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Geochimica et Cosmochimica Acta 71 (2007) 3557–3569
Geochimica et Cosmochimica Acta
www.elsevier.com/locate/gca

An isopiestic study of aqueous NaBr and KBr at 50 °C: Chemical equilibrium model of solution behavior and solubility in the NaBr–H_2O, KBr–H_2O and Na–K–Br–H_2O systems to high concentration and temperature

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Received 7 February 2007; accepted in revised form 1 May 2007; available online 17 May 2007

Abstract

The isopiestic method has been used to determine the osmotic coefficients of the binary solutions NaBr–H_2O (from 0.745 to 5.953 mol kg^{-1}) and KBr–H_2O (from 0.741 to 5.683 mol kg^{-1}) at the temperature $t = 50$ °C. Sodium chloride solutions have been used as isopiestic reference standards. The isopiestic results obtained have been combined with all other experimental thermodynamic quantities available in literature (osmotic coefficients, water activities, bromide mineral's solubilities) to construct a chemical model that calculates solute and solvent activities and solid–liquid equilibria in the NaBr–H_2O, KBr–H_2O and Na–K–Br–H_2O systems from dilute to high solution concentration within the 0–300 °C temperature range. The Harvie and Weare [Harvie C., and Weare J. (1980) The prediction of mineral solubilities in naturalwaters: the Na–K–Mg–Ca–Cl–SO_4–H_2O system from zero to high concentration at 25 °C. *Geochim. Cosmochim. Acta* **44**, 981–997] solubility modeling approach, incorporating their implementation of the concentration-dependent specific interaction equations of Pitzer [Pitzer K. (1973) Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem.* **77**, 268–277] is employed. The model for binary systems is validated by comparing activity coefficient predictions with those given in literature, and not used in the parameterization process. Limitations of the mixed solutions model due to data insufficiencies are discussed. This model expands the variable temperature sodium–potassium model of Greenberg and Moller [Greenberg J., and Moller N. (1989) The prediction of mineral solubilities in natural waters: a chemical equilibrium model for the Na–K–Ca–Cl–SO_4–H_2O system to high concentration from 0 to 250 °C. *Geochim. Cosmochim. Acta* **53**, 2503–2518] by evaluating Br^- pure electrolyte and mixing solution parameters and the chemical potentials of three bromide solid phases: NaBr–$2H_2O$ (cr), NaBr (cr) and KBr (cr).

1. INTRODUCTION

Comprehensive thermodynamic models that accurately predict bromide aqueous chemistry and bromide mineral's solubilities as a function of composition and concentration and to high temperature are critical for understanding many important geochemical, environmental and industrial processes. For example, the investigation of the solubility diagrams of bromide salts is of practical importance with a view to explain the distribution of bromide ions in natural evaporate deposits during crystallization of salts as a result of sea water evaporation and during treatment of natural deposits (Balarew et al., 1993). The behavior of bromide as trace element in evaporating seawater and diagenetic reactions of evaporates is of prime importance for geochemical studies in marine chemical sediments. The conservative vertical distribution in the oceans (the high concentration of 0.84 mmol/kg H_2O; Bruland, 1983), and

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doi:10.1016/j.gca.2007.05.007

one of the highest residency times [from 1.0×10^8 (Chester, 2000) to 7.9×10^8 yr (Taylor and McLennan, 1985)] in the ocean makes Br the most important trace element in chemically precipitated marine Cl sediments. The geochemical study of bromide is traditionally focused on its fractionation between brines and chloride salts, especially halite (NaCl(cr)) (Bratish and Herrmann, 1963; Kuhn, 1968; Siemann and Schramm, 2000). The results on the evaporation experiments for distribution of Br in the systems with precipitation of sylvie (KCl(cr)), kainite (KCl–$MgSO_4$–$3H_2O$(cr)), carnallite (KCl–$MgCl_2$–$6H_2O$(cr)) and bischofite ($MgCl_2$–$6H_2O$(cr)) minerals are also reported in literature (Siemann and Schramm, 2002). Geochemists have generally used the empirical distribution coefficient to predict Br contents in chloride minerals (salt) precipitating from a brine (solution). The distribution coefficient D_{Br} is defined by ratios of Br:Cl as (see Stoessell and Carpenter, 1986):

$$D_{Br} = [(Br/Cl)salt]/[(Br/Cl)solution] \quad (1)$$

From a practical viewpoint, it is more useful to predict Br content on the basis of thermodynamic equilibrium than to use an empirical D_{Br} coefficient, and therefore there are many works on theoretical discussions and stoichiometric saturation in solid solution–aqueous solution systems (Thostensen and Plummer, 1977; Stoessell and Carpenter, 1986; Glynn and Reardon, 1990a,b; Koenigsberger and Gamsjaeger, 1990). All these equilibrium models are aimed on correct determination of activity coefficients of bromide ($\gamma(Br^-)$) and chloride ($\gamma(Cl^-)$) ions in brine solutions and of thermodynamic solubility product of solid-solution's end-members (for example $\ln K^{\circ}_{sp}$ (halite), and $\ln K^{\circ}_{sp}$ (NaBr–$2H_2O$(cr) or $\ln K^{\circ}_{sp}$ (NaBr(cr) for the bromide distribution in the system NaCl–NaBr–H_2O))).

In the late 1990s, the role of halogen species, especially bromide, in the ozone layer depletion became evident. For example, Vogt et al. (1996) described a mechanism of halogen release from sea-salt aerosols. Honninger et al. (2004) measured a significant emission of bromide from the giant salar de Uyuni in the Bolivian Altiplano. Risacher et al. (2006) measured a significant release of bromide from surface waters and brines of Central Andes. According to Risacher et al. (2006), "the question which arises is to what extent bromide behaves conservatively in geochemical processes". Construction of comprehensive thermodynamic model for bromide brine system that describe solution behavior and bromide minerals solubility to high temperature can be powerful predictive tool to solve the above geochemical and environmental problems.

In this article, a chemical equilibrium model, incorporating the Pitzer solution equations, that calculates Br-interactions in the NaBr–H_2O and KBr–H_2O binary, and in the Na–K–Br–H_2O ternary systems to high solution concentration in the 0–300 °C temperature range is described (see Section 4). Evaluations of temperature functions for the chemical potentials of three bromide solid phases (NaBr–$2H_2O$(cr), NaBr (cr) and KBr (cr)) are also discussed in Section 3. Osmotic coefficients, water activities and bromide minerals solubility data are used in parameterization. To validate the model, the activity coefficients predictions are compared with those given in literature and not used in the model parameterization.

Several authors (Pitzer and Mayorga, 1973; Kim and Frederick, 1988; Balarew et al., 1993; Christov, 1996, 2005) have constructed 25 °C models for Na–Br and K–Br interactions. The extended ion-interaction model (see Section 3) of Rard and Archer (1995) for NaBr–H_2O system, and the standard Pitzer model of Holmes and Mesmer (1998) for NaBr–H_2O and KBr–H_2O systems are the only temperature variable models available in literature. Only the 25 °C models of Balarew et al. (1993) (for KBr–H_2O system), Christov (1996, 2005) (for NaBr–H_2O and KBr–H_2O systems) and the sodium bromide model of Rard and Archer (1995) (0–300 °C) included the bromide minerals solubility. The 25 °C low concentration (I (max) = 4 m) model of Pitzer and Kim (1974) for NaBr–KBr–H_2O system is the only model available in literature for mixed solutions studied here.

2. EXPERIMENTAL

Low and high molality osmotic/activity coefficients data, determined on the basis of isopiestic measurements, are the most reliable thermodynamic data, which can be used in parameterization of equilibrium models which can accurately predict not only solution behavior but also solid–liquid equilibria in binary and complex systems. Unfortunately, most of the isopiestic results for aqueous solutions of sodium bromide and potassium bromide are at standard temperature (25 °C) and at elevated temperatures. In the compilations of the Hamer and Wu (1972); Mikulin (1968) and Robinson and Stokes (1949) the osmotic coefficients of NaBr(aq) and KBr(aq) at 25 °C are given up to saturation of the binary solutions. In their comprehensive isopiestic study Holmes and Mesmer (1998) determined the osmotic coefficients of NaBr(aq) and KBr(aq) at saturation pressure from 110 to 225 °C and up to ≈6.2 m NaBr and ≈7.4 m KBr. In intermediate temperature range (from 25 to 110 °C) the osmotic data of Voigt et al. (1990) for NaBr(aq) (at 100.3 °C), of Fanghanel and Grojtheim (1990) for KBr(aq) (at 100.3 °C) and of Hellams et al. (1965) for KBr(aq) (at 45 °C) are the only isopiestic method based data available in literature. Isopiestic results for the bromide solutions under investigation could not be found at temperatures below 25 °C.

Rard and Archer (1995) reported the results on isopiestic investigation of aqueous sodium bromide at 25 °C. They also present a comprehensive extended Pitzer ion interaction model (using two C^{φ} parameters; see next section) for the thermodynamic properties of NaBr(aq) which is valid to temperatures of about 330 °C and pressures of 150 MPa. To construct their model at elevated temperatures and pressures Rard and Archer used enthalpy, heat capacity, volumetric properties and vapor pressure results for sodium bromide solutions. Using their own isopiestic results from 110 to 225 °C and some of the low temperature osmotic coefficients data available in literature, Holmes and Mesmer (1998) constructed an ion-interaction model for calculation of the activity coefficients of unsaturated (m(max) ≈ 5 m) NaBr(aq) and KBr(aq) solutions. Note

that their model does not consider solid–liquid equilibria in bromide systems. At high temperature and molalities the model of Holmes and Mesmer (1998) predicts much higher activity coefficients (γ) of NaBr(aq) than those determined by the model of Rard and Archer (1995) (difference of about 15%). The authors concluded that the main source of disagreement at high temperature is the fundamental difference of the data used in parameterization of both thermodynamic models. The temperature variable model of Holmes and Mesmer is constructed using only osmotic coefficients data. The main source in constructing of high temperature model of Rard and Archer is the enthalpy of dilution.

Therefore, we concluded that isopiestic results for aqueous solutions of sodium bromide and potassium bromide at intermediate temperature range (from 25 to 110 °C) are critical for developing a comprehensive ion-interaction model which accurately describe solution behavior and solid–liquid equilibria in temperature range from 0 to 300 °C. We perform our experimental investigation at the temperature of 50 °C.

The osmotic coefficients of the NaBr(aq) and KBr(aq) solutions were determined by the isopiestic method described in our previous studies (Christov et al., 1999; Ojkova et al., 1999; Barkov et al., 2003). The experimental procedure, method, and apparatus are very similar to those described in the excellent studies of Rard and co-workers (Rard and Archer, 1995) and of ORNL (Oak Ridge National Laboratory) (see Holmes and Mesmer, 1998; Palmer et al., 2002; Gruszkiewicz and Simonson, 2005).

Sodium chloride solutions were used as isopiestic reference standards. Stock solutions of aqueous NaBr, KBr and NaCl were prepared from solid samples and deionized water. Merck (A.R.) solid sodium chloride were used. The solid bromide samples were Aldrich 99.99^{+}%. The solids were used without further purification. Note that purification of solid bromides by re-crystallization enriches the chloride content (see Rard and Archer, 1995). To remove the residual moisture in the NaCl(s), NaBr(s) and KBr(s), the salts were dried slowly (for several hours) in air at the temperature 160 °C. The solutions were prepared by the gravimetric method. The salts were weighed with an accuracy of $\pm 1 \times 10^{-5}$ 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. Four copper cups (two for tested solutions and two for isopiestic standard solutions) have been used for each experiment. After attaining equilibrium, the samples were weighed again and the concentrations of the isopiestic solutions obtained were calculated. Tables 1 and 2 show the isopiestic equilibrium molalities of NaBr(aq) and KBr(aq), respectively, with NaCl(aq) reference solutions. Reported molalities are the average of duplicate determinations. We found that an equilibrium period of 20 days yielded results with a good agreement of molalities for duplicate samples of the same electrolyte. This relatively long time needed to obtain equilibrium can be attributed to the fact that we have not shaken the desiccator with solutions investigated. We weight 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 concentrations in Tables 1 and 2 are accurate to within ±0.2% or better. The osmotic coefficients ϕ of MBr(aq) (M = Na, K) were calculated from the equation:

$$\phi = (m^*\phi^*)/(m) \quad (2)$$

where m is the molality of MBr(aq), 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. Osmotic coefficients ϕ^* for the isopiestic standard NaCl(aq) were calculated from the model of Pitzer et al. (1984). Tables 1 and 2 contain the derived values of ϕ for the NaBr(aq) and KBr(aq) solutions, respectively.

Table 1
Isopiestic molalities m of aqueous NaBr, with molalities m of NaCl reference solutions and the osmotic coefficients φ of NaBr at 50 °C[a]

m(NaCl)/(mol kg^{-1})	m(NaBr)/(mol kg^{-1})	φ(NaBr)
0.7482	0.7450	0.9351
1.0789	1.088	0.9376
1.1386	1.1559	0.9402
1.2913	1.3074	0.9456
1.5289	1.5623	0.9493
1.7687	1.7536	0.9911
2.8395	2.8393	1.0467
3.2420	3.1914	1.0897
5.0885	4.8682	1.2545
5.1083	4.8643	1.2616
6.2803	5.9528	1.355

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

Table 2
Isopiestic molalities m of aqueous KBr, with molalities m of NaCl reference solutions and the osmotic coefficients φ of KBr at 50 °C[a]

m(NaCl)/(mol kg^{-1})	m(KBr)/(mol kg^{-1})	φ(KBr)
0.71498	0.7410	0.8982
1.0385	1.0821	0.9061
1.7254	1.8382	0.9204
1.8548	1.9762	0.9262
2.9775	3.1788	0.9892
4.9774	5.6597	1.0484
4.9992	5.6826	1.0504

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

3. MODELLING APPROACH

Pitzer (1973), Pitzer (1975); Pitzer (1991) created a method that allows the calculation of the activity coefficients in unsaturated solutions of electrolytes with an accuracy of (2–6)% (Pitzer and Kim, 1974). Pitzer and co-authors determined the ion interaction parameters for a large number of binary (Pitzer and Mayorga, 1973) and ternary (Pitzer and Kim, 1974) solutions. The specific interaction approach for

describing aqueous solutions to high concentration, introduced by Pitzer, represents a significant advance in physical chemistry that has facilitated the construction of accurate thermodynamic models. The small number of parameters taking into account the ion interactions even in highly concentrated multicomponent solutions and the not complicated fundamental equations allowing relatively easy computerization, have contributed to the model becoming a real hit in the scientific literature. The Pitzer model is used successfully for the solution of various theoretical and practical tasks. Harvie and Weare (1980) showed that the Pitzer specific interaction approach for describing aqueous solutions to high concentration could be expanded to calculate accurately mineral solubilities in complex brines. Weare and co-workers successfully applied their models at $t = 25$ °C to the interpretation of natural and industrial processes (e.g., Harvie and Weare, 1980; Harvie et al., 1984; Felmy and Weare, 1986). Since 1980, using the same approach, many chemical models of solid–liquid equilibria in multicomponent brines have been developed that incorporate the excess Gibbs free energy equations of Pitzer. These models extend from subzero temperatures (Spenser et al., 1990; Marion, 2001) to high temperatures below $t = 350$ °C (e.g., Pabalan and Pitzer, 1987; Moller, 1988; Greenberg and Moller, 1989; Millero and Pierrot, 1998; Koenigsberger et al., 1999; Christov and Moller, 2004a,b; Moller et al., 2006; Christov et al., accepted for publication). The applicability of Pitzer equations to the simulation of solutions from which solid solutions crystallize was also demonstrated (Christov, 2005).

In this study, I use the solubility modeling approach of Harvie and Weare (1980) and Harvie et al. (1984) and their implementation of the Pitzer (1973), Pitzer (1991) specific interaction equations. These equations and the modeling approach have been discussed in detail by us (Christov and Moller, 2004a,b, Christov, 2005) and by others in many publications. Because the Pitzer formalism is based on the excess free energy, all the activity expressions are consistent, allowing different kinds of data (e.g., osmotic, e.m.f. and solubility measurements) to be used in the parameter evaluations and other thermodynamic functions to be calculated.

To extend the application of the model for predictions of solution properties at very high concentrations Pitzer and Simonson (1986) introduced in their approach mole fraction concentrations. Their approach has been used successfully for modeling $CaCl_2$(aq) (Rard and Clegg, 1997) and aerosol mixtures (Clegg et al., 1998). In the parameterization presented here we used a standard molality—based ion interaction model. To fit the binary solution properties with lower sigma value and to high concentration, some authors used in their single electrolyte parameterization an extended version of Pitzer model, introducing two C^{φ} parameter values (see Rard and Archer, 1995; Palmer et al., 2002). In our single electrolyte parameterization, we used standard Pitzer approach with one C^{φ} parameter. In our previous studies (Christov and Moller, 2004a,b; Christov, 2005; Christov et al., accepted for publication) we show that the above standard Pitzer approach gives excellent model reliability to very high concentration (for example to 64 m in the NaOH–H_2O system: Christov and Moller, 2004a). Note that in the model presented, we accepted that the electrolytes are completely dissociated and there are only independent ions in the solution, i.e. the equilibrium constant of complexes (such as NaBr°(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. The systems presented here do not include neutral species, therefore neutral species—ion interaction parameters (λ and ξ': see Felmy and Weare, 1986) are not introduced in our models.

In our modeling approach, the standard chemical potentials (μ°/RT) of the independent ions (such as Na^+, K^+, Cl^-, and Br^-) are assigned values equal to zero. However, when ions are related by equilibrium reactions, such as H^+ and OH^- for the H_2O dissociation reaction ($H_2O = H^+ + OH^-$) the dependent standard chemical potential must be determined from equilibrium data. Similarly, the chemical potentials of the solid phases are referenced to a chosen set of independent ions and are established in parameterization process. With this approach the chemical potentials for nonhydrated solid phases that do not contain dependent species (such as NaBr(s) and KBr(s)) are equal to the logarithm of the solubility product ($\ln K_s$). For hydrated solid phases calculation of the salt chemical potential must include water dissociation. For example, with $\mu^{\circ}(Na^+)/RT$ and $\mu^{\circ}(Br^-)/RT$ set equal to zero, $\ln K_s(\text{NaBr–2H}_2\text{O(s)}) = \mu^{\circ}(\text{NaBr–2H}_2\text{O(s)})/RT - 2\mu^{\circ}(\text{H}_2\text{O})/RT$. Note that to compare chemical potentials of bromide salts (given in Table 5) with those reported using other reference systems, the nonzero standard chemical potentials of the independent ions must be considered.

Temperature dependence for the bromide ion-interaction parameters and chemical potentials of solids is built into the model by adjusting selected constants in the following equation, where T is the Kelvin temperature:

$$\text{Parameter } (T) = a_1 + a_2 T + a_5/T \tag{3}$$

Note that the constants $a_3(T^2)$, $a_4(T^3)$, $a_6(\ln T)$, $a_7(1/T - 263)$ and $a_8(1/680 - T)$ used in the acid base model of Christov and Moller (2004a,b) and in aluminum speciation model of Christov et al. (accepted for publication) are not used in the model presented here.

4. MODEL PARAMETERIZATION

In constructing the model of the Na–K–Br–H_2O system, the temperature function for $\mu^{o}_{H_2O}/RT$ (Table 5) is taken from Moller (1988) as adapted from the Busey and Mesmer (1978) study. The temperature function for the Debye–Huckel constant, A^{φ} (see Table 5), is also taken from Moller (1988). See also the discussion of Christov and Moller (2004a) for A^{φ} parameterization and validation. Temperature variable mixing parameter of Na–K interactions ($\theta_{Na,K}$) is the same as in Greenberg and Moller (1989).

The standard chemical potentials of the independent ionic species (Na^+, K^+, Br^-) are all set equal to zero from 0 to 300 °C. 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 ion interactions Na–Br and K–Br (see Table 3); the mixed solution model parameter $\psi_{Na,K,Br}$ for ion interactions in NaBr–KBr–H_2O ternary solutions (see Table 3); and the standard chemical potentials of the sodium and potassium bromide solid phases (see Table 5) contained within the Na–K–Br–H_2O system.

Model parameterization is discussed below. Activity data (osmotic coefficients, water activity) are used when available to evaluate solution parameters for low and moderate bromide concentration (see Table 6). Solubility data in binary and mixing solutions are also used to broad temperature and concentration range of parameterization. Activity coefficients values, presented in literature and not used in parameterization process, are used here to validate the solution model (see Table 4). The solubility model predictions at temperatures which are outside the temperature range of the data are also given. The differences between calculated and experimental solubility and activity data are summarized in Table 6 in terms of sigma (σ) (for definition of sigma see Christov and Moller, 2004b).

4.1. Evaluation of parameters in the NaBr–H_2O system

The NaBr–H_2O binary solution interaction parameters are evaluated from osmotic coefficients data in this binary. To better reflect the high concentration behavior of the system, we include in parameterization solubility measurements of sodium bromide salts in this system. All the data used in parameterization are summarized in Table 6. References, molality and temperature range of the experiments, and number n of experimental data points are also given in the table.

Osmotic coefficient data for binary solutions are used to help define the concentration variation of $\beta^{(0)}{}_{NaBr}$, $\beta^{(1)}{}_{NaBr}$, and $C^{\varphi}{}_{NaBr}$ with temperature. The osmotic coefficient data sets which are determined directly from isopiestic measurements of sodium bromide solutions and included in parameterization are: (1) our isopiestic results at 50 °C and up to 5.953 m NaBr given in Table 1; (2) Hamer and Wu's (1972) recommended values to 9 m NaBr at 25 °C: (3) Rard and Archer's (1995) isopiestic measurements data to 9.1701 m NaBr at 25 °C (4) Holmes and Mesmer's (1998) isopiestic study data measurements up to 6.2 m NaBr at 110, 140, 170, 200 and 225 °C and (5) Voigt et al. (1990) osmotic coefficients data at 100.3 °C and to 10.62 m NaBr. There is good agreement between both sets of osmotic coefficient data at 25 °C [sets (2) and (3)]. Note also that the 25 °C recommended values of Hamer and Wu's (1972) and the data of Rard and Archer's (1995) are in good agreement with the φ data of Robinson and Stokes (1949) (to 4.0 m NaBr) and with recommendations of Mikulin (1968) (to 9.0 m NaBr) at the same temperature. Therefore last two sets of data are not included in parameterization process. In addition to above isopiestic study data measurements we include in our parameters evaluation the osmotic coefficients determined on the basis of vapor pressure measurements. The φ values are taken from Jakli and Van Hook (from 0 to 101 °C and to 7.0 m NaBr), Patll et al. (1991) (from 30 to 70 °C and to 8.0 m NaBr), and from Apelblat and Korin (1998) (from 5° to 50 °C in saturated NaBr solutions). Note that in our final parameterization the osmotic data of Rard and Archer's (1995) in the supersaturated solution ($9.18 < m\text{NaBr} < 9.35$) are not considered. Some of osmotic data points of Apelblat and Korin (1998) (solution saturation at 45 and 50 °C) and of Patll et al. (1991) (at 30, 40, and 50 °C and 8.0 m NaBr) are not consistent with other data and model predictions and are also excluded in evaluation process.

The solubility data in the NaBr–H_2O system from 0 to 250 °C and up to 15.86 m NaBr are used to evaluate temperature functions for the Na–Br pure electrolyte parameters and the chemical potentials of two sodium bromide salts (NaBr–$2H_2O$ (s) and NaBr(s)). Solubility data, which are in very good agreement, are taken from Linke (1965). According to the data, NaBr–$2H_2O$(s) is stable phase from 0 to 51 °C where it undergoes a phase transformation to NaBr(s).

The model's $\beta^{(0)}{}_{NaBr}$, $\beta^{(1)}{}_{NaBr}$, and $C^{\varphi}{}_{NaBr}$ parameterization for the binary NaBr–H_2O system (Table 3) gives excellent agreement with the data for unsaturated binary solutions. The sigma values for the fit of the osmotic data

Table 3
Values of the fitting constants [Eq. (3)] for the binary and ternary solution interaction parameters[a]

Parameters	Constants (T in degrees Kelvin)		
	$a_1(-)$	$a_2(T)$	$a_5(1/T)$
$\beta^{(0)}$(NaBr) (0–300 °C)	7.11600256d−01	−7.51986135d−04	−1.09266366d+02
$\beta^{(1)}$(NaBr) (0–300 °C)	−4.97335195d00	8.57795255d−03	7.38610135d+02
C^{φ} (NaBr) (0–300 °C)	−7.34172496d−02	8.71449532d−05	1.33019597d+01
$\beta^{(0)}$(KBr) (0–300 °C)	4.79896100d−01	−4.17396303d−04	−9.05196847d+01
$\beta^{(1)}$(KBr) (0–300 °C)	−4.13092017d00	6.85308052d−03	7.04957954d+02
C^{φ}(KBr) (0–300 °C)	−5.93226684d−02	6.33899074d−05	1.17934031d+01
$\theta_{Na,K}$[b] (0–250 °C)	−5.02312111d−02	0	1.40213141d+01
$\psi_{Na,K,Br}$ (0–75 °C)	−1.73305922d−02	3.50504594d−05	1.28020967d00

[a] The constants a_3, a_4, and a_6–a_8 in Eq. (3) 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 Greenberg and Moller (1989).

Table 4
Predicted mean activity coefficient ($\gamma_{\pm}$) of MBr (M = Na, K) in binary MBr–H_2O solutions as a function of molality (mol kg^{-1}) and temperature

Recommended values of:	T (°C)	Activity coefficient						
		"Added" [MBr] 0.1 mol kg^{-1}	"Added" [MBr] 0.5 mol kg^{-1}	"Added" [MBr] 1.0 mol kg^{-1}	"Added" [MBr] 2.0 mol kg^{-1}	"Added" [MBr] 4.0 mol kg^{-1}	"Added" [MBr] 5.0 mol kg^{-1}	"Added" [MBr] 8.0 mol kg^{-1}
				$\gamma_{\pm}$(NaBr)				
This study[a]	25	0.774	0.673	0.662	0.711	0.918	1.049	1.613
Calc.[b]		0.783	0.697	0.687	0.730	0.934	1.083	1.694
This study[a]	100	0.741	0.6417	0.6340	0.6857	0.8854	1.038	1.4637
Calc.[c]		0.7559	0.6747	0.6707		0.9234		1.506
Calc.[d]		0.753	0.669	0.664	0.717	0.917	1.051	
This study[a]	200	0.687	0.582	0.561	0.574	0.674	0.7271	1.024
Calc.[c]		0.6797	0.5612	0.5324		0.6123		0.828
Calc.[d]		0.676	0.571	0.549	0.563	0.661	0.727	
This study[a]	250	0.641	0.523	0.488	0.4722	0.510	0.556	
Calc.[d]		0.634	0.521	0.488	0.4748	0.515	0.556	
				$\gamma_{\pm}$(KBr)				
This study[a]	25	0.774	0.664	0.624	0.600	0.613	0.633	
Calc.[b]		0.771	0.658	0.617	0.593	0.608	0.626	
This study[a]	100	0.742	0.628	0.5939	0.582	0.613	0.637	
Calc.[d]		0.746	0.639	0.608	0.600	0.640	0.668	
This study[a]	200	0.679	0.554	0.513	0.489	0.498	0.512	
Calc.[d]		0.676	0.551	0.510	0.485	0.495	0.507	
This study[a]	250	0.629	0.492	0.443	0.405	0.392	0.397	
Calc.[d]		0.610	0.466	0.416	0.380	0.378	0.385	

[a] Predictions of the model presented here.
[b] Recommended values of Hamer and Wu (1972).
[c] Predictions of the model of Rard and Archer (1995).
[d] Predictions of the model of Holmes and Mesmer (1998).

from 0 to 225 °C are given in Table 6. It was established that introducing in the temperature function [Eq. (3)] for parameters of Na–Br interactions of constants $a_3(T^2)$, $a_4(T^3)$, $a_6(\ln T)$, $a_7(1/T - 263)$ and $a_8(1/680 - T)$ do not improve considerably the fit of the experimental data used in evaluations. Therefore, the temperature functions for pure electrolyte parameters of Na–Br interactions include only three constants (a_1, a_2, and a_5). The same approach (with three temperature parameters) was used for all parameters and standard chemical potentials established here (see next sections).

Fig. 1 compares calculated and experimental osmotic coefficients at 50 °C and up to saturation of NaBr–H_2O (m(sat) ≈ 11.2). The predicted osmotic coefficients are in excellent agreement with our data presented in Table 1, and those of Jakli and Van Hook (1972) and Patll et al. (1991). At saturation the model predicts higher value of osmotic coefficient than the data point of Apelblat and Korin (1998) (not used in parameterization). On Fig. 2 we compare the calculated dependence of NaBr mean activity coefficients ($\gamma_{\pm}$) vs. temperature (from 25 to 250 °C) and molality of NaBr–H_2O solutions and values recommended by Hamer and Wu (1972) (to 9 m NaBr at 25 °C), Rard and Archer's (1995) (to 8 m NaBr at 100, and 200 °C), and by Holmes and Mesmer (1998) (to 5 m NaBr at 100, 200 and 250 °C). To show the models agreement at low molality, where the data are too compressed, we also compare the critically evaluated activity coefficients in Table 4. Note that activity coefficients, calculated by using different thermodynamic models and reported in literature, are not used in parameterization of our NaBr–H_2O model. Therefore, these data are used here to validate the solution model predictions. Fig. 2 and Table 4 show that in temperature ranging from 25° to 100 °C and up to 5 m NaBr the temperature dependence of sodium bromide mean activity coefficients is small. The present model is in excellent agreement with the $\gamma_{\pm}$ evaluations of Hamer and Wu (1972) (at 25°), of Rard and Archer's (1995) (at 100 °C) and with the recommendations of Holmes and Mesmer for all temperature and molality range. Similarly to the model of Holmes and Mesmer (see their Fig. 2) at 200 °C and high molality our NaBr–H_2O model predicts higher activity coefficients than the model of Rard and Archer (see the solid line and open circles at 4 and 8 m NaBr on Fig. 2 and Table 4). The difference between both models increase with concentration and at 200 °C it is 9% at 4 m and 19% at 8 m NaBr (Table 4).

A temperature function for the standard chemical potential of sodium bromide dihydrate and anhydrous sodium bromide is determined by fitting binary solutions solubility data and are presented in Table 5. The predicted

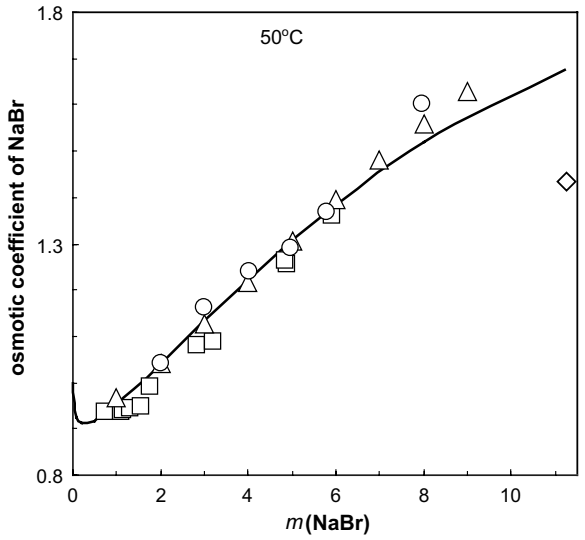

Fig. 1. The calculated (solid line) and experimental (symbols) osmotic coefficients (φ) of NaBr against molality m of NaBr–H_2O at 50 °C. Experimental data: squares, this study (see Table 1); triangles, Jakli and Van Hook (1972); circles, Patll et al. (1991); diamond, Apelblat and Korin (1998) (not included in parameterization).

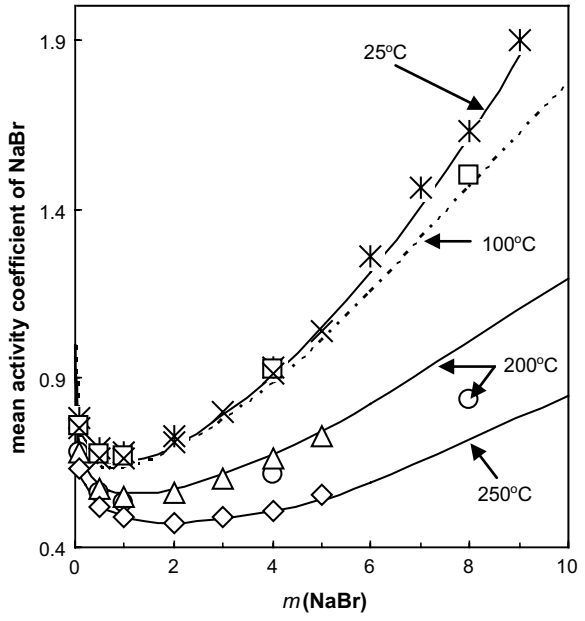

Fig. 2. Comparison of mean NaBr activity coefficients in NaBr–H_2O solutions calculated by the model (solid lines: 25, 200 and 250 °C; dotted line: 100 °C) with the reference values (symbols) from 25 to 250 °C (symbols: stars, Hamer and Wu (1972) at 25 °C; open squares and open circles, Rard and Archer (1995) at 100 and 200 °C, respectively; crosses, open triangles and open diamonds, Holmes and Mesmer (1998) at 100, 200 and 250 °C, respectively).

NaBr–$2H_2O$(s) ↔ NaBr(s) transition in water occurs at 51.4 °C and at 11.41 m NaBr. This is in excellent agreement with the data of Linke (1965) (e.g., $t = 51$ °C and 11.36 m NaBr). Kirgintsev et al. (1972) reported temperature of

Table 5
Values of fitting constants [Eq. (3)] for A^{φ}, $\ln K_w$ and for the standard chemical potentials of solid phases[a]

Parameters	Constants (T in degrees 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^{φ}[b]	3.36901532d−01	−6.32100430d−04	1.92118597d−06	9.14252359d00	−1.35143986d−02	2.26089488d−03	4.52586464d01
$\ln K_w(\mu^o/RT)$ H_2O(aq)[b]	1.04031130d03	4.86092851d−01	−2.32009393d−04	−3.26224352d04	−1.90877133d02	−5.35204850d−01	5.20549183d01
NaBr–$2H_2O$(cr) (0–51.0 °C)	3.89734390d+01	−7.97179210d−02	0	−2.23620498d+04	0	0	0
NaBr(cr) (51.0–300 °C)	2.43358712d00	3.62446066d−03	0	9.50793364d+02	0	0	0
KBr(cr) (0–275 °C)	1.89681330d+01	−1.66852903d−02	0	−3.38883924d+03	0	0	0

[a] The constant a_4 in Eq. (3) is equal to zero for all the above parameters. The temperature range of the solubility data used in parameter evaluation and validation is given.
[b] Parameter determined by Moller (1988).

50.2 °C and 11.14 m NaBr for phase transition invariant point. The parameterization established here (Tables 3 and 4) gives excellent agreement with the NaBr–$2H_2O$(s) and NaBr(s) solubility data in NaBr–H_2O(s) system from 0 to 250 °C (see Fig. 3). The model fits the solubility data with a very low sigma values (σ equal to 0.0059 and 0.022 for NaBr–$2H_2O$(s) and NaBr(s) saturated solutions, respectively) (see Table 6). Temperature extrapolation of the model gives also reasonable, but a little lower, NaBr(s) solubility at 300 °C than the data (Linke, 1965) (difference of 3.7%). Note that the model of Rard and Archer's (1995) predicts some inconsistent decrease of sodium bromide solubility at temperatures over about 220 °C (see their Fig. 7).

4.2. Evaluation of parameters in the KBr–H_2O system

The model for this binary is constructed using the same approach as for sodium bromide system. The model's $\beta^{(0)}_{KBr}$, $\beta^{(1)}_{KBr}$, and C^{φ}_{KBr} pure electrolyte parameters and standard chemical potential (μ°/RT) of KBr (s) are evaluated using activity and solubility data only in this binary system. All the data used in parameterization are summarized in Table 6.

Osmotic coefficients data sets for unsaturated solutions are taken from: (1) our isopiestic results at 50 °C and up to 5.683 m KBr given in Table 2; (2) Hamer and Wu's (1972) recommended values to 5.5 m KBr at 25 °C; (3) Holmes and Mesmer's (1998) isopiestic study data measurements up to 7.41 m KBr at 110, 140, 170, 200 and 225 °C; (4) osmotic coefficients data of Hellams et al. (1965) at 45 °C to 3.5 m KBr; and (5) φ data of Patll et al. (1991) (from 30 to 70 °C and to 4.35 m KBr). The water activity data (a_w) of Fanghanel and Grojtheim (1990) at 100.3 °C and to 8.81 m KBr are also included in our data fit. With exception of the osmotic coefficients data of Patll et al. (1991), all other activity data used in parameter's evaluation process are directly determined from isopiestic measurements of potassium bromide solutions. The osmotic coefficients reported by Patll et al. (1991) are determined on the basis of vapor pressure measurements. The 25 °C φ values of Hamer and Wu (1972) are very close to the recommendations of Mikulin (1968) (to 5.5 m KBr) and the data of Robinson and Stokes (1949) (to 5.0 m KBr) and therefore last two sets of data are not included in our data fit. Note that in our final parameterization some of high concentration activity data points of Patll et al. (1991) and of Fanghanel and Grojtheim (1990) are excluded in $\beta^{(0)}_{KBr}$, $\beta^{(1)}_{KBr}$, and C^{φ}_{KBr} evaluation process (see also Table 6).

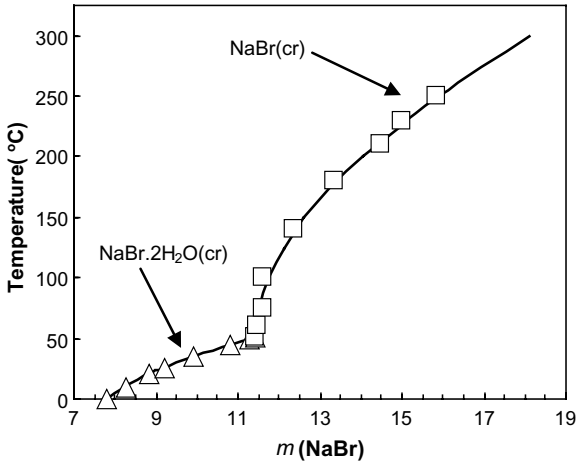

Fig. 3. The calculated (solid line) and experimental [symbols, Linke (1965)] solubility of NaBr–$2H_2O$(cr) and NaBr(cr) solid phases in the NaBr–H_2O system as a function of temperature (0–300 °C). Symbols: open triangles, NaBr–$2H_2O$(cr) precipitation; open squares, NaBr(cr) precipitation.

The resulting pure electrolyte parameterization for the binary KBr–H_2O system is given in Table 3. It gives excellent agreement with all the data for unsaturated binary solutions used in parameterization. The sigma values of fit equals to 0.0757 or less (see Table 6). On Fig. 4 we compare the model predicted and our experimental osmotic coefficients at 50 °C (see Table 2). The solution model predicts KBr mean activity coefficients which are in very good agreement with recommended values of Hamer and Wu (1972) at 25 °C (to 5.5 m KBr), and of Holmes and Mesmer (1998) at 200 and 250 °C (to 5 m KBr). The comparison is given on Fig. 5 and Table 4. At 100 °C and high potassium bromide molality the present model predicts lower activity coefficients (max difference of 4.5% at 5 m KBr). Similarly to sodium bromide mean activity coefficients, in temperature ranging from 25 to 100 °C and to molality of saturation, the temperature dependence of γ(KBr) is very small. Note that recommended potassium bromide mean activity coefficients values available in literature are not used in parameterization of our KBr–H_2O model.

Temperature function for the standard chemical potential of solid potassium bromide KBr(s) is evaluated from solubility data in the KBr–H_2O system using our evaluation of the K–Br binary interaction parameters. Solubility data from 0 to 251 °C are taken from Linke (1965). According to the data, KBr (s) is the only stable solid phase crystallizing from saturated binary KBr–H_2O solutions. The data shows that the molality of saturated KBr–H_2O binary solutions increases sharply with temperature from 0 to 251 °C (4.5 m KBr at 0 °C; 15.7 m KBr at 251 °C). The resulting temperature parameters for (μ°/RT) of KBr (s) are given in Table 5. The model also agrees very well with the binary KBr–H_2O solubility data to very high concentration (see Fig. 6). Sigma (σ) value of KBr(s) solubility data fit equals to 0.0132 (see Table 5). Temperature extension of the model to temperatures higher than 250 °C gives higher KBr(s) solubility than the data (Linke, 1965). Thus, at 275 and 290 °C the model predicts 17.56 m and 19.0 m potassium bromide solubility, respectively. The data at 275 and 301 °C are 16.9 m and 17.6 m KBr, respectively. Note that the experimental solubility data point at 301 °C (Linke, 1965) do not follow the trend of the solubility at lower temperature.

4.3. Evaluation of parameters in the Na–K–Br–H_2O system

The solubility data in this ternary are used to evaluate temperature variable $\psi_{Na,K,Br}$ mixing parameter. Solubility data in the NaBr–KBr–H_2O system were found available in the literature from 0 to 75 °C. Reported phase diagrams are

Table 6
Standard deviation (σ) values of activity (osmotic coefficients (φ); water activity (a_w)), and solubility data in NaBr–H_2O, KBr–H_2O and NaBr–KBr–H_2O systems (n is the number of experimental data points; m(sat) is the molality of solutions saturated with corresponding solid phase)

System	Method[a]	Type of data	T (°C)	Molality range	Reference	σ
Activity data						
NaBr–H_2O	iso	φ	50	m(NaBr): 0.745–6.1339	This work	0.040 ($n = 11$)
	comp	φ	25	m(NaBr): 0.001–9.0	Hamer and Wu (1972)	0.012 ($n = 32$)
	iso	φ	25	m(NaBr): 1.9551–9.1701	Rard and Archer (1995)[b]	0.029 ($n = 36$)
	iso	φ	110–225	m(NaBr): 0.65–6.20	Holmes and Mesmer (1998)	0.0076 ($n = 74$)
	iso	φ	100.3	m(NaBr): 0.47–10.62	Voigt et al. (1990)	0.0153 ($n = 9$)
	v.p.	φ	5–50	m(NaBr): 7.99–11.27	Apelblat and Korin (1998)[b]	0.107 ($n = 10$)
	v.p.	φ	30–70	m(NaBr): 2.0–7.98	Patll et al. (1991)[b]	0.0197 ($n = 71$)
	v.p.	φ	0–101	m(NaBr): 2.0–7.0	Jakli and Van Hook (1972)	
KBr–H_2O	iso	φ	50	m(KBr): 0.741–5.6826	This work	0.0096 ($n = 7$)
	comp	φ	25	m(KBr): 0.001–5.5	Hamer and Wu (1972)	0.0052 ($n = 28$)
	iso	φ	110–225	m(KBr): 0.67–7.41	Holmes and Mesmer (1998)	0.0071 ($n = 74$)
	iso	a_w	100.3	m(KBr): 1.46–8.81	Fanghanel and Grojtheim (1990)[b]	0.0757 ($n = 9$)
	iso	φ	45	m(KBr): 1.0–3.5	Hellams et al. (1965)	0.016 ($n = 12$)
	v.p.	φ	30–70	m(KBr): 1.26–4.35	Patll et al. (1991)[b]	
Solubility data						
NaBr–H_2O	sol	NaBr–$2H_2O$(cr) m(sat)	0–51	m(NaBr): 7.78–11.36	Linke (1965)	0.0059 ($n = 10$)
	sol	NaBr(cr) m(sat)	51–250	m(NaBr): 11.36–15.86	Linke (1965)	0.022 ($n = 10$)
KBr–H_2O	sol	KBr(cr) m(sat)	0–251	m(KBr): 4.51–15.74	Linke (1965)	0.0132 ($n = 22$)
NaBr–KBr–H_2O	sol	NaBr–$2H_2O$(cr) m(sat)	0–50	m(NaBr): 7.38–11.40 m(KBr): 0.00–1.59	Zdanovskii et al. (1973)	0.047 ($n = 42$)
	sol	NaBr(cr) m(sat)	50–75	m(NaBr): 10.9–12.1 m(KBr): 0.00–2.54	Zdanovskii et al. (1973)	0.118 ($n = 12$)
	sol	KBr(cr) m(sat)	0–75	m(NaBr): 0.00–11.42 m(KBr): 0.75–7.70	Zdanovskii et al. (1973)	0.124 ($n = 108$)

[a] Experimental method: iso, isopiestic; comp, compilation; v.p., vapor pressure; sol, salt solubility.
[b] Some of these data are not considered in the final parameterization.

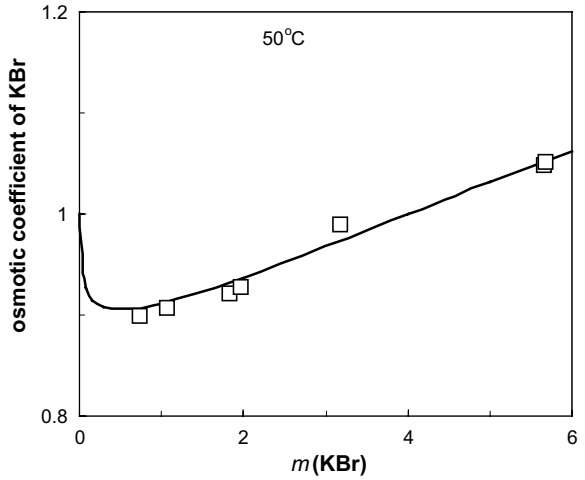

Fig. 4. The calculated (solid line) and experimental [squares, this study (see Table 2)] osmotic coefficients (φ) of KBr against molality m of KBr–H_2O at 50 °C.

a simple eutonic type, i.e. only the solid phases precipitating from corresponding binary solutions (NaBr–$2H_2O$(s), NaBr(s) and KBr(s)) crystallized from saturated mixing solutions. The NaBr–KBr–H_2O solubility data of Abliazina (1963) at 50 and 75 °C, of Agaev and Djambarov (1959) at 35 °C, of Agaev and Mamedov (1964) at 0, 25 and 50 °C, of Mukimov and Kapkaeva (1952) at 0 and 25 °C, of Muromzev (1931) at 25 °C, and of Vlasov and Bergman (1943) from 0 to 50 °C are used in parameterization. All these solubility data are summarized in Zdanovskii et al. (1973). The molality range of the data is given in Table 6. According to the data, in temperature range from 0 to 75 °C, the solubility of pure bromide salts in complex NaBr–KBr–H_2O solutions decreases, compared to the binary NaBr–H_2O and KBr–H_2O solutions solubility, with adding the second component. There are some contradictions in the data about the composition of sodium bromide solids crystallizing in the system NaBr–KBr–H_2O at 50 °C. According to the data of Vlasov and Bergman (1943), and Abliazina (1963) anhydrous sodium bromide NaBr(s) is the stable solid phase in the binary NaBr–H_2O and in ternary systems at 50 °C. Agaev and Mamedov (1964) reported precipitation of NaBr–$2H_2O$(s) from saturated binary and ternary solutions at the same temperature. However, in all three sets of data, the composition of ternary solutions, saturated with solid sodium bromide are in very good agreement. The main reason for the above

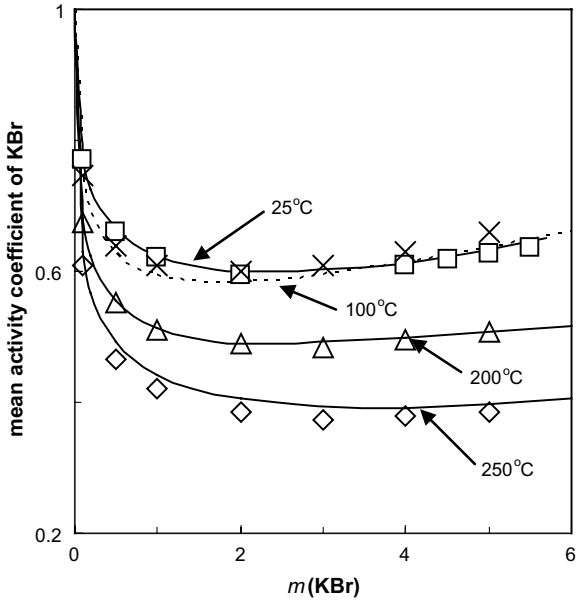

Fig. 5. Comparison of mean KBr activity coefficients in KBr–H_2O solutions calculated by the model (solid lines: 25, 200 and 250 °C; dotted line: 100 °C) with the reference values (symbols) from 25 to 250 °C (symbols: open squares, Hamer and Wu (1972) at 25 °C; crosses, open triangles, and open diamonds: Holmes and Mesmer (1998) at 100, 200 and 250 °C, respectively).

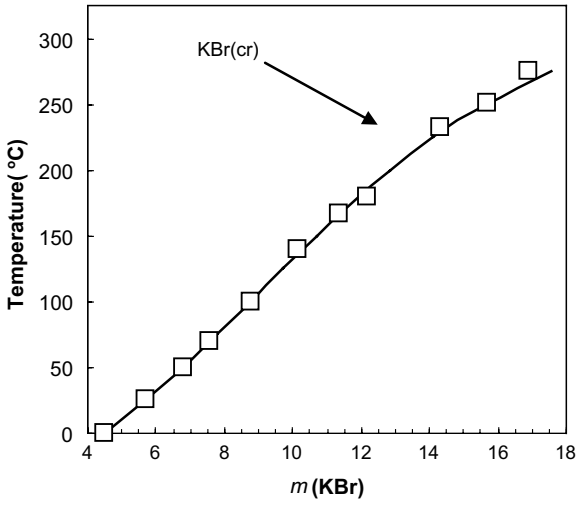

Fig. 6. The calculated (solid line) and experimental [symbols, Linke (1965)] solubility of KBr(cr) solid phase in the KBr–H_2O system as a function of temperature (0–275 °C).

contradiction is that the temperature of 50 °C is very close to the phase transition NaBr–$2H_2O$(s) ↔ NaBr(s) temperature. Our NaBr–H_2O model predicts that the stable phase at 50 °C is NaBr–$2H_2O$(s) and we use this composition in ternary system model.

In the data correlations, the evaluations of the binary parameters for aqueous NaBr and KBr, and of NaBr–$2H_2O$(s), NaBr(s) and KBr(s) standard chemical potentials established above are used. In this parameterization, the temperature function for the $\theta_{Na,K}$ mixing parameter is taken from Greenberg and Moller (1989). The resulting $\psi_{Na,K,Br}$ model (see Table 5) is in very good agreement with sodium-, and potassium-bromide solids solubility data from 0° to 75 °C in the ternary NaBr–KBr–H_2O system. The sigma values of the solubility data are given in Table 5. In Fig. 7a–c we compare the model predictions and the experimental solubility isotherms at 0, 25, 50 and 75 °C. According to the model, at 50 °C the solubility isotherm consist three branches corresponding to the crystallization of NaBr–$2H_2O$(s), NaBr(s) and KBr(s). At 75 °C and solution compositions near the invariant point, the model predicts lower NaBr(s) solubility than the data points of Abliazina (1963) (max diff of 0.6 m NaBr; see open diamonds on Fig. 7c). The temperature extrapolation of the model provides a reasonable NaBr(s) and KBr(s) solubility in the ternary NaBr–KBr–H_2O system to high temperature. Fig. 7d presents the model predictions at 100 and 200 °C. New experimental data are required to validate these model extrapolations.

5. SUMMARY AND RESTRICTIONS

In this study new osmotic coefficients data of the unsaturated binary solutions NaBr–H_2O (to 5.953 mol kg^{-1}) and KBr–H_2O (to 5.68 mol kg^{-1}) at the temperature $t = 50$ °C are reported. These data are determined directly from isopiestic measurements. Using our own results and other experimental thermodynamic quantities available in literature (osmotic coefficients, water activities, binary and ternary solutions bromide mineral's solubilities) we construct a chemical model which allows calculation of solubilities and solution activities in the NaBr–H_2O, KBr–H_2O and Na–K–Br–H_2O systems from dilute to high solution concentration up to saturation at temperature ranging from 0 to 300 °C and within experimental uncertainty (less than 4%). The Harvie and Weare (1980) solubility modeling approach is employed. The chemical potentials of three bromide salts (NaBr–$2H_2O$ (cr), NaBr (cr) and KBr (cr)) are established here from solubility data in corresponding binary solutions. Very good agreement with both the experimental activity and solubility data is achieved with temperature functions for temperature-variable ion interaction parameters and chemical potentials of solids which include only three constants (a_1, a_2, and a_5). The model for binary systems is validated by comparing activity coefficient predictions with those given in literature, and not used in the parameterization process. There is a restriction of the mixing Na–K–Br–H_2O model due to lack of solubility data at temperatures over 75 °C. However, the temperature extrapolation of the ternary system model provides reasonable mineral solubilities up to 200 °C (see Fig. 7d). When experimental data are available, extrapolations of the mixing solution model to temperatures not studied in model parameterization can be tested and validated.

As a final test of the model in Table 7 we summarized the thermodynamic properties [thermodynamic solubility product ($\ln K^{o}_{sp}$) and the standard molar Gibbs free energy of formation ($\Delta_f G^{o}_{m}$)] at 25 °C of solid phases introduced here: NaBr–$2H_2O$ (cr), NaBr (cr) and KBr (cr). The predicted and experimental molality of saturated binary

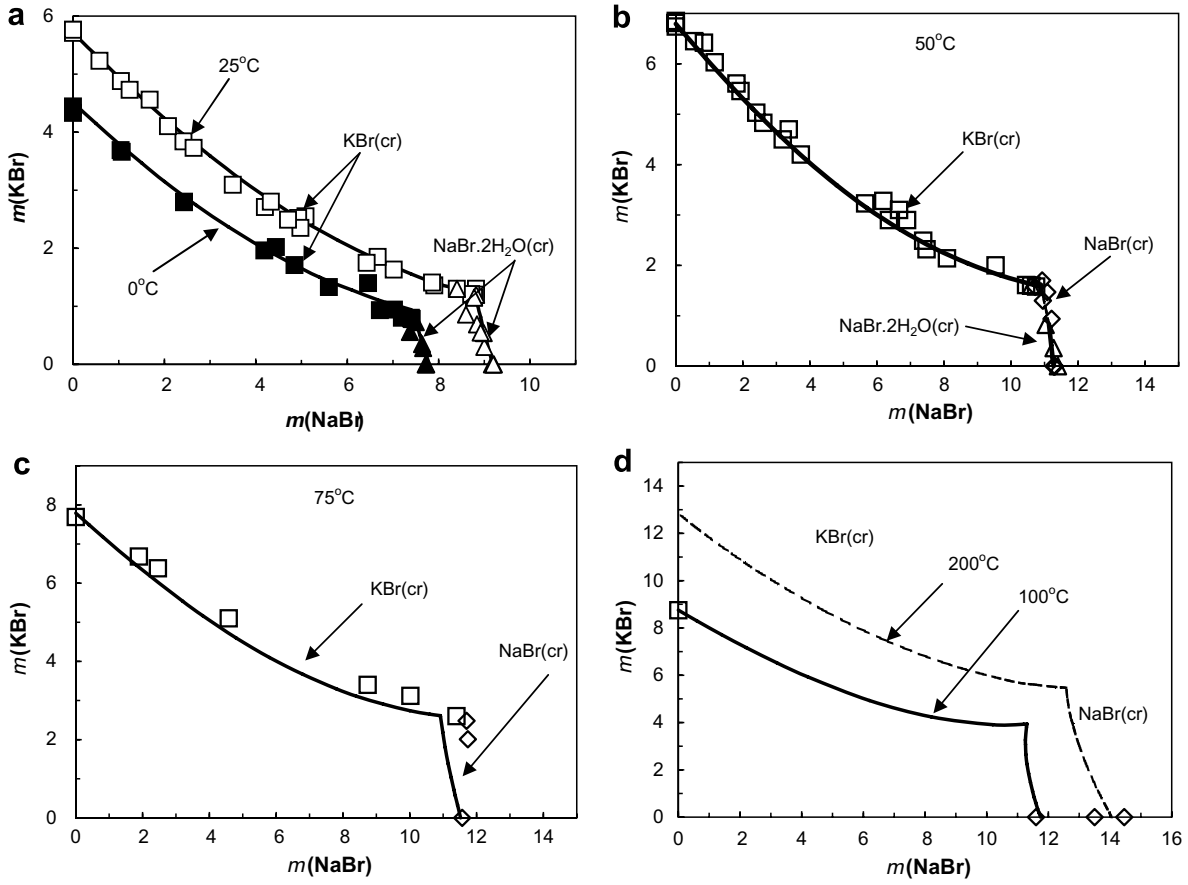

Fig. 7. The calculated (solid and dashed lines) and experimental solubility of NaBr–2H_2O(cr) (solid triangles at 0 °C and open triangles at other temperatures), NaBr(cr) (open diamonds) and KBr(cr) (solid squares at 0 °C and open squares at other temperatures) solid phases in the NaBr–KBr–H_2O system from 0 to 200 °C. (a) 0 and 25 °C; (b) 50 °C; (c) 75 °C; (d) 100 and 200 °C. The ternary system experimental solubility data are from: at 0 °C, Vlasov and Bergman (1943), Mukimov and Kapkaeva (1952) and Agaev and Mamedov (1964); at 25 °C, Muromzev (1931), Vlasov and Bergman (1943), Mukimov and Kapkaeva (1952) and Agaev and Mamedov (1964); at 50 °C, Vlasov and Bergman (1943) and Abliazina (1963); at 75 °C, Abliazina (1963). Symbols in (d) show the pure water solubility of NaBr(cr) and KBr(cr) (Linke, 1965).

Table 7
Calculated values of the logarithm of the thermodynamic solubility product ($\ln K^{o}_{sp}$), and the standard molar Gibbs free energy ($\Delta_f G^{o}_{m}$) of formation of NaBr–2H_2O(cr), NaBr(cr) and KBr(cr) at 25 °C, where m^s is the molality of the saturated binary solutions[a]

Salt composition	m^s/(mol kg^{-1})		$\ln K^{o}_{sp}$		$\Delta_f G^{o}_{m}$/(kJ mol^{-1})	
	Calculated	Experimental	Calculated	Reference data	Calculated[a]	Reference data
NaBr–2H_2O(cr)	9.188	9.193[b]	4.643	4.661[c] 4.67[d]	−828.61	−828.57[c] −828.53[d] −828.29[f]
NaBr(cr)			6.7032	6.779[c] 6.783[d]	−349.24	−349.06[c] −349.05[d] −349.31[g]
KBr(cr)	5.715	5.696[b]	2.6272	2.60[e]	−380.72	−380.78[e] −380.66[f]

[a] Calculated using standard chemical potentials for ions in solutions from Wagman et al. (1982).
[b] Linke (1965).
[c] Christov (1996).
[d] Rard and Archer (1995).
[e] Christov (2005).
[f] Wagman et al. (1982).
[g] Naumov et al. (1971).

$NaBr–H_2O$ and $KBr–H_2O$ solutions at 25 °C (m^s) is also given in Table 7. Note that for sodium dihydrate salt, in our solubility product calculations we consider the chemical potential of water given in Table 5 (see also Section 3). The $\Delta_f G^o{}_m$ values are calculated from the salt potentials (Table 5) and using the reference data for aqueous species from Wagman et al. (1982). Our calculated m^s, $\ln K^o{}_{sp}$, and $\Delta_f G^o{}_m$ values are in excellent agreement with those given in literature. The $\ln K^o{}_{sp}$ max difference of 0.08 ln units is for NaBr(cr). Note that, according to the experimental solubility data in $NaBr–H_2O$ binary and $Na–K–Br–H_2O$ ternary systems considered here NaBr(cr) is not stable solid phase at 25 °C, i.e. $\ln K^o{}_{sp}$ (NaBr(cr)) and $\Delta_f G^o{}_m$ (NaBr(cr)) calculations presented in Table 7 represent the temperature extrapolation of our solid–liquid equilibria model.

ACKNOWLEDGMENTS

This work has been supported by funds from the U.S. Department of Energy, U.S. National Science Foundation and Bulgarian Ministry of Science and Education. I thank Dr. Snejana Velikova and Dr. Kalina Ivanova for help in the isopiestic measurements. I also thank Associate Editor David J. Wesolowski and three anonymous reviewers for their constructive suggestions.

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Associate editor: David J. Wesolowski