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CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

Isopiestic investigation of the osmotic coefficients of aqueous $CaBr_2$ and study of bromide salt solubility in the $NaBr$–$CaBr_2$–H_2O system at 50 °C: Thermodynamic model of solution behavior and solid–liquid equilibria in the $CaBr_2$–H_2O, and $NaBr$–$CaBr_2$–H_2O systems to high concentration and temperature

Christomir Christov *

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, ul. "Acad. G. Bonchev", bl. 11, 1113 Sofia, Bulgaria
Geo Eco Consulting 2010, 514 E. Barham Dr. # 237, San Marcos, CA 92078, USA

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ABSTRACT

The isopiestic method has been used to determine the osmotic coefficients of the binary solution $CaBr_2$–H_2O (from 0.5121 to 2.6631 mol kg^{-1}) at a temperature $T = 50$ °C. Sodium chloride solutions have been used as isopiestic reference standards. The solubility of the system $NaBr$–$CaBr_2$–H_2O has been investigated at 50 °C by the physico-chemical analysis method. Only the crystallization of simple bromide salts, $NaBr·2H_2O(cr)$, $NaBr(cr)$ and $CaBr_2·4H_2O(cr)$, has been established. The isopiestic and solubility measurements results obtained have been combined with experimental thermodynamic quantities (osmotic coefficients, calcium and sodium bromide mineral's solubilities) available in the literature, to construct a chemical model that calculates solute and solvent activities (from 25 to 250 °C, and from dilute to high solution concentration: up to $m(CaBr_2) = 7.5$ mol kg^{-1} at 25 °C, and up to 13.33 mol kg^{-1} at 225 °C), and solid–liquid equilibria (within the 0–105 °C temperature range) in the $CaBr_2$–H_2O system. The solubility modeling approach based on the fundamental Pitzer specific interaction equations is employed. It was found, that the standard for 2-1 type of electrolytes approach with three $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} single electrolyte ion-interaction parameters gives a very good agreement with osmotic coefficients data for unsaturated solutions, and with $CaBr_2·6H_2O(cr)$, and $CaBr_2·4H_2O(cr)$ equilibrium solubility data, used in parameterization. The resulting model for $CaBr_2$–H_2O system was used without further adjustment of model parameters, to develop a model for ternary system $NaBr$–$CaBr_2$–H_2O. The model for mixed system gives a very good agreement with bromide salts equilibrium solubility data presented here (at 50 °C), and those available in the literature (at 25 °C). Temperature extrapolation of the mixed system model provides reasonable mineral solubilities at low (0 °C) and high temperatures (up to 100 °C). Limitations of the binary and the mixed system model due to data insufficiencies are discussed. The model predictions on the effect of temperature on the deliquescence relative humidity (DRH) in $CaBr_2$–H_2O solutions, saturated with highly soluble calcium bromide minerals are also given. The calculated equilibrium DRH ($CaBr_2·6H_2O(cr)$) is in good agreement with the literature data.

1. Introduction

Recent field observations show that hydrothermal water can be strongly enriched with bromide relative to seawater [1–4]. Bottomley et al. explain the elevated Br/Cl ratios in subsurface water by evaporation beyond halite saturation. Leybourne and Goodfellow suggested that elevated Br/Cl ratios of saline water compared to seawater may be explained by differential uptake of Br and Cl during groundwater evolution through water–rock

reaction. In the late 1990s, the role of halogen species, especially bromide, in the ozone layer depletion became evident. Honninger et al. [5] measured a significant emission of bromide from the giant salar de Uyuni in the Bolivian Altiplano. Risacher et al. [6] measured a significant release of bromide from surface water and brines of Central Andes. Vogt et al. [7] described a mechanism of halogen release from sea-salt aerosols. The last experimental observations of Ghosal et al. [8,9] and of Jungwirth and Tobias [10] show that there is some unsymmetrical distribution of the halide (Cl, Br) ions in solid aerosol bulk and in liquid air–water aerosol interface: the concentration of bromide ion in surface area is much higher than in the bulk solid aerosol. The questions which arise are: (1) what is the effect of bromide on the deliquescence of high soluble chloride sea-salt minerals and of the complex sea-salt, and (2) to what extent bromide behaves conservatively in geochemical

* Corresponding address: Geo Eco Consulting 2010, 514 E. Barham Dr. # 237, San Marcos, CA 92078, USA.
   E-mail addresses: christov@svr.igic.bas.bg, hristovi@sbcglobal.net.

and aerosol formation processes. Construction of comprehensive thermodynamic model for bromide brine system can be a powerful predictive tool to solve the above geochemical and environmental problems.

Computer models that predict solution behavior and solid–liquid–gas equilibria close to experimental accuracy have wide applicability. Such models can be powerful predictive and interpretive tools to study the geochemistry of natural water and mineral deposits, solve environmental problems and optimize industrial processes. The specific interaction approach for describing electrolyte solutions to high concentration introduced by Pitzer [11,12] represents a significant advance in physical chemistry that has facilitated the construction of accurate thermodynamic models. It was shown that the Pitzer approach could be expanded to accurately calculate solubilities in complex brines and to predict the behavior of natural fluids [13–20].

This paper continues our series [17–27] concerning parameterization of comprehensive XTP-variable thermodynamic solid–liquid equilibria models of high soluble chloride, bromide, and hydroxide minerals precipitating within natural system H–Li–Na–K–Mg–Ca–Fe(II)–Fe(III)–Al–OH–Cl–Br–HSO_4–SO_4–H_2O. The main objective of this study is the development of comprehensive thermodynamic model for solution behavior, and highly soluble calcium bromide minerals solubility in $CaBr_2$–H_2O binary, and NaBr–$CaBr_2$–H_2O mixed systems from 0 to 250 °C. The solubility modeling approach based on fundamental Pitzer specific interaction equations is employed. Note that, none of atmospheric chemistry [28–31], and geochemistry [13–20] comprehensive models available includes bromide interactions with major sea-salt cations (Na, K, Mg, Ca) and anions (Cl, SO_4) and the bromide minerals equilibria. Other important applications of this model include design and assessment of nuclear and acid mine waste disposal strategies, development of high concentration halide leaching processes, and water desalination, as well as production of lithium-, and other high soluble evaporate-minerals and utilization of waste solutions during treatment of natural brine-type deposits.

Several authors [32,33] have constructed 25 °C models for Ca–Br interactions. The ion-interaction solution model of Gruszkiewicz and Simonson [34] is the only temperature variable model available in the literature for $CaBr_2$–H_2O system. These authors present a variant of extended ion-interaction model to describe their own osmotic coefficients data for unsaturated $CaCl_2$–H_2O and $CaBr_2$–H_2O solutions. The model of Gruszkiewicz and Simonson consist 34 adjustable parameters, and 32 of them are used to represent only the osmotic and activity coefficients in $CaCl_2$–H_2O solutions, and 28 for $CaBr_2$–H_2O solutions. To extend their solution model from the lowest temperature of their isopiestic experiments (107 °C; m(max) = 2.346 mol kg^{-1}) to low temperatures (to 0 °C), the authors used only one set of osmotic coefficients data at 25 °C. The model presented in Ref. [34] is restricted only for activity solution calculations, i.e. solid phases are not considered. Only our 25 °C models [22,23] included the bromide minerals solubility in $CaBr_2$–H_2O system. The model for mixed NaBr–$CaBr_2$–H_2O system could not be found in the literature.

2. Experimental details

2.1. Isopiestic measurements

Low and high molality osmotic coefficients/water activity data, determined on the basis of isopiestic measurements, are the most reliable thermodynamic data, which can be used in parameterization of reliable models, which can accurately predict not only solution behavior but also solid–liquid equilibria in binary and complex systems. The isopiestic results for aqueous solutions of

calcium bromide available in the literature are at standard temperature (25 °C) and at elevated temperatures (>107 °C). At standard temperature the raw isopiestic data are given by Robinson [35] (reference standard KCl; m(max) = 2.056 mol kg^{-1} m) and by Robinson and McCoach [36] (reference standard $CaCl_2$; m(max) = 7.216 mol kg^{-1}; and reference standard H_2SO_4; m(max) = 9.21 mol kg^{-1}). Stokes [37] smoothed these data up to supersaturation zone (up to 9 mol kg^{-1}; m(sat) = 7.51–7.66 mol kg^{-1}[38,39]). The smoothed osmotic coefficients values of Stokes are accepted in the compilation of Mikulin [38]. In their evaluations Goldberg and Nuttall [39] used the original data of Robinson [35], and Robinson and McCoach [36], and recommended the 25 °C osmotic coefficients up to 9.21 mol kg^{-1} of the binary solutions. It should be noted, that following the recommendations of Robinson (their personal communications) Goldberg and Nuttall [39] clearly estimated isopiestic data beyond the molality of 7.66 mol kg^{-1} as a data for supersaturated solutions. The same estimation has been done also by Mikulin [38] and Stokes [37]. The smoothed osmotic coefficients values of Goldberg and Nuttall [39] are in good agreement with recommendations of Stokes [37], and Mikulin [38]. In their comprehensive high temperature study of $CaBr_2$–H_2O system Gruszkiewicz and Simonson [34] carried out two types of experiments. Isopiestic measurements are used to determine osmotic coefficients from 107 to 250 °C and up to relatively low molality (m(max) = 2.346 mol kg^{-1} at 107 °C and m(max) = 3.95 mol kg^{-1} at 250 °C). Vapor pressure experiments are used to determined osmotic coefficients at higher molality (up to 13.1 mol kg^{-1} at 250 °C). In intermediate temperature range (from 25 to 107 °C) the isopiestic method based data are not available in the literature. The vapor pressure data of Patil et al. [40] (m($CaBr_2$) = (1.01–4.60) mol kg^{-1}; at (30–70) °C) are the only data found in the literature. Therefore, it was concluded that isopiestic results for aqueous solutions of calcium bromide at intermediate temperature range of the data (from 25 to 107 °C) are critical for developing a comprehensive ion-interaction model from 0 to 250 °C. We perform our isopiestic measurements at the temperature of 50 °C.

The osmotic coefficients of the $CaBr_2$–H_2O solutions were determined by the isopiestic method described in our previous studies [24,25]. Sodium chloride solutions were used as isopiestic reference standards. Stock solutions of aqueous calcium bromide and sodium chloride were prepared from solid samples and deionized water. Merck (A.R.) solid sodium chloride was used. The solid calcium bromide samples were Fluka 99.99%. The solids were used without further purification. To remove the residual moisture in the solids, the salts were dried slowly (for several hours) in air at 160 °C. The solutions were prepared by the gravimetric method. The salts were weighed with an accuracy of ±1.10^{-5} g giving, after the addition of 3 ml water, a solution of the desired concentration. The samples were placed in a copper low-pressure desiccator which, after evacuation, was placed in a thermostat whose temperature was maintained at (50 ± 0.01) °C. After attaining equilibrium, the samples were weighed again and the concentrations of the isopiestic solutions obtained were calculated.

Table 1 shows the isopiestic equilibrium molalities of $CaBr_2$(aq) with NaCl(aq) reference solutions. Reported molalities are the average of duplicate determinations. We found that an equilibrium period of 20 days at 50 °C yielded results with a good agreement of molalities for duplicate samples of the same electrolyte. The molalities in Table 1 are accurate to within 0.2% or better. The relatively long time needed to obtain equilibrium can be attributed to the fact that we have not shaken the desiccator with solutions investigated. We weighed the clean and dry copper cups before and after experiments. The initial and final weights of the cups were not changed. This fact permits us a conclusion that corrosion was not a problem in our isopiestic experiments. The maximum isopiestic

$CaBr_2$(aq) molality of our experiments is 2.6631 mol kg^{-1}. It is limited by the concentration of NaCl(aq) at which reference standard solutions remained undersaturated.

The osmotic coefficients φ of $CaBr_2$–H_2O solutions were calculated from the equation [24]:

$$\varphi = (y^*m^*\varphi^*)/(ym) \qquad (1)$$

where m is the molality of calcium bromide solution in isopiestic equilibrium with reference solution, m^* is the molality of the reference solution NaCl(aq) in isopiestic equilibrium with the test solution, and φ^* is the osmotic coefficient of the isopiestic reference standard, y and y^* are the stoichiometric ionization numbers of $CaBr_2$ and NaCl ($y = 3$ for $CaBr_2$, and $y^* = 2$ for NaCl). Osmotic coefficients φ^* for the isopiestic standard NaCl(aq) were calculated from the model of Pitzer et al. [41]. Table 1 contains the derived values of φ for the $CaBr_2$(aq) solutions. The maximum uncertainty for the reported osmotic coefficients was estimated to be no more than ± 0.007 for a single experimental data point.

2.2. Solubility measurements

The solubility data in the $CaBr_2$–H_2O system are available in the literature in relatively wide temperature range [from 0 to 105 °C]. The data are given in our previous study [22], and in the compilations of Linke [42], and Zdanovskii et al. [43]. According to these data $CaBr_2 \cdot 6H_2O$(cr) (from 0 to $\approx$34.2 °C) and $CaBr_2 \cdot 4H_2O$(cr) (from $\approx$34.2 to 105 °C) are the only solids precipitating from saturated binary solutions. Note that, opposite to corresponding chloride system ($CaCl_2$–H_2O; see Fig. 3 in Ref. [19]), there are no solubility measurements data in the literature for this bromide binary system, showing metastable crystallization of low crystalline hydrate ($CaBr_2 \cdot 4H_2O$(cr)) at temperatures below phase transition (hexahydrate $\leftrightarrow$ tetrahydrate) temperature (PTT). The data show that the solubility of both calcium bromide solids sharply increases with temperature. The equilibrium solubility data for $CaBr_2 \cdot 6H_2O$(cr) are in good agreement. However, there is some inconsistency between the low ((34.2 and 40) °C) and higher ((50, 60, and 80) °C) temperature $CaBr_2 \cdot 4H_2O$(cr) solubility data. According to the data summarized in Zdanovskii et al. [43] the $CaBr_2 \cdot 4H_2O$(cr) solubility at 50 °C varies from 11.01 to 12.4 mol kg^{-1}. To validate the tendency in increasing the $CaBr_2 \cdot 4H_2O$(cr) solubility we perform the solubility measurements in $CaBr_2$–H_2O binary system at 50 °C. Equilibrium solubility data in mixed NaBr–$CaBr_2$–H_2O system were found in the literature only at 25 °C [43]. The ternary systems solubility data are critical for developing a temperature variable ion-interaction model, which describe solid–liquid equilibria of bromide minerals in brine system. To extend with temperature the application range of our bromide model we also perform the solubility measurements in NaBr–$CaBr_2$–H_2O system at 50 °C.

The solubility of bromide minerals in binary (NaBr–H_2O, and $CaBr_2$–H_2O) and mixed (NaBr–$CaBr_2$–H_2O) systems was studied by the method of isothermal decrease of the supersaturation [21,22]. Different weight ratios of solid NaBr and $CaBr_2$ were used for each experiment. Crystal salts in excess of the solubilities at 50 °C were mixed with water. The solution was heated until the solid phases were completely dissolved and then transferred to a double walled glass thermostat and cooled rapidly to the desired temperature of 50 °C. Equilibrium was attained by continuous stirring for 24 h. Samples of the liquid and wet solid phases were withdrawn for analysis. Their separation has been achieved by a Cooch filter (G-3). Weighted amounts of the liquid and the wet solid phase were diluted to a definite volume and analyzed for determining solution composition. The compositions of the saturated solutions and the corresponding wet solid phase were established using the methods described in our previous studies [22]. Calcium ion

Table 1

Isopiestic molalities m of aqueous $CaBr_2$, with molalities m of NaCl reference solutions and the osmotic coefficients φ (exp) of $CaBr_2$ at 50 °C[a].

m(NaCl)/(mol kg^{-1})	m($CaBr_2$)/(mol kg^{-1})	φ(exp)($CaBr_2$)
0.7620	0.5121	0.9409
1.0944	0.7149	0.9812
1.2913	0.7952	1.0540
1.3975	0.8146	1.1102
1.5289	0.9105	1.0980
1.8202	1.0259	1.1736
1.7687	1.0293	1.1314
2.9143	1.4713	1.3853
2.8395	1.5199	1.3097
2.9475	1.5472	1.3400
3.2420	1.6887	1.3845
4.9896	2.3628	1.6802
4.9825	2.3833	1.6600
4.9642	2.3847	1.6494
5.4117	2.4498	1.7995
5.9944	2.6631	1.9086

[a] The reported molalities are the average of duplicate determinations.

was determined by complexometric titration with eriochrome black T as indicator [44]. Merck ammonium buffer solution (ammonium chloride/ammonia) was used for maintaining the high pH (pH = 10–11) of solutions in the complexometric titration process. The amount of bromide was found by titration with silver nitrate solution (the Mohr method) [44]. The compositions of the thoroughly suction dried solid phases (simple and double salts) were specified by the Schreinemakers graphic method ([45]; see also Refs. [21,22]). The results from the solubility measurements in the NaBr–$CaBr_2$–H_2O system at 50 °C are presented in Table 2.

The experimental error is within the limits of (0.1–0.3)%. Each of our experimental results represents the arithmetical mean of three parallel determinations. The $CaBr_2 \cdot 4H_2O$(cr) pure water solubility determined in this study (11.8 $\pm$ 0.12 mol kg^{-1}) lies between the values given in Zdanovskii et al. [43] at the same temperature. The solubility isotherm of NaBr–$CaBr_2$–H_2O system at 50 °C consists a field of equilibrium crystallization of anhydrous sodium bromide (NaBr(cr)), in addition to the stable in binary sub-systems at 50 °C simple salts NaBr$\cdot$2H_2O(cr) and $CaBr_2 \cdot 4H_2O$(cr). It can be seen from the data (Table 2) that even very low concentrations of Ca^{2+} lead to the dehydration of NaBr$\cdot$2H_2O(cr).

3. Modeling approach

The model presented here incorporates the concentration-dependent specific interaction equations of Pitzer [11,12] for aqueous solutions. Since the Pitzer's representation of the aqueous phase is based on the excess free energy, all the activity expressions are consistent, allowing different kinds of data {e.g., activity (water activity (a_w); osmotic (φ), and activity ($\gamma_\pm$) coefficients), voltage, and solubility measurements} to be used in the parameter evaluations and other thermodynamic functions to be calculated. Model validation involves comparison of model predictions with data not used in parameter evaluation process.

In constructing the temperature variable model for $CaBr_2$–H_2O and NaBr–$CaBr_2$–H_2O systems, the solubility approach is used. According to this approach, which is described previously in many publications [13–26], all ion-interaction pure electrolyte and mixing parameters are adjusted to fit the available activity and solubility data in the system under investigation.

To extend the application of the model for predictions of solution properties at very high concentrations and to fit the binary solution properties with lower sigma value some authors used in their single electrolyte parameterization different variants of extended version of Pitzer model (introducing two C^φ parameter values [46]; multi-parameters ion-interaction model [34]), or introducing in their approach mole fraction concentrations [47]. In

Table 2
Experimental solubility of NaBr·2H$_2$O(cr), NaBr(cr) and CaBr$_2$·4H$_2$O(cr) solid phases in the NaBr–CaBr$_2$–H$_2$O system at 50 °C.

Liquid phase, mass per cent (mass%)		Liquid phase, molality (m/mol kg^{-1})		Wet solid phase, mass per cent (mass.%)		Solid phase
(1)	(2)	(1)	(2)	(1)	(2)	
54.07	0.00	11.44	0.00	68.05	0.00	NaBr·2H$_2$O(cr)
46.82	7.41	9.94	0.81	87.8	1.93	NaBr(cr)
39.84	14.60	8.48	1.59	91.0	2.84	NaBr(cr)
28.53	26.22	6.13	2.90	83.9	6.08	NaBr(cr)
19.91	35.08	4.29	3.89	80.4	9.12	NaBr(cr)
10.84	46.48	2.47	5.45	83.1	9.60	NaBr(cr)
7.97	50.37	1.86	6.05	79.3	11.8	NaBr(cr)
4.85	53.07	1.12	6.31	75.8	14.2	NaBr(cr)
4.29	55.62	1.04	6.94	77.5	13.8	NaBr(cr)
2.04	61.17	0.54	8.32	74.1	16.75	NaBr(cr)
1.26	65.64	0.37	9.92	72.5	18.9	NaBr(cr)
1.78	66.75	0.55	10.61	69.3	21.4	NaBr(cr)
1.11	68.19	0.35	11.11	70.4	21.3	NaBr(cr)
0.91	69.68	0.15	11.85	7.40	69.9	NaBr(cr) + CaBr$_2$·4H$_2$O(cr)
0.00	70.22	0.00	11.8	0.00	72.6	CaBr$_2$·4H$_2$O(cr)

(1) NaBr; (2) CaBr$_2$.

the single electrolyte Ca–Br parameterization presented here, I use the standard molality-based Pitzer approach with one C^φ parameter. In our previous studies we show that the described previously modeling technology, based on the standard Pitzer approach (i.e. using max four single electrolyte interaction parameters: $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^φ) gives excellent model reliability from 0 °C to very high temperature (up to 300 °C), and from extremely low {[Al$_{total}$] $\approx$ 10^{-7} mol kg^{-1} and up to 290 °C in the aluminum hydroxide speciation model [16]} to very high concentration (for example, to 64 mol kg^{-1} in the NaOH–H$_2$O system [18]; up to 110 °C and $\approx$14.5 mol kg^{-1} in the CaCl$_2$–H$_2$O system [19]; up to 100 °C and 7.64 mol kg^{-1} in the MgCl$_2$–H$_2$O system [26]; up to 300 °C and 18 mol kg^{-1} in the NaBr–H$_2$O, and KBr–H$_2$O systems [24]; and up to 100 °C and 23 mol kg^{-1} HCl in the HCl–MgCl$_2$–H$_2$O mixed system [26]). Note that to avoid over-parameterization of the model at one single temperature at which experimental activity data are more complete and cover wide concentration range of solutions (mostly at 25 °C), in all these temperature variable models the pure electrolyte parameters are determined using activity data at much lower molality regions up to saturation, and always excluding the activity data for supersaturated solutions and metastable equilibrium solubility data. For example, temperature variable (0–250 °C) Na–OH and H–Cl binary parameters are evaluated using activity data only up to 8 mol kg^{-1}, although the data at 25 °C are available up to m(NaOH) = 23 mol kg^{-1} and m(HCl) $\approx$ 19 mol kg^{-1} [18]. The variable temperature parameters of Ca–Cl interactions are determined using activity data only up to 4 mol kg^{-1} and excluding in parameterization the metastable CaCl$_2$·4H$_2$O(cr) and CaCl$_2$·2H$_2$O(cr) crystallization solubility data, and the activity data in supersaturation zone (available up to 10 mol kg^{-1} at 25 °C) [15,19]. However, these high molality data are used in validation of the parameterization of our solution and solid–liquid equilibria models. In the model presented, it is accepted that the calcium bromide is completely dissociated and there are only independent ions in the solution, i.e. the equilibrium constant of complexes (such as CaBr$_2$°(aq)) are not included in the model. Therefore, at constant temperature and pressure, the solution model parameters to be evaluated are $\beta^{(0)}$, $\beta^{(1)}$, and C^φ for each cation–anion pair; θ for each unlike cation–cation or anion–anion pair; ψ for each triple ion-interaction where the ions are all not of the same sign.

Temperature dependence for the Ca–Br binary, and Na–Ca–Br interaction parameters and chemical potentials of calcium bromide solids is built into the model by adjusting selected constants in the following equation, where T is the Kelvin temperature [18]:

$$\text{Parameter } (T/K) = a_1 + a_2(T/K) + a_3(T/K)^2 + a_4(T/K)^3$$
$$+ a_5/(T/K) + a_6 \ln(T/K) + a_7/[(T/K) - 263]$$
$$+ a_8/[680 - (T/K)] + a_9/[(T/K) - 227]. \quad (2)$$

Note that the constants $a_3(T/K)^2$, $a_4(T/K)^3$, $a_7/[(T/K) - 263]$, $a_8/[680 - (T/K)]$, and $a_9/[(T/K) - 227]$ used in our acid–base [18,19] and, in aluminum speciation [16,20] models are not used in the calcium bromide solution-, and solid–liquid equilibria model presented here.

4. Model parameterization and results

In constructing the model of the binary CaBr$_2$–H$_2$O, and mixed NaBr–CaBr$_2$–H$_2$O systems, the temperature function for $\mu°_{H_2O}/RT$ and for the Debye–Huckel constant, A^φ is taken from Moller [15]. See also the discussion of Christov and Moller [18] for A^φ parameterization and validation. The model for mixed systems is developed using the (0–250 °C) NaBr–H$_2$O parameterization from Christov [24]. Temperature independent mixing parameters of Na–Ca interactions ($\theta_{Na,Ca}$) is the same as in Moller [15] and in Christov and Moller [19] (equals to 0.05).

Evaluations of temperature functions for the remaining model parameters are discussed in the sections below. They are the binary solution model parameters, $\beta^{(0)}$, $\beta^{(1)}$, and C^φ, for the Ca–Br ion interactions; the mixed solution model parameter $\psi_{Na,Ca,Br}$ for ion interactions in NaBr–CaBr$_2$–H$_2$O ternary solutions; and the standard chemical potentials of CaBr$_2$·6H$_2$O(s) and CaBr$_2$·4H$_2$O(s) bromide solid phases contained within CaBr$_2$–H$_2$O, and NaBr–CaBr$_2$–H$_2$O systems. The differences between calculated and experimental activity data for binary CaBr$_2$–H$_2$O system are summarized in terms of sigma (σ) [18,19].

Following the approach in our previous studies [17,23–26] to avoid overlapping effect of pure electrolytes and mixing solution parameters, the model for binary CaBr$_2$–H$_2$O system was developed using only the data for this binary system, and mixed solutions model was parameterized on the basis of the data only for NaBr–CaBr$_2$–H$_2$O system. Note that in our binary and mixed systems model parameterization we used only raw experimental thermodynamic quantities (osmotic coefficients, and minerals solubility), which are directly derived from experimental measurements (isopiestic and vapor pressure studies, and solubility experiments). The calculated mean activity/osmotic coefficients recommendations are model dependent, and therefore are not used in parameterization process. The solubility model predictions for mixed NaBr–CaBr$_2$–H$_2$O system at temperatures which are outside the temperature range of the data are also given.

4.1. Evaluation of parameters in the CaBr$_2$–H$_2$O system

In constructing the model of the CaBr$_2$–H$_2$O system from 0 to 250 °C, single electrolyte parameters ($\beta^{(0)}$(Ca, Br), $\beta^{(1)}$(Ca, Br), and

Table 3
Standard deviation (σ) values of osmotic coefficients (φ) data in CaBr$_2$–H$_2$O system (n is the number of experimental data points).

Method[a]	Type of data	$T/(°C)$	Molality range/(mol kg^{-1})	Reference	σ
iso	φ	50	m (CaBr$_2$): 0.512–2.663	This work (Table 1)	0.048 ($n = 16$)
comp	φ	25	m (CaBr$_2$): 0.1–7.00	Mikulin [38] (used in parameterization)	0.056 ($n = 55$)
comp	φ	25	m (CaBr$_2$): 0.001–7.50	Goldberg and Nuttall [39] (not used in parameterization)	
iso	φ	107–250	m (CaBr$_2$): 2.154–3.95	Gruszkiewicz and Simonson [34]	0.028 ($n = 32$)
v.p.	φ	140–250	m (CaBr$_2$): 2.54–13.33	Gruszkiewicz and Simonson [34]	0.067 ($n = 112$)
v.p.	φ	30–70	m (CaBr$_2$): 1.01–4.60	Patil et al. [40]	0.084 ($n = 40$)

[a] Experimental method: iso—isopiestic; comp—compilation; v.p.—vapor pressure.

C^φ(Ca, Br)) are adjusted to fit the available activity and solubility data in CaBr$_2$–H$_2$O system. Temperature and concentration variable reference osmotic coefficients data for unsaturated solutions are used to evaluate solution parameters for low and moderate calcium bromide concentration. Equilibrium solubility measurements of bromide minerals CaBr$_2$·6H$_2$O(cr) and CaBr$_2$·4H$_2$O(cr) precipitating in this binary system are also used to broad concentration and temperature range of parameterization.

The osmotic data used in parameterization are summarized in Table 3. References, molality and temperature range of the experiments, and number n of experimental data points are also given in the table. The osmotic coefficient data sets which are determined directly from isopiestic measurements of calcium bromide solutions and included in parameterization are: (1) our isopiestic results at 50 °C and up to 2.6631 mol kg^{-1} given in Table 1; (2) the 25 °C recommendations of Mikulin [38] up to $m = 7$ mol kg^{-1}; and (3) high temperature/low molality isopiestic data of Gruszkiewicz and Simonson [34] (from 107 to 250 °C, and up to $m = 3.95$ mol kg^{-1}). In addition to above isopiestic study data we include in our parameters evaluation the osmotic coefficients determined on the basis of vapor pressure measurements. For a broad concentration and temperature ranges of pure electrolyte parameterization the high temperature/high molality φ values of Gruszkiewicz and Simonson [34] (from 140 to 250 °C, and up to $m = 13.33$ mol kg^{-1}) are used (set 4). The vapor pressure data in intermediate temperature range given by Patil et al. [40] up to $m = 4.60$ mol kg^{-1}, and from 30 to 70 °C are also included (set 5). Note that in our final parameterization of the temperature variable equilibrium model for CaBr$_2$–H$_2$O system the 25 °C osmotic data in the supersaturated solutions are not considered (i.e. two data points in the recommendations of Mikulin [38] at m (CaBr$_2$) = (8 and 9) mol kg^{-1}).

The CaBr$_2$·6H$_2$O(cr) and CaBr$_2$·4H$_2$O(cr) solubility data in the CaBr$_2$ + H$_2$O system at (0–105) °C are used to evaluate the chemical potential of solid minerals. The obtained in this study CaBr$_2$·4H$_2$O(cr) solubility at 50 °C, 25 °C CaBr$_2$·6H$_2$O(cr) solubility given in our previous study [22], and the data summarized by Linke [42] at (0, 10, 20, 25, 34, 40, 60, 80, and 105) °C, and by Zdanovskii et al. [43] at (40, and 60) °C are used in parameterization. Note that the CaBr$_2$·4H$_2$O(cr) solubility data point at 105 °C given in Linke [42] does not follow the trend of the solubility at lower temperatures.

The resulting $\beta^{(0)}$(Ca, Br), $\beta^{(1)}$(Ca, Br), and C^φ(Ca, Br) parameterization for the binary CaBr$_2$–H$_2$O system is presented in Table 4. On Fig. 1(a)–(c) we plot the temperature dependence of pure electrolyte $\beta^{(0)}$, $\beta^{(1)}$, and C parameters, established in this study. The 25 °C recommendations of Pitzer and Mayorga [32] and Kim and Frederick [33] are also given on Fig. 1(a)–(c). Note that C(Ca, Br) parameter is related to tabulated in Table 4 C^φ parameter by the equation: $C(MX) = C^\varphi(MX)/2(|Z_M Z_X|)^{1/2}$ and in case of calcium bromide: C^φ(Ca, Br) $\approx C$(Ca, Br) $\times$ 2.82843. As is shown on Fig. 1, the regression of activity and solubility data used in parameterization gives a temperature variation of all three $\beta^{(0)}$(Ca, Br), $\beta^{(1)}$(Ca, Br) and C(Ca, Br) binary parameters, which is well smoothed throughout the (0–150) °C temperature range. The

values of all three parameters are within the acceptable range values for whole temperature range. The $\beta^{(0)}$ parameter has a positive value and smoothly increase with temperature from 0 to 125 °C through a maximum at about 125 °C (max value of 0.38); $\beta^{(1)}$ smoothly decrease with temperature from 0 to 100 °C and do not exceed the value of 4.1 (at 0 °C); and C^φ consistently decrease with temperature and has a max value of 0.019 at 0 °C. The evaluated in this study values of $\beta^{(0)}$(Ca, Br), and C^φ(Ca, Br) at 25 °C are very close to those recommended by Kim and Frederick [33]. The relatively high difference of $\beta^{(1)}$ and C^φ values established here and those evaluated by Pitzer and Mayorga [32] is not surprising since the Ca–Br parameterization uses different concentration range of experimental data. Following our solubility approach, the pure electrolyte Ca–Br parameters are evaluated in this study using binary system activity data for unsaturated solutions (up to 7 mol kg^{-1} at 25 °C) and CaBr$_2$·6H$_2$O(cr) solubility data. Therefore, the established Ca–Br parameterization is valid up to saturated binary solutions. Kim and Frederick [33] evaluated their Ca–Br interaction parameters using activity data up to 6.0 mol kg^{-1}. The parameterization of Pitzer and Mayorga [32] is valid only up to 2.0 mol kg^{-1}, and therefore their C^φ (Ca, Br) parameter, which is much more sensitive pure electrolyte parameter to the higher molality data, has much smaller value than those determined here and by Kim and Frederick.

It was established that introducing in the temperature function (Eq. (2)) for parameters of Ca–Br interactions of constants a_3, a_4, a_6, a_7 and a_8 do not improve considerably the fit of the experimental data used in evaluations. Therefore, the temperature functions for pure electrolyte parameters of Ca–Br interactions include only three constants (a_1, a_2, and a_5). The $\beta^{(0)}$ (Ca, Br), $\beta^{(1)}$ (Ca, Br), and C^φ (Ca, Br) parameterization gives a good agreement with all the data for unsaturated binary solutions used in evaluation process. The sigma values for the fit of the osmotic data sets from 0 to 250 °C and up to 13.33 mol kg^{-1} are 0.084 (for set 6) or less (given in last column of Table 3). Note that the model at standard temperature was parameterized using only the osmotic data of Mikulin [38] up to 7 mol kg^{-1}. However, to check the consistency of the model presented here and smoothed osmotic coefficients values available in the literature, we determined the sigma value for the fit of the recommended data of Mikulin [38], and of Goldberg and Nuttall [39] (up to 7.5 mol kg^{-1}). The final smoothed with temperature solution model fits both sets of data with a low sigma value of 0.056. The comparison between experimental osmotic coefficients data (symbols) and predictions of solution model (solid lines) are also given on Fig. 2 (at 50 °C) and Fig. 3 (from 25 to 250 °C). To show the model agreement at low molality, where the data are too compressed, we also compare critically evaluated and experimental osmotic coefficients in Table 5. At 50 °C the predicted osmotic coefficients are in excellent agreement with our data presented in Table 1 (open squares), and those of Patil et al. [40] (closed triangles) (see Fig. 2). The 25 °C activity model gives a very a good agreement with the recommendations of Mikulin [38], and Goldberg and Nutall [39] up to very high molality of unsaturated solutions (see Table 5 up to 7.0 mol kg^{-1}, and Fig. 3 up to 7.5 mol kg^{-1}). The predicted concentration dependence of osmotic coefficients is also in very good agreement with the

Table 4
Values of the fitting constants (Eq. (2)) for the binary and ternary solution interaction parameters[a].

Parameters	Constants (T in Kelvin)			
	$a_1(-)$	$a_2(T)$	$a_5(1/T)$	$a_6(\ln T)$
$\beta^{(0)}$(Na, Br)[b] ((273.15–573.15) K)	7.11600256d−01	−7.51986135d−04	−1.09266366d+02	0
$\beta^{(1)}$(Na, Br)[b] ((273.15–573.15) K)	−4.97335195d00	8.57795255d−03	7.38610135d+02	0
C^{φ}(Na, Br)[b] ((273.15–573.15) K)	−7.34172496d−02	8.71449532d−05	1.33019597d+01	0
$\beta^{(0)}$(Ca, Br) ((273.15–523.15) K)	1.93796297d00	−2.02463996d−03	−2.97733495d+02	0
$\beta^{(1)}$(Ca, Br) ((273.15–523.15) K)	−5.32419836d+01	7.54397694d−02	1.00344685d+04	0
$C^{(\varphi)}$(Ca, Br) ((273.15–523.15) K)	−2.49439694d−01	2.61696289d−04	5.37832428d+01	0
$\theta_{Na,Ca}$[c] ((273.15–523.15) K)	5.00d−02	0	0	0
$\psi_{Na,Ca,Br}$ ((298.15–323.15) K)	6.06567329d+01	1.79115831d−02	−1.56036933d+03	−1.06670101d+01

[a] The constants a_3, a_4, and a_7 – a_8 in Eq. (2) are equal to zero for all the above parameters. The temperature range listed with each parameter indicates the temperature range of experimental data used in model parameterization and/or validation.
[b] Parameter determined by Christov [24].
[c] Parameter determined by Moller [15], and validated by Christov and Moller [19].

Table 5
Predicted osmotic coefficient (φ) of CaBr$_2$ in binary CaBr$_2$–H$_2$O solutions as a function of molality m (in mol kg^{-1}) and temperature.

Cal/measured values of:	$T/(°C)$	Osmotic coefficient φ (CaBr$_2$)						
		0.1 mol kg^{-1}	0.5 mol kg^{-1}	1.0 mol kg^{-1}	4.0 mol kg^{-1}	7.0 mol. kg^{-1}	8.0 mol kg^{-1}	12.0 mol kg^{-1}
This study[a]	25	0.915	1.007	1.145	2.551	4.414	–	–
Calcd[b]		0.869	0.9598	1.1265	2.6078	4.463	–	–
Calcd[c]		0.863	0.958	1.131	2.584	4.4254	–	–
This study[a]	50	0.874	0.9590	1.1154	2.440	3.951	4.369	6.603
Data[d]			0.941[f]	1.17–1.19	≈2.39[f]			
This study[a]	100	0.835	0.899	1.055	2.211	3.334	3.523	4.378
This study[a]	200	0.797	0.823	0.897	1.693	2.272	2.413	2.4406
Data[e]						2.271		
This study[a]	250	0.697	0.766	0.770	1.374	1.898	2.055	2.113
Data[e]					1.389	≈1.87[f]		≈2.08[f]

[a] Predictions of the model presented here (Table 3).
[b] Recommended values of Goldberg and Nuttall [39].
[c] Recommended values of Mikulin [38].
[d] This study (Table 2) and Patil et al. [40].
[e] Gruszkiewicz and Simonson [34].
[f] Data at 0.51, 3.95, 6.90, and 11.79 mol kg^{-1}.

available high temperature (from 107 to 250 °C) and high molality ($m \geq 2.154$ mol kg^{-1}) experimental data of Gruszkiewicz and Simonson [34] (see the comparison in Table 5 and Fig. 3).

A temperature function for the standard chemical potential of calcium bromide hexahydrate, and tetrahydrate are presented in Table 6. On Fig. 4 we plot the temperature dependence of thermodynamic solubility product (as $\ln K°_{sp}$) of CaBr$_2$·6H$_2$O(cr) and CaBr$_2$·4H$_2$O(cr). The model predicts solubility product values for hexahydrate, which very smoothly decrease with temperature from 13.41 at 0 °C to 13.0 at 50 °C. The $\ln K°_{sp}$ of CaBr$_2$·4H$_2$O(cr) increases smoothly from Phase Transition Temperature (PTT) to about 50 °C having a maximum value of about 19.37. At $T > 50$ °C $\ln K°_{sp}$ (CaBr$_2$·4H$_2$O(cr)) decreases with temperature and at 100 °C has a value of 14.44. The variation temperature model predicts $\ln K°_{sp}$ (CaBr$_2$·6H$_2$O(cr) value at 25 °C (equals to 13.19), which is very close to those calculated on the basis of isothermal 25 °C Pitzer model and given in our previous study [22] (equals to 13.05; see closed diamond on Fig. 4). Note that in development of our standard temperature mixed solution model for LiBr–CaBr$_2$–H$_2$O system [22] we used Ca–Br pure electrolyte parameterization of Kim and Frederick [33]. Using the reference data for aqueous species from Wagman et al. [48], and $\ln K°_{sp}$ values determined here, we also calculated the standard molar Gibbs free energy of formation ($\Delta_f G°_m$) at 25 °C of solid phases introduced into a present model: CaBr$_2$·6H$_2$O(cr), and CaBr$_2$·4H$_2$O(cr). The calculated $\Delta_f G°_m$ value of CaBr$_2$·6H$_2$O(cr) (−2151.57 kJ mol^{-1}) is very close to those determined in our previous studies [22,23] (−2151.93 kJ mol^{-1}) and lies between the recommendations of Mikulin [38] (−2150.79 kJ mol^{-1}) and

Wagman et al. [48] (−2152.8 kJ mol^{-1}). For tetrahydrate the model predicts $\ln K°_{sp}$ equals to 17.612 and $\Delta_f G°_m$ equals to: −1666.36 kJ mol^{-1}. Note that, according to the experimental solubility data available in the literature CaBr$_2$·4H$_2$O(cr) is not a stable solid phase at 25 °C, i.e. $\ln K°_{sp}$ (CaBr$_2$·4H$_2$O(cr)) and $\Delta_f G°_m$ (CaBr$_2$·4H$_2$O(cr)) calculations represent the temperature extrapolation of our tetrahydrate solid–liquid equilibria model.

The established solution (Table 4) and solid–liquid (Table 6) parameterization gives very good agreement with the pure water solubility data for both hydrates from 0 to 105 °C (see Fig. 5). According to the model, the pure water solubility of calcium bromide solids very sharply increases with temperature, e.g. CaBr$_2$·6H$_2$O(cr) from 6.24 mol kg^{-1} at 0 °C to 8.5 mol kg^{-1} at 32 °C, and CaBr$_2$·4H$_2$O(cr) from 8.5 mol kg^{-1} at 32 °C to 16.45 mol kg^{-1} at 95 °C. At higher temperature, the equilibrium model predicts decreasing of solubility of tetrahydrate. The predicted solubility of CaBr$_2$·4H$_2$O(cr) at 105 °C (equals to 15.49 mol kg^{-1}) is very close to those recommended by Linke [42] (equals to 15.58 mol kg^{-1}). This maximum on solubility curve at about 95 °C and 16.45 mol kg^{-1} can be explained by the crystallization of low calcium hydrate solid. CaBr$_2$·2H$_2$O(cr) can be suggested. New experimental solubility measurements data are needed to validate this model prediction. Above 105 °C, which is the highest temperature of the solubility data available in the literature, the model does not predict the precipitation of CaBr$_2$·4H$_2$O(cr) from binary solutions. At standard temperature the predicted molality of solutions saturated with CaBr$_2$·6H$_2$O(cr) (7.596 mol kg^{-1}) lies between recommended m(sat) values of Mikulin (7.57 mol kg^{-1}) and Goldberg and Nutall (7.66 mol kg^{-1}). At 50 °C the model

Table 6
Values of fitting constants (Eq. (2)) for Debye–Huckel constant (A^φ), ln Kw and for the standard chemical potentials of calcium bromide solid phases[a].

Parameters	Constants (T in Kelvin)						
	a_1 (–)	a_2 (T)	a_3 (T^2)	a_5 ($1/T$)	a_6 ($\ln T$)	a_7 ($1/(T-263)$)	a_8 ($1/(680-T)$)
$A^{\varphi\,b}$ ((273.15–523.15) K)	3.36901532d–01	–6.32100430d–04	1.92118597d–06	9.14252359d00	–1.35143986d–02	2.26089488d–03	4.52586464d+01
ln Kw(μ°/RT) H$_2$O(aq)[b] ((273.15–523.15) K)	1.04031130d+03	4.86092851d–01	–2.32009393d–04	–3.26224352d+04	–1.90877133d+02	–5.35204850d–01	5.20549183d+01
NaBr·2H$_2$O(cr)[c] ((273.15–324.15) K)	3.89734390d+01	–7.97179210d–02	0	–2.23620498d+04	0	0	0
NaBr(cr)[c] ((298.15–573.15) K)	2.43358712d00	3.62446066d–03	0	9.50793364d+02	0	0	0
CaBr$_2$·6H$_2$O(cr) ((273.15–305.25) K)	–2.07465165d+03	–9.37826320d–01	0	–8.10542764d+03	3.86360340d+02	0	0
CaBr$_2$·4H$_2$O(cr) ((305.25–378.15) K)	5.02886383d+04	1.20621172d+01	0	–1.53132394d+06	–8.57557029d+03	0	0

[a] The constant a_4 in Eq. (2) is equal to zero for all the above parameters. The temperature range listed with each parameter indicates the temperature range of the experimental data used in model parameterization and/or validation.
[b] Parameter determined by Moller [15] and validated by Christov and Moller [18].
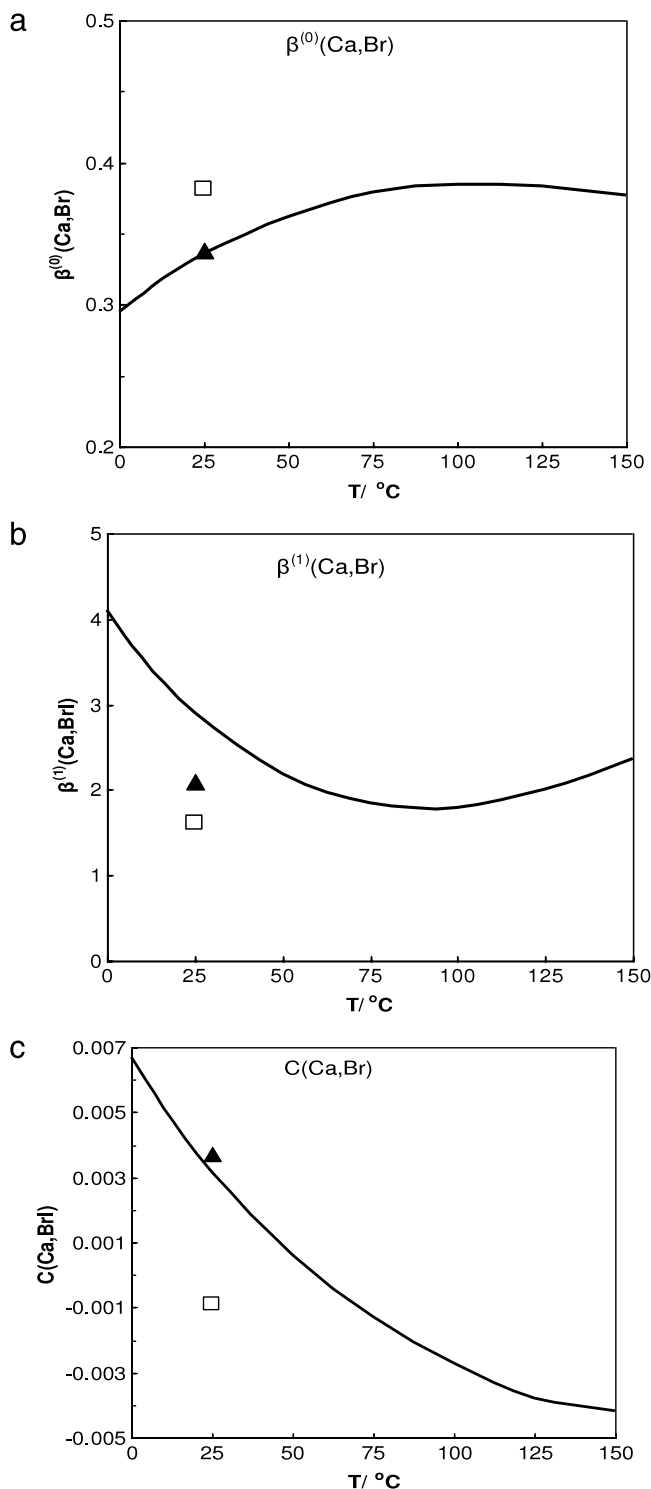[c] Parameter determined by Christov [24].

a

b

c

Fig. 1. (a)–(c). Comparison of $\beta^{(0)}$ (Mg, Cl) (a), $\beta^{(1)}$ (Mg, Cl) (b) and C(Ca, Br) (c) pure electrolyte parameters evaluated in this study and presented in Table 4 [solid lines: (0–150) °C] with the recommended values of Pitzer and Mayorga [32] (open squares) and Kim and Frederick [33] (closed triangles) at 25 °C.

Fig. 2. The calculated (solid line) and experimental (symbols) osmotic coefficients (φ) of CaBr$_2$ against molality m of CaBr$_2$–H$_2$O at 50 °C. Experimental data: open squares, this study (see Table 1), closed triangles, Patil et al. [40].
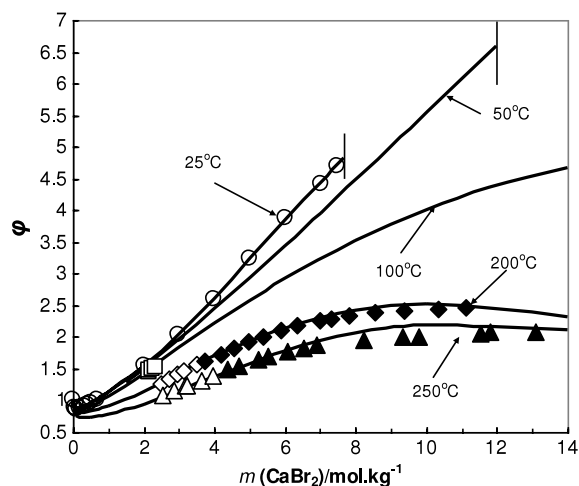
Fig. 3. Comparison of osmotic coefficients (φ) of CaBr$_2$ in CaBr$_2$–H$_2$O solutions calculated by the model [solid lines: (25, 50, 100, 200, and 250) °C] with the reference values. Open symbols denote osmotic coefficients derived from isopiestic measurements. Closed symbols are osmotic coefficients determined on the basis of vapor pressure experiments. Circles, squares, diamonds, and triangles denote the recommendations of Goldberg and Nuttall [39] at 25 °C, and data of Gruszkiewicz and Simonson [34] at (107, 200 and 250) °C, respectively. The vertical lines show the molality of the saturated CaBr$_2$–H$_2$O solutions at (25 and 50) °C.

predicted (11.96 mol kg^{-1}) and measured in this study (11.8 ± 0.12 mol kg^{-1}) molality of CaBr$_2$·4H$_2$O(cr) saturation are also in good agreement. The (CaBr$_2$·6H$_2$O(cr) $\leftrightarrow$CaBr$_2$·4H$_2$O(cr)) phase transition in water is predicted to occur at a temperature of 32.1 °C, which is only 2.1 °C lower than the transition temperature measured by Kremers [49] (see also Linke [42]) and accepted in compilation of Kirgintsev et al. [50] (e.g., $T = 34.2$ °C).
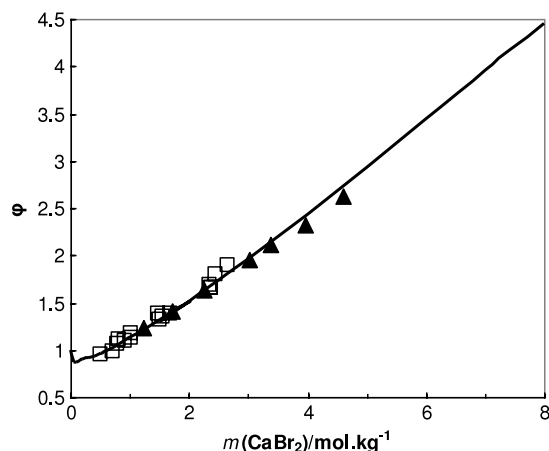
In development of our variable temperature model we used in single electrolyte parameterization all available in the literature activity (from 25 to 250 °C; see Table 6) and solubility (from 0 to 105 °C) data and excluded the osmotic coefficients data points at supersaturation. Note that inclusion of such a data beyond equilibrium molality is in contradiction with the rules of the solubility approach used here (see Modeling Approach section). However, following our model parameterization technology, which includes critical evaluation of consistency of all the data available, we included in our preliminary model the 25 °C osmotic coefficients data at supersaturation. We found that inclusion of only two osmotic coefficients data points (at (8 and 9) mol kg^{-1} from Ref. [38]) leads to: (1), increasing the standard deviation of fit of all activity datasets at lower molality and from 25 to 70 °C (sigma value of fit of complete activity data set of Mikulin [38] at 25 °C increases almost two times up to 0.08), and (2), completely destroying the consistence of solid–liquid equilibria model. The model "blow up" and cannot predict precipitation of bromide minerals even at a little higher temperature of about 32 °C, which is close to PTT. It was concluded that the 25 °C activity data for supersaturated

Table 7

Experimental and model predicted compositions (units: mol kg^{-1}) of invariant points for the NaBr–CaBr$_2$–H$_2$O system at (25 and 50) °C.
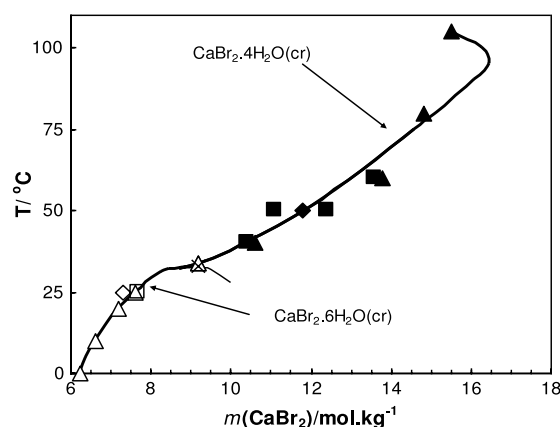
Cal/Exp values	$T/(°C)$	m(NaBr)	m(CaBr$_2$)	Solid phases
Calculated	25	2.18	4.74	NaBr·2H$_2$O(cr) + NaBr(cr)
Experimental[a]		2.03	4.83	
Experimental[b]		1.67	4.85	
Calculated	25	0.17	7.57	NaBr(cr) + CaBr$_2$·6H$_2$O
Experimental[a]		0.50	6.93	
Experimental[b]		0.18	7.46	
Calculated	50	10.41	0.65	NaBr·2H$_2$O(cr) + NaBr(cr)
Calculated	50	0.173	11.98	NaBr(cr) + CaBr$_2$·6H$_2$O
Experimental[c]		0.15	11.85	

[a] Bogoiavleskii and Feduniak [51].
[b] Ksenzenko et al. [52].
[c] This study (Table 2).
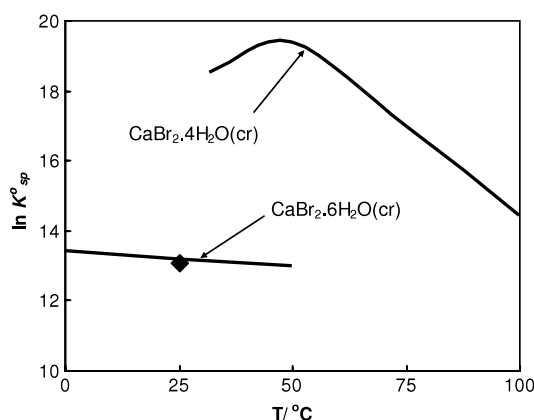
Fig. 4. Calculated thermodynamic solubility product ($\ln K°_{sp}$) of CaBr$_2$·6H$_2$O(cr) and CaBr$_2$·4H$_2$O(cr) vs. temperature [solid lines: (0 to 100) °C)]. The closed diamond denotes the recommended value of Christov et al. [22] at 25 °C.

Fig. 5. The calculated (heavy solid line) and experimental (symbols) solubility of CaBr$_2$·6H$_2$O(cr) and CaBr$_2$·4H$_2$O(cr) solid phases in the CaBr$_2$–H$_2$O system as a function of temperature ((0 to 105) °C). Open symbols: CaBr$_2$·6H$_2$O(cr) precipitation. Solid symbols: CaBr$_2$·4H$_2$O(cr) precipitation. Diamonds, Christov et al. [22] (25 °C) and this study (50 °C). Triangles, Linke [42] ((0 to 105) °C). Squares: Zdanovskii et al. [43] ((40 to 60) °C). Cross denotes experimental (CaBr$_2$·6H$_2$O(cr) + CaBr$_2$·4H$_2$O(cr)) invariant point [42,49]. The light solid line represents the temperature extrapolation of CaBr$_2$·6H$_2$O(cr) model.

solutions ($\approx$7.60 mol kg$^{-1} \leq m \leq$ 9.21 mol kg^{-1}) are not consistent with all other activity and solubility data available in the literature. Therefore, the 25 °C data at supersaturation are excluded from the database, used in parameterization. The activity properties of supersaturated solutions data are beyond the concentration limits of T-variable solid–liquid equilibria model for CaBr$_2$–H$_2$O system, presented in Tables 4 and 6. Although at low temperature, with exception at 25 °C, the activity data used in parameter evaluations cover concentration range up to relatively low molality (up to 4.60 mol kg^{-1}), using solubility approach (i.e. equilibrium solubility data), we extend our pure electrolyte parameterization up to saturation, in the range of temperatures at which such a solubility data are available (from 0 to 105 °C).

4.2. Evaluation of parameters in the NaBr–CaBr$_2$–H$_2$O system

The solubility data for ternary system NaBr–CaBr$_2$–H$_2$O are used to evaluate temperature variable $\psi_{Na,Mg,Br}$ mixing parameter. The data obtained in this study at 50 °C (Table 2) are combined with those available in the literature to develop the solid–liquid equilibria model for mixed systems. The activity data for mixed solutions cannot be found in the literature. The reference solubility data in this ternary system are available only at 25 °C. The data given by Bogoiavleskii and Feduniak [51], and by Ksenzenko et al. [52] (summarized in Zdanovskii et al. [43]) are in good agreement. According to the reported data, the phase diagram of NaBr–CaBr$_2$–H$_2$O system consists a narrow field of crystallization of anhydrous sodium bromide (NaBr(cr)) in addition to the stable in binary sub-systems at standard temperature solids (NaBr·2H$_2$O(cr)) and CaBr$_2$·6H$_2$O(cr) (see symbols on Fig. 6(a)). The same type of phase diagram, with precipitation of three bromide

solids, is also established in this study at 50 °C (see Table 2 and Fig. 6(b)). According to the data, the increasing of temperature from 25 to 50 °C leads to increasing the stability of NaBr(cr) in mixed system.

In the data correlations, the evaluations of the binary parameters for aqueous CaBr$_2$ and of the CaBr$_2$·6H$_2$O(cr) and CaBr$_2$·4H$_2$O(cr) standard chemical potential established above are used. In this parameterization, the temperature functions for Na–Br pure electrolyte parameters and standard chemical potential of NaBr·2H$_2$O(cr), and NaBr(cr) are taken from previous study of the author [24]. The temperature independent $\theta_{Na,Ca}$ (equals to 0.05) mixing parameter is taken from Moller [15]. The resulting $\psi_{Na,Mg,Br}$ model is presented in Table 4. The model provides very good agreement with bromide solids solubility data at 25 and 50 °C in the ternary NaBr–CaBr$_2$–H$_2$O system. On Fig. 6(a) and (b) we compare the model predictions and the experimental solubility isotherms at 25, and 50 °C. Table 7 compare the calculated and experimental composition of invariant points in ternary system. The temperature extrapolation of the model provides reasonable bromide minerals solubility in the ternary system at lower and higher temperature. Fig. 6(c) presents the model predictions at 0 and 100 °C. According to the model predictions NaBr(cr) is a stable phase in NaBr–CaBr$_2$–H$_2$O system from 0 to 100 °C (Fig. 6(a)–(c)). The model predicts that the temperature of $\approx$0 °C is very close to phase transition (NaBr·2H$_2$O(cr) $\leftrightarrow$ NaBr(cr)) temperature (PTT) of dihydrate solid in ternary system NaBr–CaBr$_2$–H$_2$O. New low temperature data are needed to validate this prediction. According to
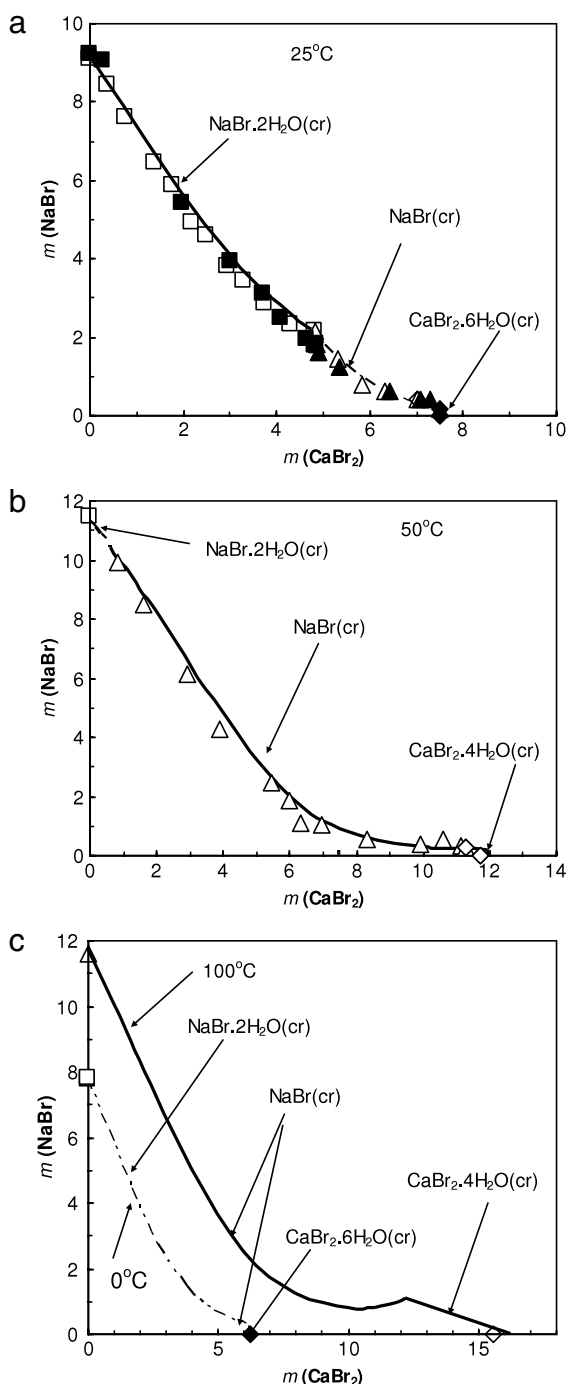
Fig. 6. The calculated (solid and dashed lines) and experimental solubility of NaBr·2H$_2$O(cr) (solid and open squares), NaBr(cr) (solid and open triangles), CaBr$_2$·6H$_2$O(cr) (solid diamonds) and CaBr$_2$·4H$_2$O(cr) (open diamonds) solid phases in the NaBr–CaBr$_2$–H$_2$O system from 0 to 100 °C. (a) 25 °C; (b) 50 °C; (c) 0 and 100 °C. The ternary system experimental solubility data at 50 °C are from this study (see Table 2). The data at 25 °C are from Bogoiavleskii and Feduniak [51], and Ksenzenko et al. [52]. Symbols in (c) show the pure water solubility of NaBr·2H$_2$O(cr), NaBr(cr), CaBr$_2$·6H$_2$O(cr) and CaBr$_2$·4H$_2$O(cr) (see Linke [42]).

Fig. 7. Comparison of model predicted (solid line) equilibrium relative humidity of saturated CaBr$_2$·6H$_2$O(cr) solutions with the literature data (closed diamonds and closed circle: recommendations of Mikulin [38] and Goldberg and Nuttall [39], respectively; open triangles: data of Hedlin and Trofimenkoff [53]; open squares: smoothed values of Greenspan [54]).

ature (25 °C) and without any adjustment of $\mu°$(NaBr(cr))/RT. Therefore, the good agreement with the solubility data at 25 °C represents another step of validation of temperature extrapolation of previously developed NaBr(cr) model to lower temperature. In the development of the model for mixed system NaBr–CaBr$_2$–H$_2$O we used pure electrolyte parameters of Ca–Br interactions and chemical potential for calcium bromide solids, which are evaluated using activity and solubility data only for binary CaBr$_2$–H$_2$O system, and without further adjustments. The established previously parameterization for binary calcium bromide system provides excellent agreement with high calcium concentration solubility data in mixed system (Table 7 and Fig. 6), for which Ca–Br interaction parameters are highly important. This agreement represents a good test for reliability of binary CaBr$_2$–H$_2$O system parameterization, established here.

5. Model applications

As a final test of consistency of T-variable solution and solid–liquid equilibrium models for CaBr$_2$–H$_2$O binary system, we calculate deliquescence relative humidity (DRH) of CaBr$_2$·6H$_2$O(cr), and CaBr$_2$·4H$_2$O(cr) in their saturated binary solutions. Within the salt-solution model, relative humidity is related to water activity, a_w, according to the equation [28]:

$$a_w = P_w/P°_w = RH/100,\tag{3}$$

where P_w and $P°_w$ are the vapor pressure of the saturation solution and pure water, respectively, at given temperature.

The results of DRH(CaBr$_2$·6H$_2$O(cr)), and DRH(CaBr$_2$·4H$_2$O(cr)) calculations from 0 to 75 °C are presented in Table 8. The model predicted thermodynamic solubility products of solids are also given in Table 8. Fig. 7 compare the model predictions (solid line) on equilibrium relative humidity of hexahydrate with the literature data (see also the values given in brackets in Table 8). These data are taken from Hedlin and Trofimenkoff [53] (from −3.9 to 21.66 °C; raw data obtained using calibrated humidity sensor), Greenspan [54] (smoothed (10–25) °C data), from Mikulin [38], (recommended water activity values at m(sat) of CaBr$_2$–H$_2$O solution equals to 7.57 mol kg^{-1}; at 25 °C), and from Goldberg and Nutall [39] (25 °C; recommended water activity value in equilibrium solution; m(sat) equals to 7.66 mol kg^{-1}). The dashed–dotted line on Fig. 7 shows the temperature extension of DRH(CaBr$_2$·6H$_2$O(cr)) function from 0 to −5 °C. According to the

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solubility data and solid–liquid equilibrium model for NaBr–H$_2$O system [24] NaBr(cr) is a stable solid phase in this binary at temperatures ranging from 51 to 300 °C. Therefore, at temperatures above 51 °C the system NaBr–CaBr$_2$–H$_2$O is of a simple type (see Fig. 6(c) at 100 °C). Note that the standard chemical potential of NaBr(cr) has been determined previously using only the pure water solubility data [24]. In this study we develop the model for mixed NaBr–CaBr$_2$–H$_2$O system using solubility data at lower temper-

Table 8

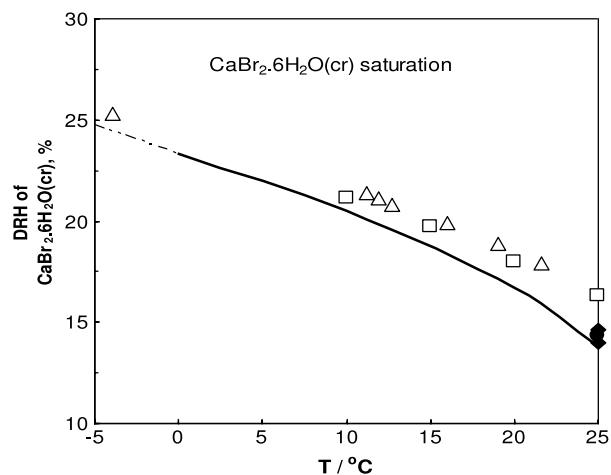Predicted Deliquescence Relative Humidity (DRH, %) values of $CaBr_2 \cdot 6H_2O(cr)$ and $CaBr_2 \cdot 4H_2O(cr)$ from 0 to 75 °C. The literature data are given in brackets.

$T/(°C)$	0	10	20	25	50	75
Precipitated mineral	$CaBr_2 \cdot 6H_2O(cr)$				$CaBr_2 \cdot 4H_2O$	
$\ln K°_{sp}$	13.41	13.25	13.21	13.19	19.37	16.96
DRH	23.23	20.5	16.73	13.81	1.40	0.77
	$(-3.9 °C: 25.3)^b$	$(21.6 \pm 0.5)^a$	$(18.5 \pm 0.5)^a$	$(16.5 \pm 0.2)^a$		
		$(11.2 °C: 21.4)^b$	$(19 °C: 18.9)^b$	$(14.0; 14.6)^c$		
				$(14.33)^d$		

[a] Smoothed values of Greenspan [54].
[b] Hedlin and Trofimenkoff [53].
[c] Mikulin [38].
[d] Goldberg and Nuttall [39].

temperature variation model, the equilibrium relative humidity of $CaBr_2 \cdot 6H_2O(cr)$ very smoothly decrease with temperature within (0 to 25) °C range (from 23.23% at 0 °C to 13.81% at 25 °C) and follow the trend of the data of Hedlin and Trofimenkoff [53], and Greenspan [54]. The model predicts lower relative humidity values than the data (max difference is $\approx$2.5% at 25 °C). Taking into account the very high complicity of DRH experiments and extremely high solubility of calcium bromide minerals, the agreement with these data can be accepted as very good. Note also that the calculated DRH $(CaBr_2 \cdot 6H_2O(cr))$ at 25 °C is in very good agreement with the recommendations given in Mikulin [38], and Goldberg and Nutall [39]. The predicted DRH of calcium bromide hexahydrate is much lower than those of calcium chloride hexahydrate at 25 °C. In our previous study [25] we determined stable equilibrium DRH $(CaCl_2 \cdot 6H_2O(cr))$ equals to 22.4% at standard temperature. According to the equilibrium model DRH $(CaBr_2 \cdot 4H_2O(cr))$ in binary system is extremely low at 50 and 75 °C. Another important comment here is that the authors [53,54] reported DRH values at 25 °C and at lower temperatures, which according to the present solid–liquid equilibria model, and available water activity recommendations at 25 °C correspond more probably to unsaturated $CaBr_2$–H_2O solutions, than to supersaturated solutions. For example, Greenspan recommended DRH value of 16.5% at 25 °C (i.e. water activity $a_w = 0.165$). According to tabulated water activity values of Mikulin and Goldberg and Nuttall, and the model presented here $a_w = 0.165$ corresponds to deeply unsaturated solutions with concentrations between 7.25 and 7.35 mol kg^{-1}. According to the high molality isopiestic data of Robinson and McCoach [36], if supersaturation phenomena play some role in determination of RH behavior of calcium bromide hexahydrate, the measured DRH value should be less than 10%. Therefore, it can be concluded that similarly to deliquescence behavior of high soluble bischofite mineral $(MgCl_2 \cdot 6H_2O(cr))$ in binary $MgCl_2$–H_2O system (see refs. [25–27]), and in mixed $MgCl_2$–$CaCl_2$–H_2O [25], and $MgCl_2$–HCl–H_2O [26] systems, and of complex sea salt at high humidity conditions (see Ref. [27]), the deliquescence behavior of calcium bromide minerals is determined in highest degree by their equilibrium crystallization, and not by metastable crystallization of some lower crystalline hydrate solid in supersaturation solutions zone.

Acknowledgements

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