

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

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Abstract

The models described in this study are of high importance in the development of thermodynamic database needed for nuclear waste geochemical storage, as well as for technology for extracting cesium resources from saline waters. In this study we developed new, not concentration restricted thermodynamic models for solution behavior and solid-liquid equilibrium in CsF-H₂O, CsOH-H₂O and Cs₂SO₄-H₂O systems at 25 °C. To parameterize models, we used all available experimental osmotic coefficients data for whole concentration range of solutions, and up to saturation point. The new models are developed on the basis of Pitzer ion interactions approach. The predictions of new developed here models are in excellent agreement with experimental osmotic coefficients data (φ) in binary solutions from low to extremely high concentration (up to 21.8 mol.kg⁻¹ for CsOH-H₂O, and up to 35.6 mol.kg⁻¹ for CsF-H₂O). The previously developed by Christov, by Christov and co-authors, and by other authors Pitzer approach based thermodynamic models for five (5) cesium binary systems (CsCl-H₂O, CsBr- H₂O, CsI-H₂O, CsNO₃-H₂O, and Cs₂SeO₄- H₂O) are tested by comparison with experimental osmotic coefficients data and with recommendations on activity coefficients (γ_{\pm}) in binary solutions. The models which give the best agreement with (φ)-, and (γ_{\pm})-data from low to high concentration, up to m(sat), are accepted as correct models, which can be used for solubility calculations in binary and mixed systems and determination of thermodynamic properties of precipitating cesium solid phases. The thermodynamic solubility products ($\ln K_{sp}^{\circ}$), and the Deliquescence Relative Humidity (DRH) of solid phases, precipitating from saturated

cesium binary solutions ($\text{CsF}(\text{cr})$, $\text{CsCl}(\text{cr})$, $\text{CsBr}(\text{cr})$, $\text{CsI}(\text{cr})$, $\text{CsOH}(\text{cr})$, $\text{CsNO}_3(\text{cr})$, $\text{Cs}_2\text{SO}_4(\text{cr})$, and $\text{Cs}_2\text{SeO}_4(\text{cr})$) have been determined on the basis of evaluated and accepted binary parameters and using experimental solubility data. The reported mixing parameters [$\theta(\text{Cs}, \text{M}^{2+})$ and $\psi(\text{Cs}, \text{M}^{2+}, \text{X})$], evaluated by solubility approach for 15 cesium mixed ternary systems ($\text{CsCl-MgCl}_2\text{-H}_2\text{O}$, $\text{CsBr-MgBr}_2\text{-H}_2\text{O}$, $\text{CsCl-NiCl}_2\text{-H}_2\text{O}$, $\text{CsBr-NiBr}_2\text{-H}_2\text{O}$, $\text{CsCl-MnCl}_2\text{-H}_2\text{O}$, $\text{CsCl-CoCl}_2\text{-H}_2\text{O}$, $\text{CsCl-CuCl}_2\text{-H}_2\text{O}$, $\text{CsCl-CsBr-H}_2\text{O}$, $\text{CsCl-RbCl-H}_2\text{O}$, $\text{Cs}_2\text{SO}_4\text{-CoSO}_4\text{-H}_2\text{O}$, $\text{Cs}_2\text{SeO}_4\text{-CoSeO}_4\text{-H}_2\text{O}$, $\text{Cs}_2\text{SO}_4\text{-NiSO}_4\text{-H}_2\text{O}$, $\text{Cs}_2\text{SeO}_4\text{-NiSeO}_4\text{-H}_2\text{O}$, $\text{Cs}_2\text{SO}_4\text{-ZnSO}_4\text{-H}_2\text{O}$, and $\text{Cs}_2\text{SeO}_4\text{-ZnSeO}_4\text{-H}_2\text{O}$) are tabulated.

Keywords

Cesium binary and mixed systems, computer thermodynamic modeling, geochemical nuclear waste sequestration, Pitzer approach

Introduction

Radioactive waste is a by-product of the nuclear fuel cycle and the production of weapons and medical radioisotopes. As nuclear technologies become more widespread, so does the production of waste materials. In Europe, nuclear waste is classified into 1) high-level; 2) intermediate level; 3) low-level, and 4) transitional radioactive waste. The long-term storage of high-level waste is still experimental. Radiocesium isotopes, particularly ^{137}Cs , form part of the high-level nuclear waste group. Crucially, the storage of high-level waste in liquid form poses serious risks. On 29 September 1957 a liquid storage tank exploded at the Mayak facility (Chelyabinsk-40), contaminating more than 52,000 square kilometers with ^{137}Cs and ^{90}Sr (Kostyuchenko and Krestinina 1994). This is known as the Kyshtym accident and is the second most serious radiation disaster after Chernobyl at 1986. On 1987 a release of ^{137}Cs occurred as a result of improper disposal of radiotherapy source (Rosenthal et al. 1991). This is known as Goiânia accident in Brazil. According to Schrage et al. (2012) among the more common fission products from spent nuclear fuels, the radionuclide ^{137}Cs with half-lives of 30.17 years, is mostly critical for the design of the nuclear waste repository because of the intense γ and β radiation and the heat generated by the decay process, as well as the high solubilities of cesium halides. Thus, modelling the properties of cesium atoms in salts and solutions is a current, pertinent question in theoretical chemistry.

A long term safety assessment of a repository for radioactive waste requires evidence that all relevant processes are known and understood, which might have a significant positive or negative impact on its safety (Altmaier et al. 2011a, b; Lach et al. 2018; Donchev and Christov 2020; Donchev et al. 2021b). It has to be demonstrated, that the initiated chemical reactions don't lead to an un-due release of radionuclides into the environmental geo-, hydro-, and bio-sphere. One key parameter to assess the propagation of a radionuclide is its solubility in solutions interacting with the waste. Solubility estimations can either be based on experimental data determined at conditions close to those in the repository or on thermodynamic calculations. The thermodynamic database created from experimental data is the basis for thermodynamic model calculations.

Since the disposal of radioactive waste is a task encompassing decades, the database is projected to operate on a long-term basis. Chemical models that predict equilibrium involving mineral, gas and aqueous phases over a broad range of solution compositions and temperatures are useful for studying the interactions between used nuclear fuel waste and its surroundings. The reliability of such predictions depends largely on the thermodynamic database. An accurate description of highly concentrated waters should be required for modeling of chemical interactions in and around nuclear repositories. The modeling of dissolution and precipitation processes in concentrated solutions requires an adequate thermodynamic model for the prediction of activities and solubilities (Lach et al. 2018; Donchev and Christov 2020; Donchev et al. 2021b). This requirement is fulfilled by the ion interaction model of Pitzer (Pitzer 1973). Extensive thermodynamic databases, which are based on the Pitzer ion interaction model, were developed within the Yucca Mountain Project (YMTDB: data0.ypf.r2) (Sandia National Laboratories (2005, 2007), Thereda project (THERmodynamic REference DAtabase, THEREDA-Final Report) (Altmaier et al. 2011a, b), and ANDRA project (Lach et al. 2018). However, the subject of long-term radioactive waste storage still has many questions left for scientists to solve. Unfortunately, many of the Pitzer models introduced in YMTDB and in THEREDA databases for cesium binary and mixed systems are concentration restricted and cannot describe correctly the solid-liquid equilibrium in geochemical and industrial systems of interest for nuclear waste programs.

This paper presents a comprehensive analysis and evaluation of existent thermodynamic database for cesium binary and mixed systems. It should be noted, that the thermodynamic properties, solubility isotherms and their simulation by thermodynamic model of the cesium binary and mixed brine type systems (s.a. CsX-MgX₂-H₂O (X =Cl,Br,I) ternary systems) are also of significant importance for extracting cesium resources from brine type solutions (Balarew et al. 1993; Christov et al. 1994; Christov 1995a, b, 1996a, 2005; Guo et al. 2017). According to Baranauskaite et al. (2021) carnalite type minerals of the type MX.MgX₂.6H₂O (cr) (M=Li, K,NH₄,Rb,Cs) (Christov and Balarew 1995; Christov 2012; Lassin et al. 2015) “are interesting not only as natural sources of chemical compounds, but also they can be made use of in renewable thermochemical energy storage since their hydration reactions are exothermic”.

In this study we developed new, not concentration restricted thermodynamic models for solution behavior and solid-liquid equilibrium in CsF-H₂O, CsOH-H₂O and Cs₂SO₄-H₂O systems at 25 °C. The new models are developed on the basis of Pitzer ion interactions approach. The previously developed by Christov (2003a, 2005), and Christov and co-authors (Balarew et al. 1993; Barkov et al. 2001; Donchev and Christov 2020) and by other authors (Pitzer and Mayorga 1973; Scharge et al. 2012; Palmer et al. 2002) Pitzer approach based thermodynamic models for five (5) cesium binary systems (CsCl-H₂O, CsBr-H₂O, CsI-H₂O, CsNO₃-H₂O, and Cs₂SeO₄-H₂O) are tested by comparison with experimental osmotic coefficients data and with recommendations on activity coefficients (γ_{\pm}) in binary solutions. The models that give the best agreement with (ϕ)-, and (γ_{\pm}) data from low to high concentration, up to m(sat),

are accepted as correct models, which can be used for solubility calculations in binary and mixed systems. We also summarized the previously established by the main author (C. Christov) solid-liquid equilibrium model for 15 cesium mixed ternary systems at 25 °C. The evaluated mixing parameters [$\theta(\text{Cs}, \text{M}^{2+})$ and $\psi(\text{Cs}, \text{M}^{2+}, \text{X})$], determined by solubility approach are tabulated.

Methodology

The models for cesium binary systems 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 shown 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; Christov et al. 1994, 1998; Christov 1995a, 1996a, 1998, 1999, 2002, 2003a, b, 2005, 2007, 2009, 2012, 2020; Barkov et al. 2001; Park et al. 2009; Lach et al. 2018; Donchev and Christov 2020; Donchev et al. 2021a, b), and from 0 to 290 °C (Christov and Moller 2004; Moller et al. 2006; Lassin et al. 2015). Several extensive parameter databases have been reported. These include: 25 °C database of Pitzer and Mayorga (1973, 1974), of Kim and Frederick (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 and Moller 2004; Moller et al. 2006; Christov 2009)], YMTDB (Sandia National Laboratories 2005, 2007), and THEREDA (2011a, b).

According to Pitzer theory, electrolytes are completely dissociated and in the solution there are only ions interacting with one 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 ($\text{MX}(\text{aq})$) are determined by Pitzer using the binary parameters of ionic interactions ($\beta^{(0)}, \beta^{(1)}, C^\phi$). The Pitzer's equations are described and widely discussed in the literature (Harvie et al. 1984; Christov and Moller 2004; Christov 2005; Moller et al. 2006; Donchev et al. 2021b). 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; Donchev et al. 2021b).

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 $\beta^{(2)}(\text{M},\text{X})$, 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 , Na_2SO_4 , or MgCl_2), the standard Pitzer approach use 3 parameters (i.e. omit the $\beta^{(2)}$ term) and α_1 is equal to 2.0. For 2-2 type of electrolytes the model includes the $\beta^{(2)}$ parameter and α_1 equals to 1.4 and α_2 equals to 12. This approach provides accurate models for many 2-2 binary sulfate (Pitzer and Mayorga 1974; Christov 1999, 2003a) and selenate (Christov et al. 1998; Barkov et al. 2001; Christov 2003a) 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 for strong association reactions at high molality, Christov (1996b, 1998a, b, 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 (see Eqns. (3) and (3A) in Donchev et al. 2021b). 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 $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{O}$: (Christov 1998)}, 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 2002, 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.

Results and discussions

Model parameterization for cesium binary $\text{CsF-H}_2\text{O}$, $\text{CsOH-H}_2\text{O}$ and $\text{Cs}_2\text{SO}_4\text{-H}_2\text{O}$ systems at 25 °C

In this study we developed new, not concentration restricted thermodynamic models for solution behavior and solid-liquid equilibrium in $\text{CsF-H}_2\text{O}$, $\text{CsOH-H}_2\text{O}$ and $\text{Cs}_2\text{SO}_4\text{-H}_2\text{O}$ systems at 25 °C. The new models are developed on the basis of Pitzer ion interactions approach. To parameterize models for cesium binary systems we used

all available experimental osmotic coefficients data for whole concentration range of solutions, and up to saturation point. Raw data at low molality from Hamer and Wu (1972) and Mikulin (1968), and extrapolated data from Mikulin (1968) are used to parameterize the model for CsF-H₂O system. The model for CsOH-H₂O has been constructed using low molality data from Hamer and Wu (1972) and Mikulin (1968), and osmotic coefficients data-point at saturation from Mikulin (1968). The new model for Cs₂SO₄-H₂O system has been developed using low molality data from Palmer et al. (2002) and Mikulin (1968), and extrapolated osmotic coefficients data-up to saturation from Mikulin (1968). To construct the models, we used different versions of standard molality-based Pitzer approach. It was established that for CsF-H₂O system 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. For CsOH-H₂O and Cs₂SO₄-H₂O system a standard approach with 3 interaction parameters was used. The predictions of new developed here models are in excellent agreement with experimental osmotic coefficients data (ϕ) in binary solutions from low to extremely high concentration (up to 21.8 mol.kg⁻¹ for CsOH-H₂O, and up to 35.6 mol.kg⁻¹ for CsF-H₂O) (see Fig. 1a, b, g, h, k). As it is shown on Fig. 1 for CsF-H₂O, CsOH-H₂O systems the new models are in pure agreement at high concentration with the low molality models of Pitzer and Mayorga (1973). For Cs₂SO₄-H₂O system the new model is again in pure agreement at high concentration with the low molality models of Palmer et al. (2002) and Scharge et al. (2012). New activity data are needed to validate the model for this binary.

Validation of models for cesium binary systems CsCl-H₂O, CsBr-H₂O, CsI-H₂O, CsNO₃-H₂O, and Cs₂SeO₄-H₂O

The previously developed by Christov (2003a, 2005), and Christov and co-authors (Balarew et al. 1993; Barkov et al. 2001; Donchev and Christov 2020) and by other authors (Pitzer and Mayorga 1973; Kim and Frederick 1988; Sharge et al. 2012) Pitzer approach based thermodynamic models for five (5) cesium binary systems (CsCl-H₂O, CsBr-H₂O, CsI-H₂O, CsNO₃-H₂O, and Cs₂SeO₄-H₂O) are tested in this study by comparison with experimental osmotic coefficients data and with recommendations on activity coefficients (γ_{\pm}) (for CsNO₃-H₂O) in binary solutions (Fig. 1). The models which give the best agreement with (ϕ)-, and (γ_{\pm}) - data from low to high concentration, up to m(sat), are accepted as correct models, which can be used for solubility calculations in binary and mixed systems and determination of thermodynamic characteristics of precipitating cesium solid phases. The following models are accepted as correct models: model of Balarew et al. (1993) and Christov et al. (1994) for CsCl-H₂O, and CsBr-H₂O systems (see heavy solid line on Fig. 1c,d,e); model of Pitzer and Mayorga (1973) for CsI-H₂O (see heavy solid line on Fig. 1f); model of Donchev and Christov (2020) for CsNO₃-H₂O (see heavy solid line on Fig. 1i), and the model of Barkov et al. (2001) for Cs₂SeO₄-H₂O system (see heavy solid line on Fig. 1j).

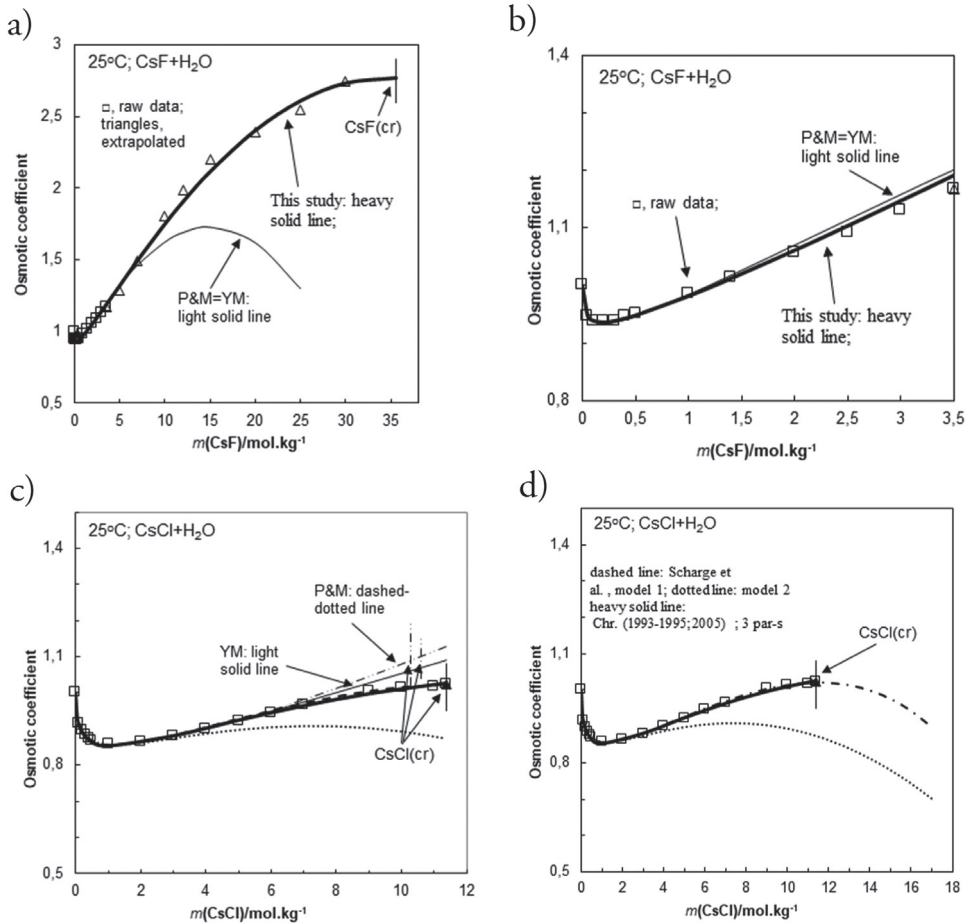


Figure 1. (a,b,c,d,e,f,g,h,i,j,k). Comparison of model calculated (lines) for activity coefficients (Fig. i) and for osmotic coefficients (φ) in cesium binary solutions (CsF-H₂O, CsCl-H₂O, CsBr-H₂O, CsI-H₂O, CsOH-H₂O, CsNO₃-H₂O, Cs₂SO₄-H₂O, and Cs₂SeO₄-H₂O) against molality at $T = 298.15$ K with recommendations in literature (symbols). For CsF-H₂O (Fig. b) and CsOH-H₂O (Fig. h) systems an enlargement of the low molality corner is also given. Heavy solid lines represent the predictions of the developed in this study (for CsF-H₂O, CsOH-H₂O, and Cs₂SO₄-H₂O systems) and previously reported and accepted models constructed by Christov and co-authors (Christov 2003a, 2005; Balarew et al. 1993; Barkov et al. 2001; Donchev and Christov 2020) and by Pitzer and Mayorga (1973) (for CsI-H₂O). Dashed-dotted, dashed and light solid lines represent the predictions of the reference models of Pitzer and Mayorga (1973) (as P&M on Fig. a,b,c,f, g and h), of Scharge et al. (2012) (for CsCl-H₂O and for Cs₂SO₄-H₂O (Fig. c, d and k)), and of Palmer et al. (2002) (for Cs₂SO₄-H₂O (Fig. k)) and of YMTB (given as YM on Fig. c and g) (Sandia National Laboratories (2005)). Experimental data (symbols) are from Hamer and Wu (1972) (for 1-1 systems), Robinson and Stokes (1959), Mikulin (1968), Palmer et al. (2002) (for Cs₂SO₄-H₂O), Partanen (2010) (recommended values for CsI-H₂O) and from Barkov et al. (2001) (for Cs₂SeO₄-H₂O). The molality of stable crystallization of solid cesium phases is given on all figures by vertical lines (see Table 1 for $m(\text{sat})$ sources).

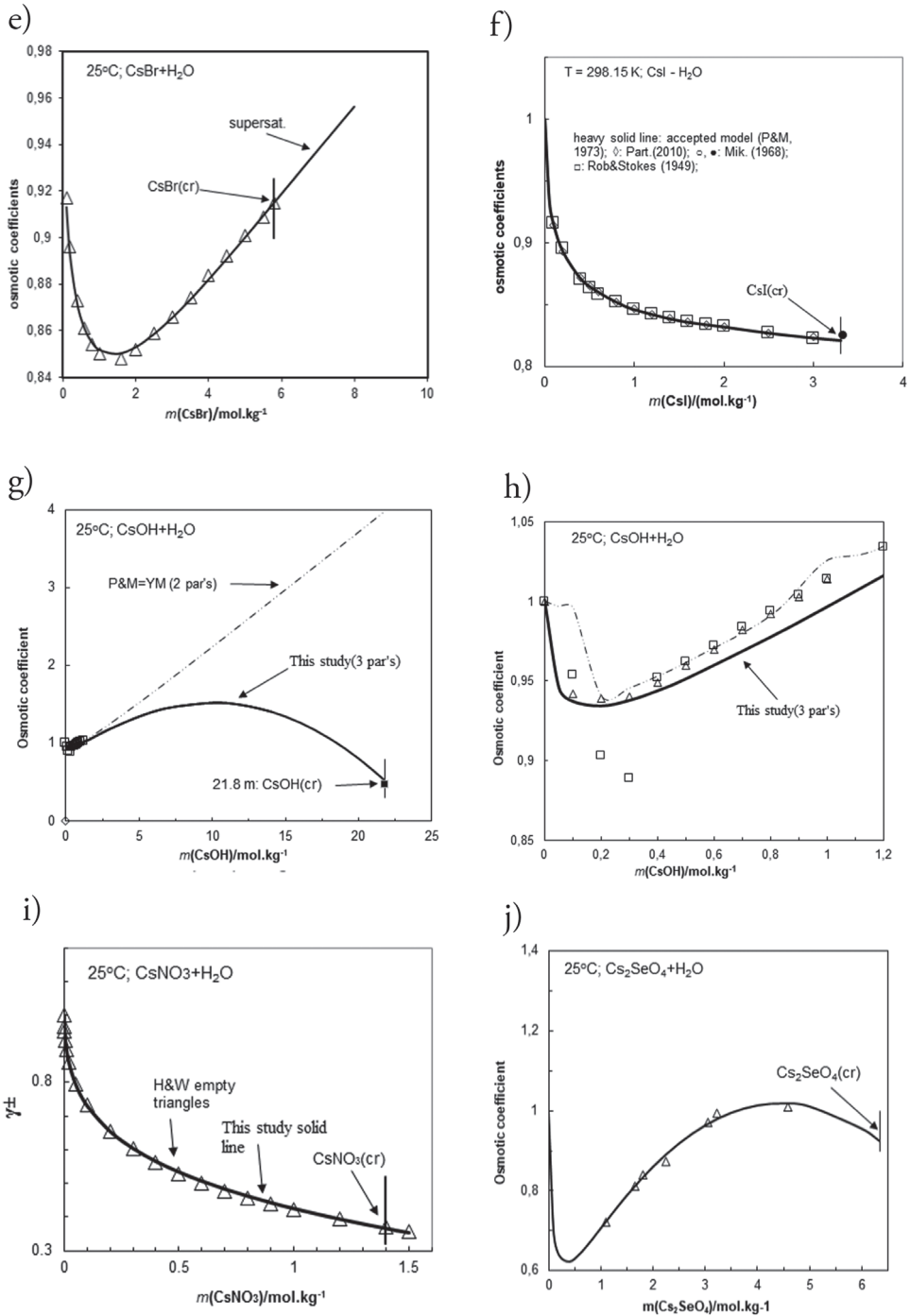


Figure I. Continued.

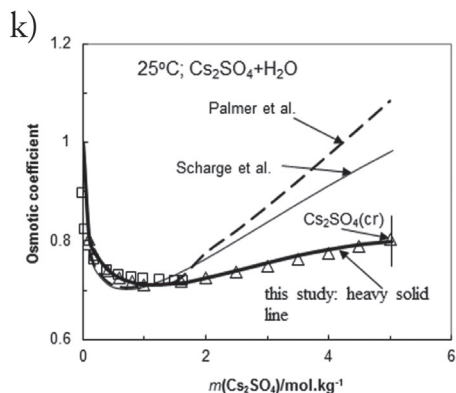


Figure 1. Continued.

Deliquescence Relative Humidity (DRH (%)) and thermodynamic solubility product ($\ln K_{sp}^o$) of cesium solid phases

On the basis of evaluated previously and accepted models (see previous paragraph) and evaluated in this study binary parameters we determine water activity (a_w) and Deliquescence Relative Humidity (DRH (%)) of solid phases crystallizing from saturated binary solutions. According to Christov (2009, 2012), Donchev and Christov (2020) and Donchev et al. (2021b): $\text{DRH} (\%) = a_w (\text{sat}) \times 100$; where $a_w (\text{sat})$ is activity of water at saturation. The results of DRH calculations are given in Table 1. The DRH predictions of new and accepted models 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 extremely low relative humidity of environment. As a next step, using the accepted and new developed parameterizations, and experimentally determined molalities ($m(\text{sat})$) of the saturated binary solutions (Mikulin 1968; Balarew et al. 1993; Barkov et al. 2001; Palmer et al. 2002) we calculate the logarithm of the thermodynamic solubility product ($\ln K_{sp}^o$) of cesium solid phases crystallizing from saturated binary solutions at 25 °C. The calculation approach is the same as in Christov (1995a, 1996a, 2005, 2009, 2012), in Donchev and Christov (2020), and in Donchev et al. (2021b). The model calculations are given in Table 1.

Models for cesium ternary systems

In previous studies of Christov (1996bc, 2003a, 2005) and Christov and co-authors (Balarew et al. 1993; Christov et al. 1994; Christov and Petrenko 1996; Barkov et al. 2001), a solid-liquid equilibrium Pitzer approach models for 15 cesium mixed ternary (CsCl-MgCl₂-H₂O, CsBr-MgBr₂-H₂O, CsCl-NiCl₂-H₂O, CsBr-NiBr₂-H₂O,

Table 1. Model calculated logarithm of the thermodynamic solubility product (as $\ln K_{sp}^{\circ}$), and model calculated and recommended values of the Deliquescence Relative Humidity (DRH) of the of cesium solid phases crystallizing from saturated binary solutions at $T = 25^{\circ}\text{C}$.

| Salt composition | m (sat) (exp) (mol.kg ⁻¹) | Calculated $\ln K_{sp}^{\circ}$ | DRH(%) | |
|---------------------------------------|---------------------------------------|---------------------------------|--------------------|--------------------------------|
| | | | Calculated | Experimental data ^a |
| CsF (cr) | 35.6 ^a | 14.74 | 2.46 | 4.0 |
| CsCl (cr) | 11.37 ^b | 3.49 | 65.69 | 65.80 |
| CsBr(cr) | 5.79 ^b | 1.905 | 82.62 | 82.6 |
| CsI(cr) | 3.305 ^a | 0.675 | 90.71 | 90.60 |
| CsOH(cr) | 21.8 ^a | 6.067 | 66.57 | - |
| CsNO ₃ (cr) | 1.40 ^a | -1.328 ^c | 96.54 ^e | 96.50 |
| Cs ₂ SO ₄ (cr) | 5.0 ^c | 0.9424 ^f | 80.60 ^f | 80.40 |
| | | 1.971 ^g | 74.59 ^g | |
| | | 1.486 ^h | 76.74 ^h | |
| Cs ₂ SeO ₄ (cr) | 6.34 ^d | 1.45 | 72.86 | - |

^aExperimental data of Mikulin (1968); ^bExperimental data of Balarew et al. (1993) and Christov (2005); ^cExperimental data of Palmer et al. (2002) and Christov (2003,2005); ^dExperimental data of Barkov et al. (2001) and Christov (2003); ^eFrom Donchev and Christov (2020);

^fCalculated using binary parameters determinate in this study (heavy solid line on Fig. 1k);

^gCalculated using binary parameters from Palmer et al. (2002) (dashed line on Fig. 1k);

^hCalculated using 4 parameters model of Sharge et al. (2012) (light solid line on Fig. 1k).

CsCl-MnCl₂-H₂O, CsCl-CoCl₂-H₂O, CsCl-CuCl₂-H₂O, CsCl-CsBr-H₂O, CsCl-RbCl-H₂O, Cs₂SO₄-CoSO₄-H₂O, Cs₂SeO₄-CoSeO₄-H₂O, Cs₂SO₄-NiSO₄-H₂O, Cs₂SeO₄-NiSeO₄-H₂O, Cs₂SO₄-ZnSO₄-H₂O, and Cs₂SeO₄-ZnSeO₄-H₂O systems at 25 °C are reported. The validated here parameterization for binary systems CsCl-H₂O, CsBr-H₂O, and Cs₂SeO₄-H₂O have been used without adjustment to develop a model for mixed systems. The Pitzer mixing ion interaction parameters ($\theta(\text{Cs}, \text{M}^{2+})$ and $\psi(\text{Cs}, \text{M}^{2+}, \text{X})$ for the cesium common anion ternary 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, 1996a, b, 1998, 1999, 2005, 2012).

The values of evaluated mixing parameter are summarized in Table 2. The mixed solution models are developed using our own solubility data (Balarew et al. 1993; Barkov et al. 2001), or the reference data from Zdanovskii et al. (2003), and Silcock (1979). The choice of the mixing parameters is based on the minimum deviation of the logarithm of the solubility product ($\ln K_{sp}^{\circ}$) for the whole crystallization curve of the component from its value for the binary solution. See Table 1 for $\ln K_{sp}^{\circ}$ values for cesium simple salts. In addition, the $\ln K_{sp}^{\circ}$ value for the cesium double salts crystallizing from the saturated ternary solutions has to be constant along the whole crystallization branch of the double salt. Since the parameters $\theta(\text{M}, \text{M}')$ take into account only the ionic interactions of the type M-M' in mixing solutions, their values have to be constant for the chloride, bromide, sulfate and selenate solutions with the same cations (M⁺ and M²⁺). Therefore, for common cation systems in constructing the mixing model, we keep the same value of $\theta(\text{M}, \text{M}')$, and only the $\psi(\text{M}, \text{M}', \text{X})$ have been varied. In our θ and ψ evaluation the unsymmetrical mixing terms (${}^E\theta$ and ${}^E\theta'$) have been

Table 2. Solutions mixing parameters [$\theta(\text{Cs}, \text{M}^{2+})$ and $\psi(\text{Cs}, \text{M}^{2+}, \text{X})$] evaluated on the basis of the m (sat) molality in cesium common anion ternary systems at 25 °C.

| System | $\theta(\text{Cs}, \text{M}^{2+})$ | $\psi(\text{Cs}, \text{M}^{2+}, \text{X})$ | Reference |
|---|------------------------------------|--|--|
| CsCl-MgCl ₂ -H ₂ O | -0.1260 | 0.0000 | Balarew et al. (1993) |
| CsBr-MgBr ₂ -H ₂ O | -0.1260 | -0.0367 | Balarew et al. (1993) |
| CsCl-MnCl ₂ -H ₂ O | 0.00 | 0.00 | Christov and Petrenko (1996) |
| CsCl-CoCl ₂ -H ₂ O | 0.00 | 0.00 | Christov and Petrenko (1996) |
| Cs ₂ SO ₄ -CoSO ₄ -H ₂ O ^a | (I) 0.00 (II) -0.05 | (I) -0.09 (II) -0.04 | Christov (2003a, 2005) |
| Cs ₂ SeO ₄ -CoSeO ₄ -H ₂ O ^a | (I) 0.00 (II) -0.05 | (I) 0.04 (II) -0.02 | Christov (2003a, 2005) |
| CsCl-NiCl ₂ -H ₂ O | -0.23 | 0.0000 | Christov (1996b) |
| CsBr-NiBr ₂ -H ₂ O | -0.23 | -0.0199 | Christov (1996b) |
| Cs ₂ SeO ₄ -NiSO ₄ -H ₂ O ^a | (I) -0.23 (II) -0.05 | (I) 0.015 (II) -0.05 | Christov (2003a, 2005) |
| Cs ₂ SeO ₄ -NiSeO ₄ -H ₂ O ^a | (I) -0.23 (II) -0.05 | (I) 0.015 (II) -0.13 | Barkov et al. (2001) Christov (2003a, 2005) |
| Cs ₂ SO ₄ -ZnSO ₄ -H ₂ O | -0.05 | -0.05 | Christov (2003a) |
| Cs ₂ SeO ₄ -ZnSeO ₄ -H ₂ O | -0.05 | -0.08 | Christov (2003a) |
| CsCl-CuCl ₂ -H ₂ O | 0.00 | -0.050 | Christov and Petrenko (1996) |
| CsCl-CsBr-H ₂ O ^b | -0.0001 | 0.00001 | Christov (1996c, 2005) |
| CsCl-RbCl-H ₂ O ^b | 0.00025 | -0.00060 | Christov et al. (1994) |

^a Two sets of mixing parameters (I and II) are evaluated in Christov (2003, 2005); ^bMixing solution parameters calculated by using the Zdanovskii rule (Christov et al. 1994; Christov (1996c, 2005)).

included (2003a, b, 2005). Mixing solution parameters for systems with precipitation of solid solutions (CsCl-CsBr-H₂O and CsCl-RbCl-H₂O) calculated by using the Zdanovskii rule (Christov et al. 1994; Christov 1996c, 2005) are also given in Table 2.

Summary and conclusions

In this study we developed new, not concentration restricted thermodynamic models for solution behavior and solid-liquid equilibrium in CsF-H₂O, CsOH-H₂O and Cs₂SO₄-H₂O systems at 25 °C. To parameterize models for cesium binary systems we used all available experimental osmotic coefficients data for whole concentration range of solutions, and up to saturation point. The new models are developed on the basis of Pitzer ion interactions approach. To construct the models, we used different versions of standard molality-based Pitzer approach. It was established that for CsF-H₂O system 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. The predictions of new developed here models are in excellent agreement with experimental osmotic coefficients data (ϕ) in binary solutions from low to extremely high concentration (up to 21.8 mol.kg⁻¹ for CsOH-H₂O, and up to 35.6 mol.kg⁻¹ for CsF-H₂O). The previously developed Pitzer approach based thermodynamic models for five (5) cesium binary systems (CsCl-H₂O, CsBr-H₂O, CsI-H₂O,

$\text{CsNO}_3\text{-H}_2\text{O}$, and $\text{Cs}_2\text{SeO}_4\text{-H}_2\text{O}$) are tested by comparison with experimental osmotic coefficients data and with recommendations on activity coefficients (γ_{\pm}) in binary solutions. The models which give the best agreement with (ϕ)-, and (γ_{\pm}) data from low to high concentration, up to $m(\text{sat})$, are accepted as correct models, which can be used for solubility calculations in binary and mixed systems and determination of thermodynamic characteristics of cesium solid phases. The thermodynamic solubility products ($\ln K_{\text{sp}}^{\circ}$), and the Deliquescence Relative Humidity (DRH) of solid phases, precipitating from saturated cesium binary solutions ($\text{CsF}(\text{cr})$, $\text{CsCl}(\text{cr})$, $\text{CsBr}(\text{cr})$, $\text{CsI}(\text{cr})$, $\text{CsOH}(\text{cr})$, $\text{CsNO}_3(\text{cr})$, $\text{Cs}_2\text{SO}_4(\text{cr})$, and $\text{Cs}_2\text{SeO}_4(\text{cr})$) have been determined on the basis of evaluated binary parameters and using experimental solubility data. The previously established and validated here parameterization for binary systems $\text{CsCl-H}_2\text{O}$, $\text{CsBr-H}_2\text{O}$, $\text{Cs}_2\text{SO}_4\text{-H}_2\text{O}$, and $\text{Cs}_2\text{SeO}_4\text{-H}_2\text{O}$ have been used without adjustment to develop a solid-liquid equilibrium model for 15 cesium mixed ternary ($\text{CsCl-MgCl}_2\text{-H}_2\text{O}$, $\text{CsBr-MgBr}_2\text{-H}_2\text{O}$, $\text{CsCl-NiCl}_2\text{-H}_2\text{O}$, $\text{CsBr-NiBr}_2\text{-H}_2\text{O}$, $\text{CsCl-MnCl}_2\text{-H}_2\text{O}$, $\text{CsCl-CoCl}_2\text{-H}_2\text{O}$, $\text{CsCl-CuCl}_2\text{-H}_2\text{O}$, $\text{CsCl-CsBr-H}_2\text{O}$, $\text{CsCl-RbCl-H}_2\text{O}$, $\text{Cs}_2\text{SO}_4\text{-CoSO}_4\text{-H}_2\text{O}$, $\text{Cs}_2\text{SeO}_4\text{-CoSeO}_4\text{-H}_2\text{O}$, $\text{Cs}_2\text{SO}_4\text{-NiSO}_4\text{-H}_2\text{O}$, $\text{Cs}_2\text{SeO}_4\text{-NiSeO}_4\text{-H}_2\text{O}$, $\text{Cs}_2\text{SO}_4\text{-ZnSO}_4\text{-H}_2\text{O}$, and $\text{Cs}_2\text{SeO}_4\text{-ZnSeO}_4\text{-H}_2\text{O}$) systems at 25 °C. The evaluated previously mixing parameters [$\theta(\text{Cs}, \text{M}^{2+})$ and $\psi(\text{Cs}, \text{M}^{2+}, \text{X})$], determined by solubility approach are tabulated. The models described in this study are of high importance in development of thermodynamic database needed for nuclear waste geochemical storage. The models are also of significant importance for extracting cesium resources from saline waters.

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