Journal of Molecular Liquids 252 (2018) 362–367

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Experimental and thermodynamic modeling study of solid-liquid equilibrium in ternary systems NaBr–$SrBr_2$–H_2O and KBr–$SrBr_2$–H_2O at 288.15 K and 0.1 MPa

Dan Li [a], Lingzong Meng [a,b,*], Tianlong Deng [b], Yafei Guo [b], Yu Pan [a]

[a] School of Chemistry and Chemical Engineering, Linyi University, Linyi 276000, China
[b] Tianjin Key Laboratory of Marine Resources and Chemistry, Tianjin University of Science and Technology, Tianjin 300457, China

ARTICLE INFO

Article history:
Received 20 November 2017
Received in revised form 31 December 2017
Accepted 3 January 2018
Available online 4 January 2018

Keywords:
Solid and liquid equilibrium
Phase diagram
Strontium bromide
Solubility
Pitzer model

ABSTRACT

The solubilities and refractive indices of the NaBr–$SrBr_2$–H_2O and KBr–$SrBr_2$–H_2O systems at 288.15 K were investigated with the isothermal dissolution method. The phase diagrams and refractive index diagrams were plotted for the two systems at 288.15 K. The phase diagrams consist of one two-salt cosaturated invariant point, two univariant solubility isotherms, and two stable crystallization fields. The two systems belong to the simple eutectic type, and neither double salt nor solid solution was found. The refractive indices change regularly with the strontium bromide concentration increasing in solution, and reach the maximum value at the eutectic point. On the basis of Pitzer and Harvie-Weare (HW) model, the binary and mixing Pitzer parameters and solubility equilibrium constants of equilibrium solid salts for the two ternary systems at 288.15 K were acquired. And then, the solubilities for the ternary systems at 288.15 K were demonstrated. A comparison shows that the calculated solubilities agree well with the experimental data.

1. Introduction

Recently, bromine and strontium have been widely used in the technology fields and pharmaceuticals fields. The oilfield brines in Nanyishan Section in the Qaidam Basin of the Qinghai-Tibet Plateau, which belong to the $CaCl_2$ type, have high contents of lithium, potassium, strontium, bromine, as well as accompanying sodium, calcium, boron, and many other useful components. The concentration of bromine in the brines is up to 0.281 $g \cdot L^{-1}$, and 4.45 $g \cdot L^{-1}$ for strontium, which is much higher than those in the salt lake brines in Qinghai-Tibet Plateau [1,2]. These brines largely consist of the complex system (Li–Na–K–Ca–Sr–Cl–Br–borate–H_2O). It is well-known that phase equilibria and phase diagrams (solubility data) of brine systems are both the theoretical foundation for the exploitation of the brine resources [3]. Therefore, the investigation of the phase equilibria and phase diagrams will provide the fundamental chemical engineering thermodynamic data for the finer separation and comprehensive exploitation of brine resources using salinity-gradient solar pond technology.

The ternary systems NaBr–$SrBr_2$–H_2O and KBr–$SrBr_2$–H_2O containing strontium bromine are important subsystems of the above complex system. Although the equilibria of the quaternary system NaBr–KBr–$SrBr_2$–H_2O at 348.15 K have been reported [4], the equilibria of the above ternary systems at 288.15 K, which is nearly the same as the temperature for brine exploitation, has not been reported in the literature. Computer models on the aqueous solutions of electrolytes are reliable on predicting solution behavior and (solid + liquid) equilibria. The Pitzer and Harvie-Weare (HW) model, which is described in our study, was widely used in calculating the solubilities of the salt-water systems [5–8]. The models for the quinary system Na–K–Mg–Ca–Br–H_2O and Na–K–Ca–Br–SO_4–H_2O containing bromine have been constructed over a wide temperature range (273.15 to 373.15) K [9,10]. The thermodynamic properties of the system $SrBr_2$–H_2O, which can be used for Pitzer model construction, have been reported from 303.15 K to 343.15 K [11]. The mean activity coefficients of NaBr in NaBr–$SrBr_2$–H_2O system at 298.15 K were shown in the literature [12]. However, the models for the systems containing strontium bromine are still lacking in the literature. In this study, the solubilities and the refractive indices of the ternary systems NaBr–$SrBr_2$–H_2O and KBr–$SrBr_2$–H_2O at 288.15 K were determined, and the solubilities for the ternary systems were also calculated on the basis of Pitzer and Harvie-Weare (HW) model.

2. Experimental section

2.1. Apparatus and reagents

The phase equilibrium has been done in a magnetic stirring thermostatic bath (HXC-500-12A, Shanghai Baidian Experimental Instrument

* Corresponding author at: School of Chemistry and Chemical Engineering, Linyi University, Linyi 276000, China.
E-mail address: menglingzong@lyu.edu.cn (L. Meng).

https://doi.org/10.1016/j.molliq.2018.01.020
0167-7322/

Table 1
Chemical sample information.

Chemical name	Source	Initial purity (mass fraction)	Purity grade
NaBr	Aladdin Industrial Corp.	0.99	Analytical purity
KBr	Aladdin Industrial Corp.	0.99	Analytical purity
$SrBr_2 \cdot 6H_2O$	Aladdin Industrial Corp.	0.98	Analytical purity

Ltd., temperature uncertainty ±0.1 K). An X-ray diffractometer (X'pert PRO, Spectris. Pte. Ltd., The Netherlands) was used to identify the solid phase minerals. The chemicals used in this work were analytical purity grade, as shown in Table 1. The water used in the experiments such as chemical analysis was double distilled water (DDW) with conductivity $\leq 1.2 \times 10^{-4}\ S \cdot m^{-1}$ and pH ≈ 6.60 at 298.15 K.

2.2. Experimental methods

The isothermal dissolution method, which was described in our previous study [5], was used to measure the solubility of the systems NaBr–$SrBr_2$–H_2O and KBr–$SrBr_2$–H_2O in this study. According to the estimated solubilities of the ternary system, a series of artificial synthesized brines by mixing appropriate amount of salts and DDW were prepared, and loaded into clean glass bottles, which were placed in the thermostatic bath, with the temperature at (288.15 ± 0.1) K and stirring speed at 300 rpm to quicken the equilibrium of those brines. The solid phase in the bottle should always exist during the equilibrium process. The stirring would stop for 2 h to make the solid and liquid phases stratification, and then a sample of approximately 3.0 cm^3 of the clarified solution was taken, weighed accurately, diluted in a 250.0 cm^3 volumetric flask with DDW and measured periodically. If the difference between the concentrations of the two samples taken from the same glass bottle was within ±0.3% in mass fraction, then the equilibrium state achieved. Otherwise, the solution was stirred continually until the equilibrium state achieved. The average of the concentrations of the two samples was the solubility data of this point. Generally, it took approximately 15 days to reach the equilibrium state at 288.15 K for the two systems. Meanwhile, some of the liquid phases were taken out for refractive index measurement. And the solid phases were also sampled and identified by Schreinemaker's wet residue method [13] (the liquid phase point, the wet residue point and the solid phase mineral point in the phase diagrams are in a line) and the X-ray diffraction. The remainder of the solid and liquid phases in the bottles was used to synthesize another system point.

2.3. Analytical method

The Sr^{2+} ion concentration was measured by titration with an EDTA standard solution in the presence of $MgCl_2$ and ammonia buffer solution with the indicator Eriochrome Black-T [14]. The Br^- ion concentration determined was by titration with a standard solution of $Hg(NO_3)_2$ in the presence of mixed indicator of diphenylcarbazone and bromophenol blue [15]. The relative deviation for the Sr^{2+} and Br^- concentrations was less than ±0.003. The concentration for Na^+ and K^+ was calculated in view of the charge balance of ions with relative deviation no more than ±0.006. The refractive indices (n_D) of liquid phases were measured with a WZS-1 type abbe refractometer at (288.15 ± 0.1) K, with an uncertainty of ±0.0001.

3. Results and discussion

The solubilities for the binary systems NaBr–H_2O and KBr–H_2O at different temperatures have been studied in many references, the difference between the solubilities at the same temperature have been reported in more detail [16]. The solubilities for the two systems at 288.15 K in this study are nearly the same as those in the literature, so the difference between experimental data in this study and those in the literature for the binary systems were not discussed any more. The solubility for the $SrBr_2$–H_2O system was reported in many literature. There are solubility data from 273.15 to 373.15 K listed in the CRC Handbook of Chemistry and Physics [17]. The solubility data at 298.15 K agree well with the data (0.5160 in mass fraction) from Harkins and Pearce [18], but are higher than these from Milikan (0.4979 in mass fraction) [19], Scott and Durham (0.4993 in mass fraction) [20]. Ropp also give the solubility data for the $SrBr_2$–H_2O system from 273.15 to 363.15 K [21], which are the same as these in the handbook at 273.15 and 283.15 K, but higher at other temperatures. In this study, the equilibrium time for this system at 288.15 K was more than one month, and the solubility of $SrBr_2$ was carefully checked several times. The solubility data is 0.4927, which is close to the interpolated solubility data from the Handbook. A comparison between the solubility data at different temperatures are presented in Fig. 1. It is shown that the solubility data for $SrBr_2$ increases with increasing temperature.

The experimental solubility data and refractive indices of the NaBr–$SrBr_2$–H_2O and KBr–$SrBr_2$–H_2O systems at 288.15 K are listed in Tables 2 and 3. w_i in Tables 2 and 3 is the concentration (mass fraction) for the mineral i. According to the experimental solubility data of Tables 2 and 3, the phase diagrams of the systems were shown in Figs. 2 and 3.

The points A and B in Table 2 and Fig. 2 represent the solubilities of the binary systems NaBr–H_2O and $SrBr_2$–H_2O at 288.15 K. The phase diagram in Fig. 2 has one invariant point E cosaturated with $NaBr \cdot 2H_2O$ and $SrBr_2 \cdot 6H_2O$, two univariant solubility curves AE and EB, and two crystallization fields for $NaBr \cdot 2H_2O$ and $SrBr_2 \cdot 6H_2O$. The crystallization area of $NaBr \cdot 2H_2O$ is relatively large, while the crystallization area of $SrBr_2 \cdot 6H_2O$ are relatively small, which shows strontium bromide has a higher solubility than sodium bromide. The concentration of sodium bromide decreases with strontium bromide concentration increasing, which shows that strontium bromide has a strong salt-out effect on sodium bromide.

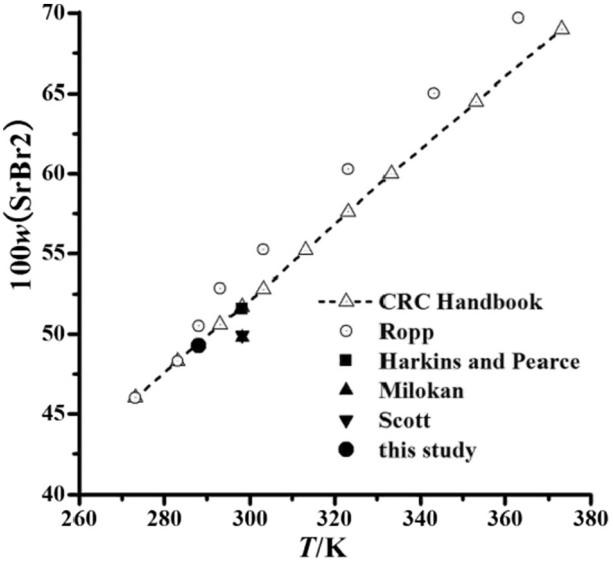

Fig. 1. Comparison of the experimental solubilities of $SrBr_2$ at different temperatures. △, Ref. 17; ○, Ref. 21; ■, Ref. 18; ▲, Ref. 19; ▼, Ref. 20; ●, this study.