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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

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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, $NaBr\cdot 2H_2O(cr)$, $NaBr(cr)$ and $CaBr_2\cdot 4H_2O(cr)$, 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 $CaBr_2\cdot 6H_2O(cr)$, and $CaBr_2\cdot 4H_2O(cr)$ 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 ($CaBr_2\cdot 6H_2O(cr)$) 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

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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}; $m(\text{sat}) = 7.51$–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 $\pm 1.10^{-5}$ 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