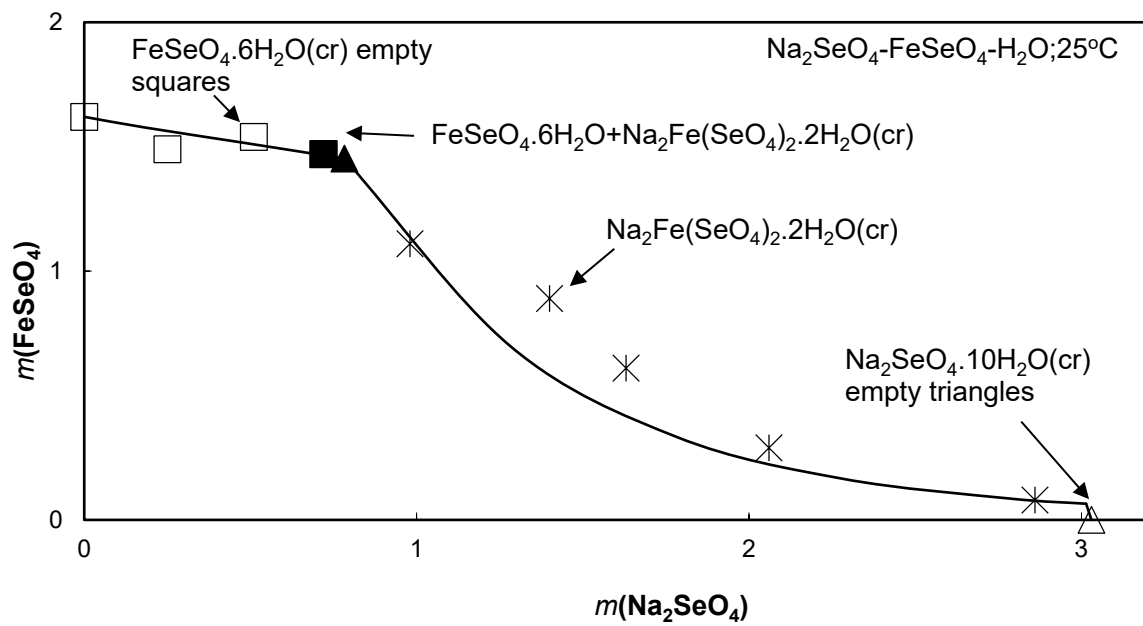
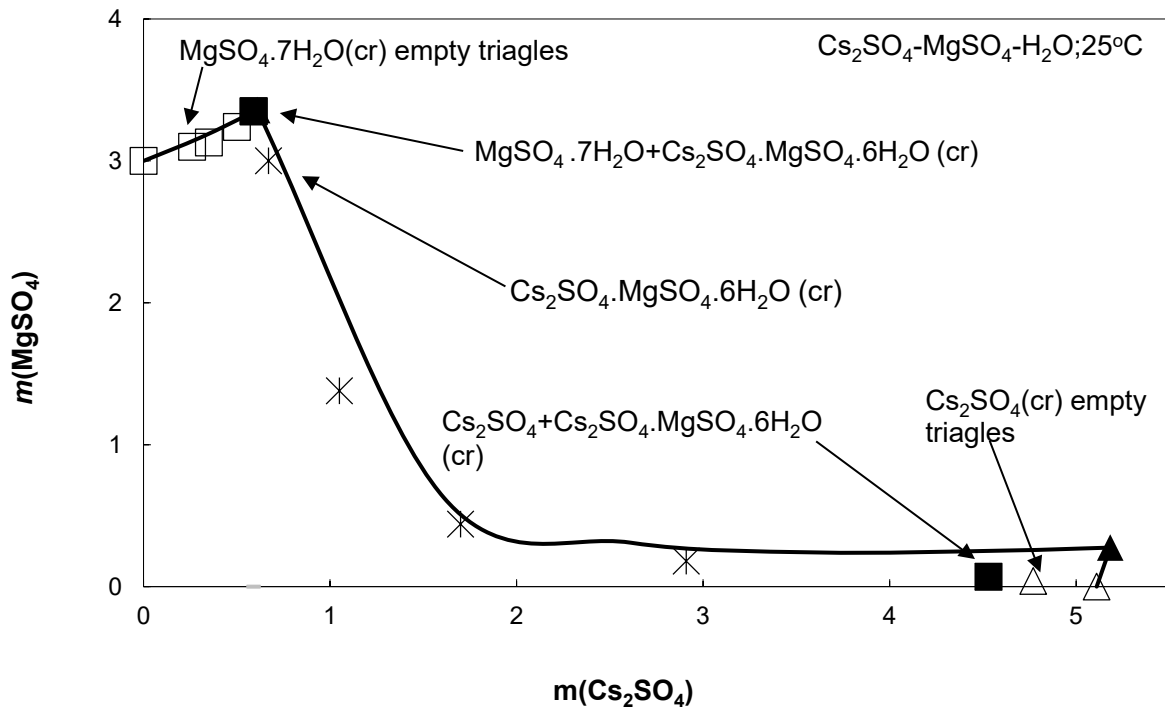
b- Wagman D., Evans W., Parker V., Schumm R., Halow I., Bayler S., Churney K., Nutall R., 1982.

c- $\Delta_f G_m^{\circ}$ are calculated using the data from Wagman et al. (1982) for chemical potential of ions in solutions.

Models for mixed systems

In this study we developed a model for for 10 mixed systems at 25°C: for 3 rubidium systems RbCl-MgCl₂-H₂O, RbBr-MgBr₂-H₂O, and Rb₂SO₄-MgSO₄-H₂O; for 3 cesium systems CsCl-MgCl₂-H₂O, CsBr-MgBr₂-H₂O, and Cs₂SO₄-MgSO₄-H₂O; and for 4 selenate mixed systems Na₂SeO₄-CdSeO₄-H₂O, Na₂SeO₄-FeSeO₄-H₂O, (NH₄)₂SeO₄-FeSeO₄-H₂O and K₂SeO₄-FeSeO₄-H₂O. The Pitzer mixing ion interaction parameters (θ and ψ) for the systems have been evaluated on the basis of the experimental data on the compositions of the saturated ternary solutions, i.e. using “solubility approach”(Harvie et al., 1984; Christov, 1995a, 1996ab, 1998, 1999, 2005, 2012). The developed and validated here parameterization for binary selenate systems Na₂SeO₄-H₂O, (NH₄)₂SeO₄-H₂O and K₂SeO₄-H₂O have been used without adjustment to develop a model for mixed systems. The parametrization for CdSO₄-H₂O (Pitzer and Mayorga, 1974) and FeSO₄-H₂O (Christov, 2004) have been approximated to describe activities in CdSeO₄-H₂O and FeSeO₄-H₂O systems and have been used in development models for selenate mixed systems. The validated here parameterization for binary rubidium and cesium systems RbCl-H₂O, RbBr- H₂O, Rb₂SO₄- H₂O; CsCl-H₂O, CsBr-H₂O, and Cs₂SO₄-H₂O have been used without adjustment to develop a model for mixed systems. Models for magnesium binary systems MgCl₂-H₂O, MgBr₂-H₂O, and MgSO₄-H₂O are taken from Christov (2009), Christov (2012) and Christov (2005), respectively. The solubility data for RbCl-MgCl₂-H₂O, RbBr-MgBr₂-H₂O, CsCl-MgCl₂-H₂O, CsBr-MgBr₂-H₂O are taken from Balarew et al. (1993) and Zdanovskii et al. (2003) and for sulphate Rb₂SO₄-MgSO₄-H₂O, and Cs₂SO₄-MgSO₄-H₂O are from Zdanovskii et al. (2003). The mixed solution models are developed using the reference solubility data from Mihov (2022) for Na₂SeO₄-FeSeO₄-H₂O, (NH₄)₂SeO₄-FeSeO₄-H₂O and K₂SeO₄-FeSeO₄-H₂O systems, and from Ojkova and Mihov (1992) for Na₂SeO₄-CdSeO₄-H₂O system. The choice of the mixing 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 from the saturated ternary solutions has to be constant along the whole crystallization branch of the double salt. According to experiment-model comparison the developed models for mixed systems under study are in a very good agreement with experimental solubility data for whole concentration range of solutions (see also Fig. 2).





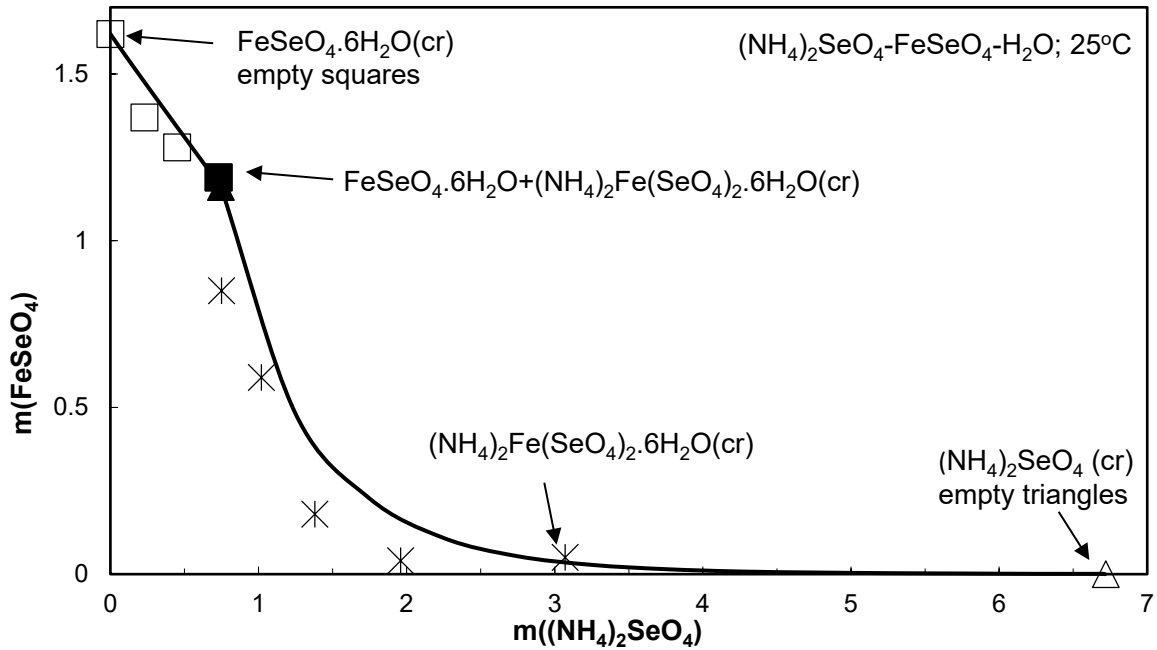


Fig. 2. Experimental (symbols) and model calculated (solid lines) solubilities in the mixed systems RbCl-MgCl₂-H₂O, CsBr-MgBr₂-H₂O, Cs₂SO₄-MgSO₄-H₂O, (NH₄)₂SeO₄-FeSeO₄-H₂O and K₂SeO₄-FeSeO₄-H₂O systems at T=25°C.

Experimental studies

Determination of solubilities in the mixed system LiBr-CaBr₂-H₂O at 35°C and 50°C.

In this study, the bromide minerals solubility in the mixed system LiBr-CaBr₂-H₂O have been investigated at T = at 35°C and 50°C by the physico-chemical analysis method (Balarew and Christov, 1992; Donchev et al., 2019). At T=35°C the equilibrium crystallization of LiBr.2H₂O (cr), LiBr.H₂O (cr), CaBr₂.4H₂O (cr) and CaBr₂.2H₂O (cr). has been established. At T = 50°C precipitation of LiBr.H₂O (cr), CaBr₂.4H₂O (cr) and CaBr₂.2H₂O (cr). has been established. The solubilities of lithium bromide solids sharply decrease in ternary system with adding calcium bromide solids at both temperatures. It was concluded that the phase transition temperature (PPT) LiBr.CaBr₂.5H₂O (cr) → LiBr.H₂O (cr) + CaBr₂.4H₂O (cr) lies at temperature range from 25°C to 35°C.

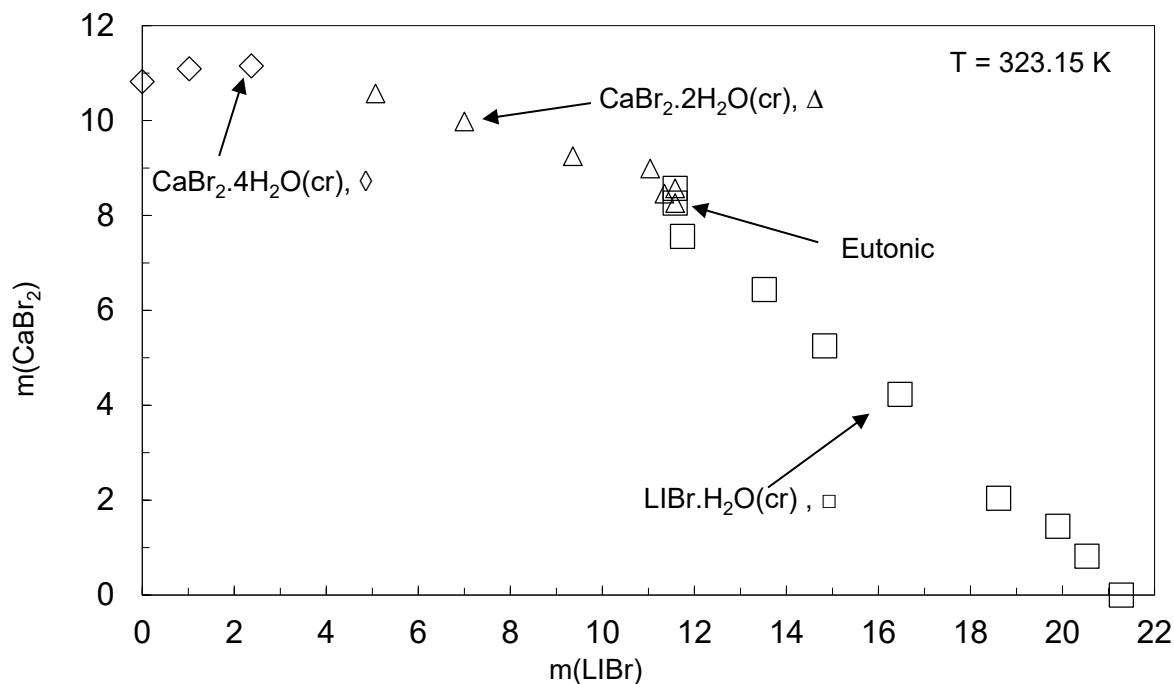


Fig. 3. Bromide minerals solubility in the mixed system LiBr-CaBr₂-H₂O at T = 323.15 K

Synthesis and characterization of selenate solid phases: Na₂SeO₄·H₂SeO₃ u Na₂Cd(SeO₄)₂·2H₂O

After powder X-ray diffraction of the synthesized material, it was found to be a mixture of two phases: Na₂Cd(SeO₄)₂·2H₂O (nanoparticles) and a new phase, Na₂SeO₄·H₂SeO₃. From the new phase a single crystal was cast. The composition of the new phase was identified by means of the X-ray diffraction, powder X-ray analysis and the infrared spectroscopy methods. The structure of the double salt was determined by quantum chemical computer modeling and thermal analysis. The experimental data show that the newly synthesized compound is with the composition Na₂SeO₄·H₂SeO₃ and possesses monoclinic symmetry (group P21/c), the parameters of the elementary cell are: a = 8,5638(6) Å, b = 6,9665(5) Å, c = 11,1596(8) Å, β = 90,149(7)°, α = γ = 90,00°. There is no data in the literature about X-ray analysis of Sodium selenate dihydrogen selenite.

The following conclusions can be drawn from the results obtained:

- Two compounds were synthesized – $\text{Na}_2\text{SeO}_4 \cdot \text{H}_2\text{SeO}_3$, from which a single crystal was cast and nanoparticles of the double salt $\text{Na}_2\text{Cd}(\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$ were obtained. The presence of two phases was established by powder X-ray analysis.
 - Sodium selenate dihydrogenselenite was characterized by X-ray diffraction analysis and infrared spectroscopy.
 - By RDG analysis, it was found that strong hydrogen (1,763Å and 1,867Å) and electrostatic bonds stabilize $\text{Na}_2\text{SeO}_4 \cdot \text{H}_2\text{SeO}_3$. The interactions between dihydrogen selenite and selenate anion are van der Waals.
 - Molecular structural and geometrical parameters of nanoparticles from $\text{Na}_2\text{Cd}(\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$ have been determined by Density Functional Theory. The electronic structure and pure atomic charges have been determined.
- The probable decomposition mechanism of the double salt was determined by thermal analysis.

Scientific contributions

In this study we developed new thermodynamic models and/or validated previously published by Christov models for solution behavior and solid-liquid equilibrium for:

1. For 24 binary systems at 25°C:
 - 1a. For 8 binary acetate systems of the type 1-1: $\text{LiCH}_3\text{COO-H}_2\text{O}$, $\text{NaCH}_3\text{COO-H}_2\text{O}$, $\text{KCH}_3\text{COO-H}_2\text{O}$, $\text{RbCH}_3\text{COO-H}_2\text{O}$, $\text{CsCH}_3\text{COO-H}_2\text{O}$ и $\text{TlCH}_3\text{COO-H}_2\text{O}$, and of the type 2-1: $\text{Ba}(\text{CH}_3\text{COO})_2\text{-H}_2\text{O}$ и $\text{Mg}(\text{CH}_3\text{COO})_2\text{-H}_2\text{O}$;
 - 1b. For binary rubidium systems $\text{RbCl-H}_2\text{O}$, $\text{RbBr-H}_2\text{O}$; and $\text{Rb}_2\text{SO}_4\text{-H}_2\text{O}$;
 - 1c. For binary cesium systems $\text{CsCl-H}_2\text{O}$, $\text{CsBr-H}_2\text{O}$ and $\text{Cs}_2\text{SO}_4\text{-H}_2\text{O}$;
 - 1d. For 10 binary selenate systems of the type 1-2: $\text{Li}_2\text{SeO}_4\text{-H}_2\text{O}$, $\text{Na}_2\text{SeO}_4\text{-H}_2\text{O}$, $(\text{NH}_4)_2\text{SeO}_4\text{-H}_2\text{O}$, $\text{K}_2\text{SeO}_4\text{-H}_2\text{O}$, $\text{Rb}_2\text{SeO}_4\text{-H}_2\text{O}$, $\text{Cs}_2\text{SeO}_4\text{-H}_2\text{O}$; and of the type 2-2: $\text{MgSeO}_4\text{-H}_2\text{O}$, $\text{CoSeO}_4\text{-H}_2\text{O}$, $\text{NiSeO}_4\text{-H}_2\text{O}$, $\text{ZnSeO}_4\text{-H}_2\text{O}$.

The models are constructed on the basis of specific interaction approach for describing electrolyte solutions from low to high concentration introduced by Pitzer. 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. To construct models, we used different versions of standard molality-based Pitzer approach. It was established that application of extended approach with 4 parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^ϕ) and variation of α_1 and α_2 terms in fundamental Pitzer equations leads to the lowest values of standard model-experiment deviation (see Table 1). On figures we present a comparison of osmotic coefficients in nitrate and fluoride binary solutions calculated by the accepted models developed here (heavy solid lines), and models developed by other authors (dashed lines and dashed-dotted lines). The models for all binary systems under study are also validated by comparison with recommendations given in literature on the mean activity coefficients (γ_{\pm}). These recommendations on γ_{\pm} are model-dependent. Therefore, they are not used in parameterization process, and only to validate the resulting models. The recommended osmotic coefficients and activity coefficients values given in literature at 25°C are given on figures by symbols. The vertical lines on the figures denote the molality of solutions saturated with corresponding solid phase (m(sat)). Excellent accepted new model (heavy solid line) – experiment (symbols) agreement has been obtained for all systems under study, and from low to very high molality (see Fig. 1). It should be noted that all reference models presented on figures by dashed, dashed-dotted, and light solid lines have been constructed on the basis of standard Pitzer approach with

3 interaction parameters. Therefore, these models cannot reproduce well the experimental data. 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 40 m in RbCH₃COO-H₂O, and up to 53 m in CsCH₃COO-H₂O).

1e. Important thermodynamic characteristics (the thermodynamic solubility products ($\ln K^{\circ}_{sp}$), the Deliquescence Relative Humidity (DRH), and standard molar Gibbs Energy of formation ($\Delta_f G^{\circ}_m$)) of solid phases, precipitating from saturated binary solutions have been determined on the basis of evaluated binary ion interaction parameters. The calculated DRH and $\Delta_f G^{\circ}_m$ values are compared with recommendations given in literature.

2. In this study we developed new thermodynamic models for solution behavior and solid-liquid equilibrium for 10 mixed systems at 25°C:

2a. For 3 rubidium systems of the type 1-1+2-1 RbCl-MgCl₂-H₂O, RbBr-MgBr₂-H₂O and of the type 1-2+2-2 Rb₂SO₄-MgSO₄-H₂O;

2b. For 3 cesium systems of the type 1-1+2-1 CsCl-MgCl₂-H₂O, CsBr-MgBr₂-H₂O, and of the type 1-2+2-2 Cs₂SO₄-MgSO₄-H₂O;

2c. For 4 selenate mixed systems of the type 1-2+2-2 Na₂SeO₄-CdSeO₄-H₂O, Na₂SeO₄-FeSeO₄-H₂O, (NH₄)₂SeO₄-FeSeO₄-H₂O and K₂SeO₄-FeSeO₄-H₂O.

Models for mixed systems are developed on the basis of solubility approach, i.e. mixing parameters are evaluated using solubility data in mixed systems. According to comparison the developed models for mixed systems are in a very good agreement with experimental solubility data for whole concentration range of solutions. (see Fig.2).

2d. Important thermodynamic characteristics (the thermodynamic solubility products ($\ln K^{\circ}_{sp}$), standard molar Gibbs Energy of synthesis reaction from simple salts ($\Delta_r G^{\circ}_m$), and standard molar Gibbs Energy of formation ($\Delta_f G^{\circ}_m$) of double salts, precipitating from saturated ternary solutions have been determined on the basis of evaluated mixing ion interaction parameters.

3. Experimental laboratory studies include:

3a. Determination of solubilities in the mixed system LiBr-CaBr₂-H₂O at 35°C and 50°C.

It was concluded that the phase transition temperature (PPT) LiBr.CaBr₂.5H₂O (cr) → LiBr.H₂O (cr) + CaBr₂.4H₂O (cr) lies at temperature range from 25°C to 35°C.

3b. Synthesis and characterization of selenate solid phases Na₂SeO₄·H₂SeO₃ and Na₂Cd(SeO₄)₂.2H₂O

Two compounds were synthesized – $\text{Na}_2\text{SeO}_4 \cdot \text{H}_2\text{SeO}_3$, from which a single crystal was cast and nanoparticles of the double salt $\text{Na}_2\text{Cd}(\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$ were obtained. The presence of two phases was established by powder X-ray analysis

References

- Altmaier, M., Brendler, V., Bube, C., Marquardt, C., Moog, H. C., Richter, A., Scharge, T., Voigt, W., Wilhelm, S. (2011) THEREDA: Thermodynamic Reference Database. Final Report (short version), 63p. (cited as THEREDA)
- Altmaier M., Brendler V., Bube C., Neck V., Marquardt C., Moog H. C., Richter A., Scharge T., Voigt W., Wilhelm S., Wilms T., Wollmann G. (2011) THEREDA- Thermodynamische Referenzdatenbasis. Report GRS 265 (German), ISBN 978-3- 939355-41-0. (cited as THEREDA)
- ANDRA. Dossier (2005) - Argile. Evaluation de La Faisabilité Du Stockage Géologique En Formation Argileuse. <https://www.andra.fr/sites/default/files/2017-12/266.pdf> (cited as ANDRA, 2005)
- André L., Christov C., Lassin A., Azaroual M. (2013) Water Rock Interaction [WRI14], *Procedia Earth and Planetary Science*, 7, 14-18.
- André L., Christov C., Lassin A., Azaroual M. (2019) *Acta Scientifica Naturalis*, vol. 6, No. 1, 26-36. DOI: <https://doi.org/10.2478/asn-2019-0004>
- Balarew C., Christov C. (1992), *Compt. rend. Acad. Bulg. Sci.* 45, 49-52
- Balarew C., Christov C., Petrenko S., Valyashko V. (1993) *J. Solution Chem.* 22 173-181. <https://doi.org/10.1007/BF00650683>
- Barkov D., Christov C., Ojkova T. (2001) *J. Chem. Thermodynamics*, 33, 1073-1080. <https://doi.org/10.1006/jcht.2000.0818>
- Christov C. (1994) *J. Chem. Thermodynamics*, 26, 1071-1080.
- Christov C. (1995) *J. Chem. Thermodynamics*, 27: 1267-1273. <https://doi.org/10.1006/jcht.1995.0133>
- Christov C. (1996a) *J. Chem. Thermodynamics*, 28, 743-752. <https://doi.org/10.1006/jcht.1996.0068>
- Christov C. (1996b) *CALPHAD*, 20: 501-509. [https://doi.org/10.1016/S0364-5916\(97\)00012-6](https://doi.org/10.1016/S0364-5916(97)00012-6)
- Christov C. (1997) *J. Chem. Thermodynamics*, 29, 481-489. <https://doi.org/10.1006/jcht.1996.0181>
- Christov C. (1998) *CALPHAD* 22, 449-457. [https://doi.org/10.1016/S0364-5916\(99\)00004-8](https://doi.org/10.1016/S0364-5916(99)00004-8)
- Christov C. (1999), *J. Chem. Thermodynamics*, 31, 71-83. <https://doi.org/10.1006/jcht.1998.0419>
- Christov C. (2000) *J. Chem. Thermodynamics*, 32, 285-295. <https://doi.org/10.1006/jcht.1999.0564>
- Christov C. (2001a) *CALPHAD*, 25, 11-17. [https://doi.org/10.1016/S0364-5916\(01\)00025-6](https://doi.org/10.1016/S0364-5916(01)00025-6)
- Christov C. (2001b) *CALPHAD*, 25, 445-454. [https://doi.org/10.1016/S0364-5916\(01\)00063-3](https://doi.org/10.1016/S0364-5916(01)00063-3)
- Christov C. (2002a) *CALPHAD*, 26, 85-94. [https://doi.org/10.1016/S0364-5916\(02\)00026-3](https://doi.org/10.1016/S0364-5916(02)00026-3)

- Christov C. (2002b) *CALPHAD*, 26, 341-352. [https://doi.org/10.1016/S0364-5916\(02\)00049-4](https://doi.org/10.1016/S0364-5916(02)00049-4)
- Christov C. (2003a) , *J.Chem. Thermodynamics*, 35, 1775-1792. <https://doi.org/10.1016/j.jct.2003.08.004>
- Christov C. (2003a) *CALPHAD*, 27, 153-160. [https://doi.org/10.1016/S0364-5916\(03\)00046-4](https://doi.org/10.1016/S0364-5916(03)00046-4)
- Christov C. (2003b) *J. Chem. Thermodynamics*, 35: 909-917. [https://doi.org/10.1016/S0021-9614\(03\)00042-9](https://doi.org/10.1016/S0021-9614(03)00042-9)
- Christov C. (2004) , *J. Chem. Thermodynamics* 36, 223-235. <https://doi.org/10.1016/j.jct.2003.11.010>
- Christov C. (2005) *J. Chem. Thermodynamics* 37, 1036-1060. <https://doi.org/10.1016/j.jct.2005.01.008>
- Christov C. (2007) *Geochim.Cosmochim. Acta*, 71, 3357-3369. <https://doi.org/10.1016/j.gca.2007.05.007>
- Christov C. (2009a) *J. Chem. Eng. Data*, 54, 627-635. <https://doi.org/10.1021/je8005634>
- Christov C. (2009b) *J.Chem. Eng. Data*, 54, 2599-2608. <https://doi.org/10.1021/je900135w>
- Christov C. (2012a) *J. Chem. Thermodynamics*, 55, 7-22. <https://doi.org/10.1016/j.jct.2012.06.006>
- Christov C. (2012b) *CALPHAD* 36, 71-81. <https://doi.org/10.1016/j.calphad.2011.11.003>
- Christov C. (2019) DOCTOR OF SCIENCES DISSERTATION, Chemical and Geochemical Modeling. Theory and Practice, Shumen University “ Episkop Konstantin Preslavski”
- Christov C. (2020) Review of the Bulgarian Geological Society, 81, 3: 69–71. ISSN 0007-3938.
- Christov C., Petrenko S., Balarew C., Valyashko V. (1994) *J. Solution Chem.*, **23** 795-812.
- Christov C., and Moller N. (2004a), *Geochim.Cosmochim. Acta*, 68, 1309-1331. <https://doi.org/10.1016/j.gca.2003.08.017>
- Christov C., and Moller N. (2004b) *Geochim.Cosmochim. Acta* 68, 3717-3739. <https://doi.org/10.1016/j.gca.2004.03.006>
- Christov C., Ojkova T. and Mihov D. (1998) *J. Chem. Thermodynamics*, 30: 73-79. <https://doi.org/10.1006/jcht.1997.0274>
- Christov C., Dickson A. and Moller N. (2007) *J. Solution Chem.* **36**, 1495-1523.
- Christov C., Zhang, M., Talman S., Reardon E., Yang T. (2012) *Mineralogical Magazine* 76, 1578. <https://goldschmidtabstracts.info/abstracts/abstractView?id=2012001520>
- D'Ans J., Busch F/ (1937) *Z. anorg. allg. Chem.* 232, 363 (in Zdanovski, 2003)
- Donchev S., Christov C. (2020) *Ecologia Balkanica*, Special Edition 3: 195-210. <http://eb.bio.uni-plovdiv.bg>
- Donchev S., Tsenov, T., Christov C. (2021) *Acta Scientifica Naturalis*, 8(2): 1-15 <https://doi.org/10.2478/asn-2021-0014>
- Donchev S., Tsenov, T., Christov C. (2022) *Biorisk*, issue 17, pp. 389-406 (doi: [10.3897/biorisk.17.77487](https://doi.org/10.3897/biorisk.17.77487))
- Donchev S., Tsenov, T., Christov C. (2023) *Acta Scientifica Naturalis*, vol. 10, Issue 1, pp. 1-15 (2023). DOI: 10.2478/asn-2023- 0002
- Goldberg, R. N. (1981) Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Thirty-Six Uni-Bivalent Electrolytes, *J. Phys. Chem. Ref. Data* 10, 671–764 <https://doi.org/10.1063/1.555646>
- Guignot S., Lassin A., Christov C., Lach A., André L., Henocq P. (2019) *J. Chem. Eng. Data*, 64, 1, 345-359. DOI: [10.1021/acs.jced.8b00859](https://doi.org/10.1021/acs.jced.8b00859)
- Hamer W.J., Wu Y-C. (1972) *J. Phys. Chem. Ref. Data* 1, 1047-1099. DOI: 10.1063/1.3253108
- Harvie C., Moller N., Weare J. (1984) *Geochim. Cosmochim. Acta* 48, 723-751. DOI: [10.1016/0016-7037\(84\)90098-X](https://doi.org/10.1016/0016-7037(84)90098-X)
- Kim H.-T., Frederick W. (1988) *J. Chem. Eng. Data* 33, 177-184. <https://doi.org/10.1021/je00052a035>

- Kolev H., Tyuliev G., Christov C., Kostov K. (2013) *Bulgarian Chem. Commun.* 45, 584–591. <http://www.bcc.bas.bg/BCC>
- Lach A., André L., Guignot S., Christov C., Henocq P., Lassin A. (2018) *J. Chem. Eng. Data* 63, 787–800. DOI: [10.1021/acs.jced.7b00953](https://doi.org/10.1021/acs.jced.7b00953)
- Lassin A., Christov C., André L., Azaroual M. (2015) *Amer. J. Sci.* 315, 204–256. DOI: [10.2475/03.2015.02](https://doi.org/10.2475/03.2015.02)
- Lassin, A., Guignot, S., Lach, A., Christov, C., André, L., Madé, B. (2020) *J. Chem. Eng. Data* 65, 7, 3613–3626 DOI: [10.1021/acs.jced.0c00180](https://doi.org/10.1021/acs.jced.0c00180)
- Mihov D. (2022) PhD Thesis "Experimental and theoretical studies of selenate systems", Burgas University "A. Zlatarov"
- Mikulín G. (1968) *Voprosy Fizicheskoi Khimii Electrolytov*, Izd. Khimiya, St.Petersburg, 417 pages.
- Moller N., Christov C., Weare J. (2006) Thermodynamic models of aluminosilicate mineral solubility for application to enhanced geothermal systems. *Proceedings 31th Workshop on Geothermal Reservoir Engineering*, Stanford University, Stanford, California, January 30 –February 1 (8 pages). SGP-TR-179 <https://pangea.stanford.edu/ERE/pdf/IGAstandard/SGW/2006/moller.pdf>
- Moller N., Christov C., Weare J. (2007) Thermodynamic model for predicting interactions of geothermal brines with hydrothermal aluminum silicate minerals. *Proceedings 32th Workshop on Geothermal Reservoir Engineering*, Stanford University, Stanford, California, January 22-24 (8 pages) GP-TR-183 <https://geo.stanford.edu/ERE/pdf/IGAstandard/SGW/2007/moller.pdf>
- Ojkova T., Staneva D. (1989) *Z. Phys. Chem. (Leipzig)* 270, 628–632.
- Oykova T., Mihov D. (1992) *Crystal Research and Technology*, page 697–701. doi:10.1002/crat.2170270522
- Ojkova T., Christov C., Mihov D. (1998) *Z. Physik. Chem.*, 203, 87-93. DOI: https://doi.org/10.1524/zpch.1998.203.Part_1_2.087
- Ojkova T., Christov C., Mihov D. (1999) *Monatsh. Chemie*, **130**, 1061-1065. <https://doi.org/10.1007/PL00010283>
- Park J.-H., Christov C., Ivanov A., Molina M. (2009) *Geophysical Research Letters*, 36 L02802, DOI: [10.1029/2009GL036160](https://doi.org/10.1029/2009GL036160). <https://doi.org/10.1029/2008GL036160>
- Pitzer K. S. (1973) *J. Phys. Chem.* 77, 2, 268–277. <https://doi.org/10.1021/j100621a026>
- Pitzer K.S., Mayorga G. (1973) *J. Phys. Chem.* 77, 2300-2308. <https://doi.org/10.1021/j100638a009>
- Pitzer, K.S., Mayorga G. (1974) *J. Soln. Chem.* 3, 539-546. <https://doi.org/10.1007/BF00648138>
- Robinson R. and Stokes R. (1959) *Electrolyte Solutions*, 2nd.ed.; Butterworths, London.
- Sandia National Laboratories (2005): Pitzer database expansion to include actinides and transition metal species (data0.ypf.R1) U.S. Department of Energy, ANL-WIS-GS-000001 REV 00(as YMTDB).
- Trendafelov D., Christov C., Balarew C., Karapetkova A. (1995b) *Coll. Czech. Chem. Commun.*, 60 (1995) 2107-2111. <https://doi.org/10.1135/cccc19952107>
- Wagman D., Evans W., Parker V., Schumm R., Halow I., Bayler S., Churney K. and Nutall R. (1982) *J. Phys. Chem. Ref. Data*, **11** (Suppl.2).
- Zdanovskii A., Soloveva E., Liahovskaia E., Shestakov N., Shleimovich P., Abutkova L. Cheremnih L. and Kulikova (2003), *Experimentalnie dannie po rastvorimosti mnogokomponentnih vodno-soleviih system*, vols. I-1 and I-2, Khimiizdat, St. Petersburg.

Publications indexed in SCOPUS AND/OR WEB OF SCIENCE AND SJR

- A1.** Tsvetan Tsenov, Stanislav Donchev, Christomir Christov, Development of Accurate Chemical Thermodynamic Database for Geochemical Storage of Nuclear Waste. Part III: Models for Predicting Solution Properties and Solid-Liquid Equilibrium in Cesium Binary and Mixed Systems, *Biorisk*, issue 17 pp. 407-422 (2022) (doi: 10.3897/biorisk.17.77523) (in US Dept. of Agriculture database: https://pubag.nal.usda.gov/?q=%22Christomir+Christov%22&search_field=author (Q2 – 20 p. in the quartil *Agricultural and Biological Sciences (miscellaneous)*)
- A2.** Rумыана Yankova, Tsvetelina Yotova, Tsvetan Tsenov, Dencho Mihov, New insight into the structure and properties of silver selenite, *Journal of Molecular Structure*, volume 1289 (2023), <https://doi.org/10.1016/j.molstruc.2023.135774> (Q2 - 20 т.)

Total 40 points

Citations in the world databases:

Публикация А1: в (EBSCO: <https://essentials.ebsco.com/search/eds/details/development-of-accurate-chemical-thermodynamic-database-for-geochemical-storage-of-nuclear-waste?searchfield=AU&language=en&query=Tsenov%2C%20Tsvetan&db=owf&an=157141449> and US Dept. of Agriculture database: https://search.nal.usda.gov/discovery/search?query=any,contains,Tsvetan%20Tsenov&tab=pubag&search_scope=pubag&vid=01NAL_INST:MAIN&offset=0

PUBLICATIONS NOT INCLUDED IN WEB OF SCI. AND SCOPUS AND INCLUDED IN CONFERENCE PROCEEDINGS AFTER PEER REVIEW

1. Stanislav Donchev, Tsvetan Tsenov, Christomir Christov, Thermodynamic models for solution behavior and solid-liquid equilibrium in cesium binary systems (CsF-H₂O, CsCl-H₂O, CsBr- H₂O, CsI-H₂O, CsOH-H₂O, CsNO₃-H₂O, Cs₂SO₄- H₂O, and Cs₂SeO₄- H₂O) from low to very high concentration at 25°C, *SocioBrains* , issue 66, pp. 32-49 (2020) (ISSN 2367- 5721).
2. Stanislav A. Donchev, Tsvetan V. Tsenov, Christomir I. Christov Thermodynamic models for solution behavior and solid-liquid equilibrium in rubidium binary systems from low to very high concentration at 25°C (Термодинамични модели за поведението на разтворите и твърдо-течното фазово равновесие в рубидиеви бинерни системи от ниски до много високи концентрации при 25°C), In proceedings of НАУЧНА КОНФЕРЕНЦИЯ С МЕЖДУНАРОДНО УЧАСТИЕ МАТТЕХ 2020 , ШУМЕНСКИ УНИВЕРСИТЕТ „ЕПИСКОП КОНСТАНТИН ПРЕСЛАВСКИ“, SECTION MATHEMATICS AND NATURAL SCIENCE, vol.1., pp. 57-74 (2020) . (ISSN 1314-3921).
3. Stanislav Donchev, Tsvetan Tsenov, Christomir Christov, MODELS FOR THE BEHAVIOR OF SOLUTIONS AND SOLID-LIQUID PHASE EQUILIBRIUM IN RUBIDIUM BINARY SYSTEMS FROM LOW TO VERY HIGH CONCENTRATION AT 25°C, PROCEEDINGS OF THIRD SCIENTIFIC CONFERENCE WITH INTERNATIONAL PARTICIPATION Geography, regional development and tourism, 27-29 Nov. 2020 pp. 45-46, (ISBN 978-619-201-447-6)
4. Stanislav Donchev, Tsvetan Tsenov, Christomir Christov, COMPUTER THERMODYNAMIC MODELS FOR PREDICTING SOLUTION PROPERTIES AND

SOLID-LIQUID EQUILIBRIUM IN BINARY RUBIDIUM AND CESIUM SYSTEMS FROM LOW TO VERY HIGH CONCENTRATION AT 25°C, Сборник с доклади на Пролетна научна сесия на ФМИ-СУ 2021, секция УНИТе

5. Tsvetan Tsenov, Stanislav Donchev, Christomir Christov, THERMODYNAMIC MODELS FOR PREDICTING SOLUTION PROPERTIES AND SOLID-LIQUID EQUILIBRIUM IN BINARY ACETATE SYSTEMS FROM LOW TO VERY HIGH CONCENTRATION AT 25°C, In proceedings of NINTH STUDENT SCIENTIFIC CONFERENCE "ECOLOGY AND ENVIRONMENT" 2021, Shumen University, Shumen, Bulgaria, pp. 107-108.

6. Tsvetan Tsenov, Stanislav Donchev, Christomir Christov, Development of Accurate Chemical Thermodynamic Database for Geochemical Storage of Nuclear Waste. Part III: Models for Predicting Solution Properties and Solid-Liquid Equilibrium in Cesium Binary and Mixed Systems. In Proceedings of International Seminar of Ecology – 2021, Current Trends of Ecology

7. Tsvetan Tsenov, Stanislav Donchev, Ismail Ismailov, Christomir Christov THERMODYNAMIC MODELS FOR PREDICTING SOLUTION PROPERTIES AND SOLID-LIQUID EQUILIBRIUM IN BINARY ACETATE SYSTEMS FROM LOW TO VERY HIGH CONCENTRATION AT 25°C (in Bulgarian), In Proceedings of 19th National Conference with International Participation "Natural Sciences 2021", (2021) pp.21-28 (ISSN 2603-2917)

8. Tsvetan Tsenov, Dencho Mihov, Stanislav Donchev, Romyana Yankova, Christomir Christov, Thermodynamic models for solution behavior and solid-liquid equilibrium in binary and mixed selenate systems from low to very high concentration at 25°C, Сборник от Конференция „География, регионално развитие и туризъм“ 2021, 3-5 Декември 2021, стр. 54-55

9. Tsvetan Tsenov, Dencho Mihov, Stanislav Donchev, Romyana Yankova, Christomir Christov, Thermodynamic study of aqueous Na and Fe(II) selenate system at the temperature 25°C, In proceedings of 10th STUDENT SCIENTIFIC CONFERENCE "ECOLOGY AND ENVIRONMENT" 2022, 29.4.2022-30.4.2022 Shumen University, Shumen, Bulgaria, pp. 59-61.

10. Tsvetan Tsenov, Dencho Mihov, Romyana Yankova, Christomir Christov, Thermodynamic study of aqueous K and Fe(II) selenate system at the temperature 25°C, In proceedings of 11th STUDENT SCIENTIFIC CONFERENCE "ECOLOGY AND ENVIRONMENT" 2023, Shumen University, Shumen, Bulgaria (2023), ISSN 2367-5209

11. Tsvetan Tsenov, Dencho Mihov, Stanislav Donchev, Romyana Yankova, Christomir Christov, Thermodynamic study of $(m_1\text{Na}_2\text{SeO}_4+m_2\text{CdSeO}_4)$ (aq) system at the temperature 25°C, XXI НАЦИОНАЛНА КОНФЕРЕНЦИЯ С МЕЖДУНАРОДНО УЧАСТИЕ "ПРИРОДНИ НАУКИ '2023", Shumen University, Shumen, Bulgaria (29-30.09.2023)

12. Christomir Christov, Tsvetan Tsenov, Nina Ivanova, Stanislav Donchev, Solid-liquid phase equilibrium in LiBr-CaBr₂-H₂O system at (35 and 50)°C, in Proceedings of INTERNATIONAL SEMINAR OF ECOLOGY- 2023, "Cutting Edge Research of Ecology", p.86 (2023).

13. Christomir Christov, Tsvetan Tsenov, Stanislav Donchev, Thermodynamic models for solution behavior and solid-liquid equilibrium in rubidium binary systems from low to very high concentration at 25°C, in Proceedings of INTERNATIONAL SEMINAR OF ECOLOGY- 2023, "Cutting Edge Research of Ecology", p.87 (2023).

14. Christomir Christov, Tsvetan Tsenov, Stanislav Donchev, Thermodynamic models for solution behavior and solid-liquid equilibrium in selenate binary systems from low to very high concentration at 25°C, in Proceedings of INTERNATIONAL SEMINAR OF ECOLOGY- 2023, "Cutting Edge Research of Ecology", p.88 (2023).

15. Christomir Christov, Tsvetan Tsenov, Stanislav Donchev, THERMODYNAMIC MODELS FOR PREDICTING SOLUTION PROPERTIES AND SOLID-LIQUID EQUILIBRIUM IN BINARY ACETATE SYSTEMS FROM LOW TO VERY HIGH CONCENTRATION AT 25°C, in Proceedings of 12th Chemistry Conference with International Participation, p.73 (2023)
16. Christomir Christov, Tsvetan Tsenov, Stanislav Donchev, THERMODYNAMICS OF FORMATION OF CESIUM SOLID PHASES (SIMPLE SALTS, DOUBLE SALTS, AND SOLID SOLUTIONS) FROM SATURATED AQUEOUS SOLUTIONS, in Proceedings of 12th Chemistry Conference with International Participation, p.67 (2023)
17. Christomir Christov, Tsvetan Tsenov, Stanislav Donchev, THERMODYNAMIC MODELS FOR SOLUTION BEHAVIOR AND SOLID LIQUID EQUILIBRIUM IN RUBIDIUM MIXED SYSTEMS FROM LOW TO VERY HIGH CONCENTRATION, in Proceedings of 12th Chemistry Conference with International Participation p.72 (2023)

Participation in scientific forums

1. Станислав Дончев, Цветан Ценов, Калин Колев, Христомир Христов, Термодинамични модели за твърдо-течно фазово равновесие в силно концентрирани Цезиеви бинерни и смесени разтвори, VII Национална Научна Студентска Конференция “От Атома до Космоса”, 17-18 Май, 2019, Шуменски Университет, Шумен, България-устен доклад.
2. Stanislav Donchev, Tsvetan Tsenov, Christomir Christov, Thermodynamic Phase Equilibrium Models for Cesium Binary and Mixed Systems, XVII National Conference with International Participation “Natural Sciences 2019”, 4.10.2019-5.10.2019, Shumen, Bulgaria, oral presentation.
3. Stanislav A. Donchev, Tsvetan V. Tsenov, Christomir I. Christov Thermodynamic models for solution behavior and solid-liquid equilibrium in rubidium binary systems from low to very high concentration at 25°C (Термодинамични модели за поведението на разтворите и твърдо-течното фазово равновесие в рубидиеви бинерни системи от ниски до много високи концентрации при 25°C), НАУЧНА КОНФЕРЕНЦИЯ С МЕЖДУНАРОДНО УЧАСТИЕ МАТТЕХ 2020, ШУМЕНСКИ УНИВЕРСИТЕТ „ЕПИСКОП КОНСТАНТИН ПРЕСЛАВСКИ“ 22 – 24 ОКТОМВРИ 2020 Г., oral presentation
4. Stanislav Donchev, Tsvetan Tsenov, Christomir Christov, Thermodynamic models for solution behavior and solid-liquid equilibrium in rubidium binary systems (RbF-H₂O, RbCl-H₂O, RbBr- H₂O, RbI-H₂O, RbNO₃-H₂O, Rb₂SO₄- H₂O, and Rb₂SeO₄- H₂O) from low to very high concentration at 25°C National Conference with International Participation “Geography, Regional Development, and Tourism 2020” 27-29 Nov., 2020, Shumen Bulgaria, oral presentation
5. Stanislav Donchev, Tsvetan Tsenov, Christomir Christov, COMPUTER THERMODYNAMIC MODELS FOR PREDICTING SOLUTION PROPERTIES AND SOLID-LIQUID EQUILIBRIUM IN BINARY RUBIDIUM AND CESIUM SYSTEMS FROM LOW TO VERY HIGH CONCENTRATION AT 25°C, Пролетна научна сесия на ФМИ-СУ, секция УНИТе, 27 март 2021-устен доклад
6. Tsvetan Tsenov, Stanislav Donchev, Christomir Christov, THERMODYNAMIC MODELS FOR PREDICTING SOLUTION PROPERTIES AND SOLID-LIQUID EQUILIBRIUM IN BINARY ACETATE SYSTEMS FROM LOW TO VERY HIGH CONCENTRATION AT 25°C, NINTH STUDENT SCIENTIFIC CONFERENCE “ECOLOGY AND ENVIRONMENT” April 23-24, 2021, Shumen University, Shumen, Bulgaria, oral presentation

7. Tsvetan Tsenov, Stanislav Donchev, Christomir Christov, Development of Accurate Chemical Thermodynamic Database for Geochemical Storage of Nuclear Waste. Part III: Models for Predicting Solution Properties and Solid-Liquid Equilibrium in Cesium Binary and Mixed Systems, International Seminar of Ecology – 2021, Current Trends of Ecology September, 2021, oral presentation.
8. Цветан Ценов, Станислав Дончев, Исмаил Исмаилов, Христомир Христов, Термодинамични модели за поведението на разтворите и твърдо-течното фазово равновесие в ацетатни бинерни системи от ниски до много високи концентрации при 25°C, 19-та Национална конференция с международно участие „Природни науки’ 2021” 1-3 Октомври 2021 г., oral presentation
9. Станислав Дончев, Цветан Ценов, Христомир Христов, Термодинамика на образуване на рублидиеви твърди фази от наситени бинерни водни разтвори при 25°C, 19-та Национална конференция с международно участие „Природни науки’ 2021” 1-3 Октомври 2021 г., oral presentation
10. Цветан Ценов, Денчо Михов, Станислав Дончев, Румяна Янкова, Христомир Христов, Термодинамични модели за поведението на разтворите и твърдо-течното фазово равновесие в селенатни бинерни системи от типа $M_2SeO_4-H_2O$ ($M = H, Li, Na, K, NH_4, Rb, Cs$) при 25°C, 19-та Национална конференция с международно участие „Природни науки’ 2021” 1-3 Октомври 2021 г., oral presentation
11. Tsvetan Tsenov, Dencho Mihov, Stanislav Donchev, Romyana Yankova, Christomir Christov, Thermodynamic models for solution behavior and solid-liquid equilibrium in binary and mixed selenate systems from low to very high concentration at 25°C, Конференция „География, регионално развитие и туризъм“ 2021, 3-5 Декември 2021, oral presentation
12. Tsvetan Tsenov, Dencho Mihov, Stanislav Donchev, Romyana Yankova, Christomir Christov, Thermodynamic study of aqueous Na and Fe(II) selenate system at the temperature 25°C, 10th STUDENT SCIENTIFIC CONFERENCE “ECOLOGY AND ENVIRONMENT” 2022, 29.4.2022-30.4.2022 Shumen University, Shumen, Bulgaria, oral presentation
13. Tsvetan Tsenov, Dencho Mihov, Romyana Yankova, Christomir Christov, Thermodynamic models for predicting solution properties and solid-liquid equilibrium in selenate systems at 25°C. Part I: Models for binary selenate systems, 20-та Национална конференция с международно участие „Природни науки’ 2022” 30.09.2022-3.10.2022г., oral presentation
14. Tsvetan Tsenov, Dencho Mihov, Romyana Yankova, Christomir Christov, Thermodynamic models for predicting solution properties and solid-liquid equilibrium in selenate systems at 25°C. Part II: Models for mixed selenate systems, 20-та Национална конференция с международно участие „Природни науки’ 2022” 30.09.2022-3.10.2022г., oral presentation
15. Tsvetan Tsenov, Dencho Mihov, Romyana Yankova, Christomir Christov, Thermodynamic study of aqueous K and Fe(II) selenate system at the temperature 25°C, In proceedings of 11th STUDENT SCIENTIFIC CONFERENCE “ECOLOGY AND ENVIRONMENT” 2023, Shumen University, Shumen, Bulgaria, oral presentation.
16. Tsvetan Tsenov, Dencho Mihov, Stanislav Donchev, Romyana Yankova, Christomir Christov, Thermodynamic study of $(m_1Na_2SeO_4+m_2CdSeO_4)$ (aq) system at the temperature 25°C, XXI НАЦИОНАЛНА КОНФЕРЕНЦИЯ С МЕЖДУНАРОДНО УЧАСТИЕ “ПРИРОДНИ НАУКИ '2023”, Shumen University, Shumen, Bulgaria, oral presentation
17. Christomir Christov, Tsvetan Tsenov, Nina Ivanova, Stanislav Donchev, Solid-liquid phase equilibrium in LiBr-CaBr₂-H₂O system at (35 and 50)°C, INTERNATIONAL SEMINAR OF ECOLOGY- 2023, "Cutting Edge Research of Ecology", September 28th - 29th, 2023. At Sofia Bulgaria oral presentation

18. Christomir Christov, Tsvetan Tsenov, Stanislav Donchev, Thermodynamic models for solution behavior and solid-liquid equilibrium in rubidium binary systems from low to very high concentration at 25°C, INTERNATIONAL SEMINAR OF ECOLOGY- 2023, "Cutting Edge Research of Ecology", September 28th - 29th, 2023. At Sofia Bulgaria oral presentation oral presentation
19. Christomir Christov, Tsvetan Tsenov, Stanislav Donchev, Thermodynamic models for solution behavior and solid-liquid equilibrium in selenate binary systems from low to very high concentration at 25°C, INTERNATIONAL SEMINAR OF ECOLOGY- 2023, "Cutting Edge Research of Ecology", September 28th - 29th, 2023. At Sofia Bulgaria oral presentation
20. Christomir Christov, Tsvetan Tsenov, Stanislav Donchev, Thermodynamics of formation of cesium solid phases (simple salts, double salts and solid solutions) from saturated aqueous solutions, 12th Chemistry Conferense with International Participation, October 13-14, 2023, Plovdiv, oral presentation.
21. Christomir Christov, Tsvetan Tsenov, Stanislav Donchev, Thermodynamic models for solution behavior and solid-liquid equilibrium in rubidium mixed systems from low to very high concentration at 25oC, 12th Chemistry Conferense with International Participation, October 13-14, 2023, Plovdiv, oral presentation.
22. Christomir Christov, Tsvetan Tsenov, Stanislav Donchev, Thermodynamic models for solution behavior and solid-liquid equilibrium in acetate binary systems from low to very high concentration at 25°C, 12th Chemistry Conferense with International Participation, October 13-14, 2023, Plovdiv, oral presentation.