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Solubility in the NH$_4$Br-CaBr$_2$-H$_2$O system at T = (298.15 and 323.15) K.

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Abstract

In this study, the bromide minerals solubility in the mixed system NH$_4$Br-CaBr$_2$-H$_2$O have been investigated at T = (298.15 and 323.15) K by the physico-chemical analysis method. According to the data obtained NH$_4$Br-CaBr$_2$-H$_2$O system is of a simple eutonic type at both temperatures. At standard temperature the equilibrium crystallization of NH$_4$Br (cr) and CaBr$_2$.6H$_2$O (cr) has been established. The crystallization of NH$_4$Br (cr) and CaBr$_2$.4H$_2$O (cr) has been identified at T = 323.15 K. The data shows that the field of crystallization of calcium bromide hydrates is very narrow on the solubility isotherm at T = (298.15 and 323.15) K.

Keywords: phase equilibrium; bromide minerals solubility; mixed system NH$_4$Br-CaBr$_2$-H$_2$O;

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INTRODUCTION

The behaviour of bromide as a trace element in vaporising seawater and diagenetic reactions of evaporates is of prime importance for geochemical studies in marine chemical sediments [1-3]. The investigation of the phase diagrams of bromide mixed systems is of practical importance with a view to explain the distribution of bromide ions in natural evaporated deposits during crystallization of salts as a result of sea water evaporation, during treatment of natural deposits and production of bromide mineral resources [1-4]. The investigation of NH_4 – Ca – chloride, and -bromide mixed diagrams is of high interest for the production of sodium carbonate using Solvay technology method [5]. Investigation of mixed ammonium (NH_4^+)– major ocean cations (Na^+, K^+, Mg^+, Ca^+) halide and sulfate mixed systems are also of high importance for atmospheric aerosol system, and especially for correct estimation of the effect of ammonia (NH_3) on the solid-liquid phase change of sea type aerosols in atmosphere [3,4,6].

The solubility data for ammonium – alkali earth metals chloride/bromide (1-1+ 2-1) mixtures of the type $NH_4X-MX_2-H_2O$ (X=Cl, Br; M = Mg, Ca, Sr, Ba) are scarce. Solubility data are available only for 5 systems: $NH_4Cl-MgCl_2-H_2O$, $NH_4Br-MgBr_2-H_2O$, $NH_4Cl-CaCl_2-H_2O$, $NH_4Cl-SrCl_2-H_2O$ (at 298.15 K only) , and $NH_4Cl-BaCl_2$-H_2O (at 298.15 K only). According to the data strontium and barium chloride ternary systems are of simple eutonic type at standard temperature [7,8]. According to the data of Zeng et al. [5] the mixed $NH_4Cl-CaCl_2-H_2O$ system is also of eutonic type in the range of temperatures from 283.15 K to 353.15 K. The available reference solubility data [1, 7-12] and solid-liquid equilibrium models [2,13] show that carnallite type double salts $NH_4X.MgX_2.6H_2O$ crystallize from mixed saturated solutions $NH_4X-MgX_2-H_2O$ from 273.15 K to 348.15 K.

According to the available reference solubility data [7,8,14] and temperature – variation (from 273.15 to 373.15) K) solid-liquid equilibrium modeling studies [3,4,13,14] for calcium bromide (1-1+ 2-1) mixtures of the type $M'Br-CaBr_2-H_2O$ (M' = Li,Na,K) double salt $LiBr.CaBr_2.5H_2O$ crystallize from saturated $LiBr-CaBr_2-H_2O$ solutions at 298.15 K [13,14], while in a wide range of temperatures (from 273 15 K to 373.15 K) from sodium bromide ($NaBr-CaBr_2-H_2O$) and potassium bromide ($KBr-CaBr_2-H_2O$) saturated solutions precipitate only simple salts [3,4]. Solubility data for mixed $NH_4Br-CaBr_2-H_2O$ system could not be found in the literature.

EXPERIMENTAL

In this study, the bromide minerals solubility in the mixed system $NH_4Br-CaBr_2-H_2O$ have been investigated at T = (298.15 and 323.15) K. The solubility of bromide minerals in ternary system was studied by the method of isothermal decrease of the supersaturation [1-4, 9-12, 14,15]. Different weight ratios of solid NH_4Br, and $CaBr_2$ were used for each experiment. Crystal salts in excess of the solubilities at T =(298.15 and 323.15) K 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 298.15 K and 323.15 K. The quick cooling of the solution followed by agitation with a magnetic stirrer ensured a fast decrease of the supersaturation. Equilibrium was attained by continuous stirring for 24 h.

The solid potassium bromide and calcium bromide samples were from Fluka with mass fraction purity 0.999. The solids were used without further purification. 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 [1-4,9-12,14]. Calcium ion was determined by complexometric titration with eriochrome black T as indicator [16]. 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) [16]. The concentration of Ammonium ion $[NH_4^+]$ was calculated by balance reaction: $[NH_4^+] = [Br^-]_{total} – 2x[Mg^{2+}]$. The compositions of the thoroughly suction dried solid phases were specified by the Schreinemackers graphic method {[17]; see also references [1-4, 14,15]}.

RESULTS AND DISCUSSION

The results from the solubility measurements in the NH_4Br-$CaBr_2$-H_2O system are presented in table 1 and 2, and figure 1 and 2 at T = (298.15 and 323.15) K, respectively. The experimental error is within the range ± (0.1 to 0.3) per cent. Each experimental result represents the arithmetical mean of three parallel determinations.

The data presented on Table 1 and 2, and Fig. 1 and 2 shows that the solubilities of ammonium bromide and calcium bromide solids in binary systems sharply increase with temperature. The determinated here solubilities of NH_4Br (cr) in binary system NH_4Br-H_2O at 298.15 K and 323.15 K are very close to those reported in literature by other authors [7, 18,19] and in our previous experimental [1,9-12] and thermodynamic modeling studies [2,13]. The determined here composition of precipitating calcium bromide solids ($CaBr_2.6H_2O$ at 298.15 K, and $CaBr_2.4H_2O$ at 323.15 K), and concentration of saturated binary $CaBr_2$-H_2O solutions at both temperatures 298.15 K and 323.15 K are in excellent agreement with solubility measurements [3,4,7,8,14,18,19] and thermodynamic phase equilibrium models at standard temperature [14], and in a wide range of temperatures from 273. 15 K to 373.15 K [3,4].

According to the data NH_4Br-$CaBr_2$-H_2O system is of a simple eutonic type at both temperatures. At standard temperature the equilibrium crystallization of NH_4Br (cr) and $CaBr_2.6H_2O$ (cr) has been established. At T = 323.15 K precipitation of NH_4Br (cr) and $CaBr_2.4H_2O$ (cr) has been established. The solubilities of ammonium bromide and calcium bromide solids in mixed system sharply decrease with the concentration of each other at both temperatures. According to the data the field of crystallization of calcium bromide hydrates is very narrow on the solubility isotherm at both temperatures. It can be seen from the data that addition of very low amount of NH_4^+ leads to the crystallization of NH_4Br (cr) at 298.15 K and at 323.15 K.The phase diagrams for NH_4Br-$CaBr_2$-H_2O system studied here at T = (298.15 and 323.15) K are very similar to the phase diagrams for NH_4Cl-$CaCl_2$-H_2O {see fig. 4 in ref. [5], for $NaBr$-$CaBr_2$-H_2O {see fig. 6 in ref. [3]} and for KBr-$CaBr_2$-H_2O (see fig. 1 in ref. [4]} systems at the same temperatures.

Table 1. Experimental mass fraction *w* and molality solubility of NH₄Br(cr), and CaBr₂.6H₂O(cr) solid phases in the NH₄Br - CaBr₂ –H₂O system at T = 298.15 K

Liquid phase, $10^2\,w$		Liquid phase, molality (m/mol·kg⁻¹)		Wet solid phase, $10^2\,w$		Solid phase
NH_4Br	$CaBr_2$	NH_4Br	$CaBr_2$	NH_4Br	$CaBr_2$	
44.0	0.0	8.02	0.0	96.6	0.0	NH_4Br(cr)
41.29	2.92	7.55	0.26	96.36	1.04	NH_4Br(cr)
38.03	5.90	6.92	0.53	96.19	0.96	NH_4Br(cr)
33.30	11.06	6.10	0.99	95.66	1.70	NH_4Br(cr)
26.10	17.80	4.75	1.59	95.40	1.20	NH_4Br(cr)
19.98	24.00	3.64	2.14	93.22	2.11	NH_4Br(cr)
14.66	29.78	2.69	2.68	90.43	3.49	NH_4Br(cr)
10.82	34.85	2.03	3.21	91.73	3.58	NH_4Br(cr)
7.51	39.88	1.46	3.79	85.86	6.23	NH_4Br(cr)
4.77	43.56	0.94	4.21	87.10	6.50	NH_4Br(cr)
3.77	45.57	0.76	4.50	89.30	5.98	NH_4Br(cr)
1.26	50.73	0.27	5.28	76.88	11.94	NH_4Br(cr)
0.70	52.92	0.15	5.71	86.1	3.53	NH_4Br(cr)
0.47	53.84	0.10	5.89	90.28	5.73	NH_4Br(cr)
0.24	56.02	0.06	6.40	84.30	9.18	NH_4Br(cr)
<0.1	57.30	0.02	6.71	0.51	62.30	$CaBr_2.6H_2O$(cr)
<0.1	57.89	<0.02	6.87	0.59	61.67	$CaBr_2.6H_2O$(cr)
0.0	59.36	0.0	7.66		63.59	$CaBr_2.6H_2O$(cr)

Table 2. Experimental mass fraction *w* and molality solubility of NH₄Br(cr), and CaBr₂.4H₂O(cr) solid phases in the NH₄Br - CaBr₂ –H₂O system at T = 323.15 K [a]

Liquid phase, $10^2 \, w$		Liquid phase, molality (m/mol·kg⁻¹)		Wet solid phase, $10^2 \, w$		Solid phase
NH₄Br	CaBr₂	NH₄Br	CaBr₂	NH₄Br	CaBr₂	
50.43	0.0	10.38	0.0	97.67	—	NH₄Br (cr)
43.88	4.75	8.71	0.46	94.92	0.84	NH₄Br (cr)
23.06	24.90	4.52	2.39	95.50	2.10	NH₄Br (cr)
8.90	41.30	1.82	4.15	90.68	4.60	NH₄Br (cr)
5.67	47.30	1.23	5.03	88.60	6.38	NH₄Br (cr)
3.12	52.90	0.72	6.01	85.40	8.40	NH₄Br (cr)
2.50	56.42	0.62	6.87	81.50	11.39	NH₄Br (cr)
1.71	59.46	0.45	7.66	65.77	23.96	NH₄Br (cr)
0.94	62.12	0.26	8.41	41.75	35.85	NH₄Br (cr)
0.71	62.93	0.20	8.66	33.20	42.60	NH₄Br (cr)
0.46	66.22	0.14	9.94	42.15	33.62	NH₄Br (cr)
0.28	67.70	0.09	10.58	37.20	47.30	E
0.18	68.96	0.06	11.18	22.45	60.80	E
<0.1	69.60	<0.05	11.45	21.1	62.60	E
<0.1	69.70	<0.05	11.50	8.60	64.30	CaBr₂.4H₂O(cr))
0.0	70.22	0.0	11.80	0.0	72.6	CaBr₂.4H₂O(cr)

[a]E= eutonic (NH₄Br (cr) + CaBr₂ 4H₂O(cr))
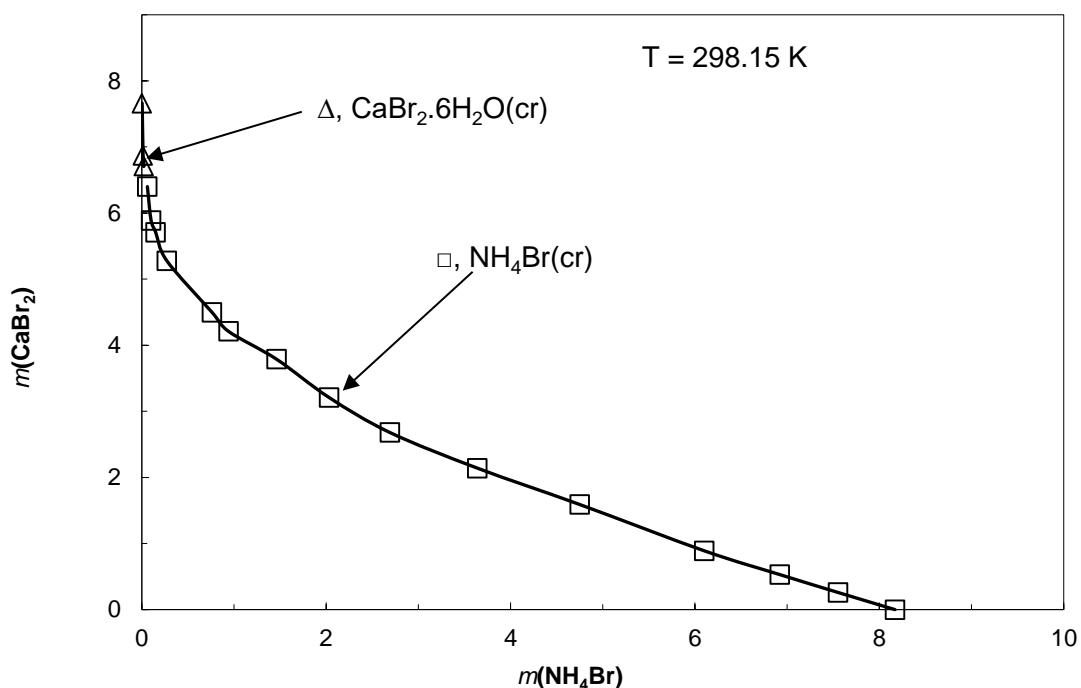
Fig. 1. Experimental molality solubility of NH₄Br(cr) (open squares), and CaBr₂.6H₂O(cr) (open triangles) solid phases in the NH₄Br - CaBr₂ –H₂O system at T = 298.15 K
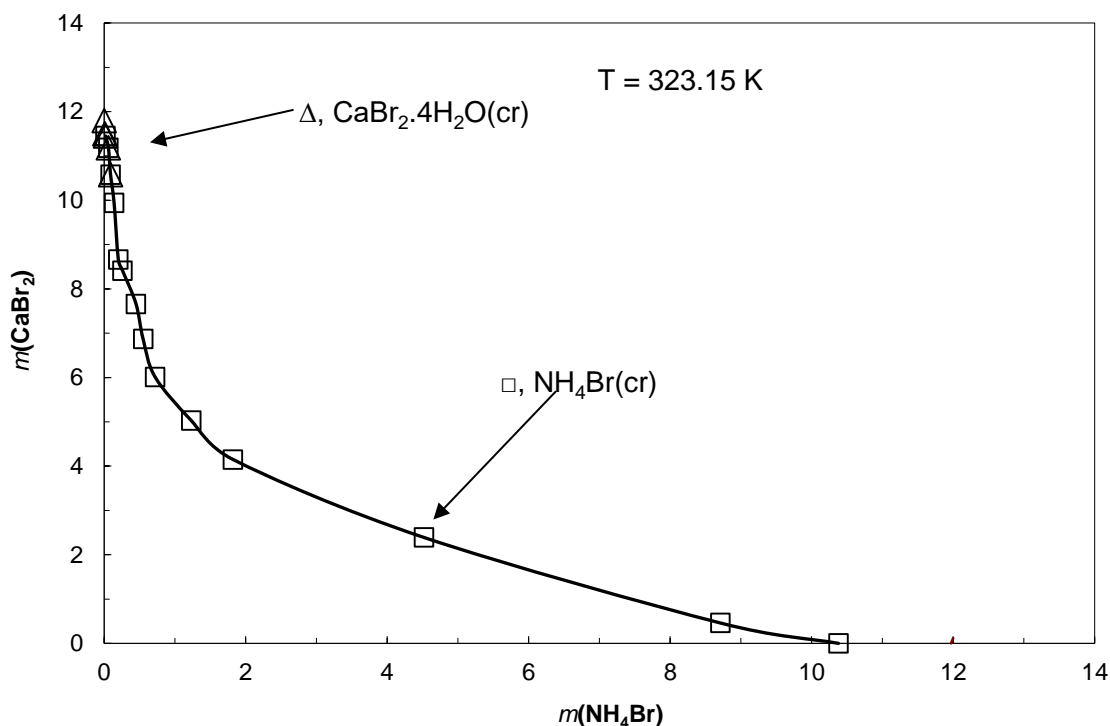
Fig. 2. Experimental molality solubility of NH₄Br(cr) (open squares), and CaBr₂.4H₂O(cr) (open triangles) solid phases in the NH₄Br - CaBr₂ –H₂O system at T = 323.15 K

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