J. Chem. Thermodynamics 90 (2015) 209–215

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

(Solid + liquid) equilibria for the ternary system (CsBr + $LnBr_3$ + H_2O) (Ln = Pr, Nd, Sm) at T = 298.2 K and atmospheric pressure, thermal and fluorescent properties of $Cs_2LnBr_5{\cdot}10H_2O$

Zhan-Ping Qiao *, Zhao-Wan Li, Xin Chen, Yuan-Lin Dang, Qi-Chao Yang

College of Chemistry and Pharmacy Engineering, Nanyang Normal University, Nanyang 473061, PR China

ARTICLE INFO

Article history:
Received 14 November 2014
Received in revised form 23 June 2015
Accepted 5 July 2015
Available online 10 July 2015

Keywords:
Phase diagram
Cesium bromide
Rare earth bromides
Standard molar enthalpy of formation
Fluorescent property

ABSTRACT

The (solid + liquid) phase equilibria of the ternary systems (CsBr + $LnBr_3$ + H_2O) (Ln = Pr, Nd, Sm) at T = 298.2 K were studied by the isothermal solubility method. The solid phases formed in the systems were determined by the Schreinemakers wet residues technique, and the corresponding phase diagrams were constructed based on the measured data. Each of the phase diagrams, with two invariant points, three univariant curves, and three crystallization regions corresponding to CsBr, $Cs_2LnBr_5{\cdot}10H_2O$ and $LnBr_3{\cdot}nH_2O$ (n = 6, 7), respectively, belongs to the same category. The new solid phase compounds $Cs_2LnBr_5{\cdot}10H_2O$ are incongruently soluble in water, and they were characterized by chemical analysis, XRD and TG-DTG techniques. The standard molar enthalpies of solution of $Cs_2PrBr_5{\cdot}10H_2O$, $Cs_2NdBr_5{\cdot}10H_2O$ and $Cs_2SmBr_5{\cdot}10H_2O$ in water were measured to be (52.49 ± 0.48) kJ · mol^{-1}, (49.64 ± 0.49) kJ · mol^{-1} and (50.17 ± 0.48) kJ · mol^{-1} by microcalorimetry under the condition of infinite dilution, respectively, and their standard molar enthalpies of formation were determined as being −(4739.7 ± 1.4) kJ · mol^{-1}, −(4728.4 ± 1.4) kJ · mol^{-1} and −(4724.4 ± 1.4) kJ · mol^{-1}, respectively. The fluorescence excitation and emission spectra of $Cs_2PrBr_5{\cdot}10H_2O$, $Cs_2NdBr_5{\cdot}10H_2O$ and $Cs_2SmBr_5{\cdot}10H_2O$ were measured. The results show that the upconversion spectra of the three new solid phase compounds all exhibit a peak at 524 nm when excited at 785 nm.

1. Introduction

Compounds, containing lanthanide ions, possessing versatility and specificity, have wide application prospects in biology, medical diagnosis, sensing, photovoltaic cells, solar energy conversion, hydrogen fuel storage, trichromatic fluorescent lamps, and other fields [1–4]. More and more efforts had been devoted in the work of searching, finding and characterizing the basic thermodynamic properties of new compounds containing lanthanides.

The phase equilibria of binary systems ($LnBr_3$ + CsBr) (Ln = La, Ce, Pr, Tb, Dy) [5–9], ternary systems (CsBr + $LnBr_3$ + H_2O) (Ln = La, Ce) [10] and quaternary systems (CsBr + $LnBr_3$ + HBr (∼13 %) + H_2O) (Ln = La, Ce, Pr, Nd, Sm, Dy) [11–16] were reported previously, and relevant results of rare earth metal halide in aqueous systems were evaluated importantly [17–18]. These studies provided the phase diagrams for scientists and engineers. In the binary systems, four types (type means the molar ratio of CsBr to $LnBr_3$) of new solid-phase compounds were obtained, including Cs_3LnBr_6 (3:1 type) (Ln = La, Ce, Pr, Tb, Dy), $Cs_3Ln_2Br_9$ (3:2 type) (Ln = Tb, Dy), Cs_2LnBr_5 (2:1 type) (Ln = La, Ce) and $CsLn_2Br_7$ (1:2 type) (Ln = La, Ce, Pr, Tb). In the ternary systems, $Cs_2LnBr_5{\cdot}10H_2O$ (2:1 type) (Ln = La, Ce) were determined. For the quaternary systems (CsBr + $LnBr_3$ + HBr (∼ 13 %) + H_2O) (Ln = La, Ce, Pr, Nd, Sm), new solid-phase compounds $Cs_5Ln_2Br_{11}{\cdot}22H_2O$ (Ln = La, Ce, Pr, Nd, Sm) (5:2 type) were affirmed, and for the quaternary system (CsBr + $DyBr_3$ + HBr (∼ 13 %) + H_2O), solid-phase compound $Cs_5Dy_3Br_{14}{\cdot}24H_2O$ (5:3 type) was confirmed. Optical investigation shows that $Cs_2CeBr_5{\cdot}10H_2O$ has upconversion fluorescence property in the visible region when being excited by the lights of near infrared region.

A comparison of the above systems, it can be found that the phase chemical reactions of the two binary systems ($LnBr_3$ + CsBr) (Ln = La, Ce) are similar in that they both have 3:1, 2:1 and 1:2 type compounds. But the system ($PrBr_3$ + CsBr) only has 3:1 and 1:2 type compounds and no 2:1 type compound. For the two binary systems ($LnBr_3$ + CsBr) (Ln = Tb, Dy), there are both similarity (both having 3:1 and 3:2 type compounds) and difference (1:2 type compound existing in the system ($TbBr_3$ + CsBr), but it disappearing in the system ($DyBr_3$ + CsBr)) in their phase

* Corresponding author. Tel./fax: +86 0377 63513540.
E-mail address: nyqiaozp@163.com (Z.-P. Qiao).

http://dx.doi.org/10.1016/j.jct.2015.07.004
0021-9614/

chemical reactions. For the ternary systems ($CsBr + LnBr_3 + H_2O$) (Ln = La, Ce), their phase chemical reactions are similar. Both of them only have 2:1 type compound. Compared with the binary systems ($LnBr_3 + CsBr$) (Ln = La, Ce), the ternary systems have a disappearance of 3:1 and 1:2 type compounds. As far as the quaternary systems ($CsBr + LnBr_3 + HBr + H_2O$) (Ln = La, Ce, Pr, Nd, Sm) are concerned, they belong to the same category, because they all have 5:2 type compound. For the quaternary system ($CsBr + DyBr_3 + HBr$ (~ 13 %) + H_2O), it has 5:3 type compound, and its phase chemical reaction is different from that of ($CsBr + LnBr_3 + HBr + H_2O$) (Ln = La, Ce, Pr, Nd, Sm) systems.

The present paper reports the solubility and phase equilibrium relations of the ($CsBr + LnBr_3 + H_2O$) (Ln = Pr, Nd, Sm) systems at T = 298.2 K and the thermodynamic and fluorescent properties of three new solid-phase compounds established in the systems.

2. Experimental

2.1. Reagents

All reagents and solvents employed were commercially available and used without further purification. Quartz double deionized water was used (resistivity = 5.7 MΩ · cm). Table 1 summarizes relevant information on sample material purity.

$PrBr_3·7H_2O$, $NdBr_3·6H_2O$ and $SmBr_3·6H_2O$ were prepared by a reaction of Pr_2O_3, Nd_2O_3 and Sm_2O_3 with hydrobromic acid, respectively. The samples were repeatedly crystallized with water and repetitively scrubbed with anhydrous ether, and were then dried in glass desiccator. The compositions were confirmed by analyzing the Br^- content by titration with a normal solution of silver nitrate, and the Pr^{3+}, Nd^{3+} and Sm^{3+} content by titration with EDTA. The molar ratio of $PrBr_3$, $NdBr_3$ and $SmBr_3$ to H_2O were 1:7.06, 1:6.13 and 1:6.13, respectively. The purity reached by this way was found to be 99.8%. The relative errors were less than ±0.22%.

2.2. Investigations on the system at 298.2 K and analysis methods

The starting materials CsBr, $LnBr_3·nH_2O$ (Ln = Pr, Nd, Sm) and H_2O were mixed in different mass ratios. Twenty five samples were prepared. Each contained solid and liquid phase that were sealed in a plastic container. Then, all the sealed samples were put in a big water tank with a thermostat fixed at T = 298.2 K and an electrical stirrer. The precision of the temperature was 0.1 K. The (solid + liquid) phase equilibrium was established for these samples after 2 to 3 days.

After that, the saturated solutions and the corresponding wet solid phases (wet residue) of the samples were removed and analyzed. The analysis methods were as follows: (1) Ln^{3+} by titration with a normal solution of EDTA, and (2) the total amount of Br^- by titration with a normal solution of silver nitrate. (3) The concentration of Cs^+ was determined by gravimetry with the precipitation of $CsB(C_6H_5)_4$. The compositions of solid phases were determined by the Schreinemakers wet residues technique [19].

2.3. Equipments and conditions

Thermogravimetric/differential thermogravimetric (TG-DTG) analysis was undertaken with a NETZSCH STA449C thermal

TABLE 2
Solubility data, in mass fraction, for the ternary system ($CsBr + PrBr_3 + H_2O$) at T = 298.2 ± 0.1 K and p = 0.1 ± 0.005 MPa.[a]

Composition of saturated solution/100·w[b]			Composition of wet residue/100·w		Solid phase[c]
No.	CsBr	$PrBr_3$	CsBr	$PrBr_3$	
1	55.51	0.00			A
2	47.46	7.34	90.54	1.51	A
3	39.84	14.46	92.03	2.06	A
4	33.84	20.73	92.36	2.59	A
5	28.64	26.74	93.59	2.66	A
6	24.75	31.97	89.70	4.78	A
7	21.22	37.22	77.13	11.03	A
8	19.48	41.50	90.80	4.97	A
9	17.91	45.08	85.69	8.16	A
10	17.07	47.39	83.39	9.74	A
11	17.32	47.37	41.76	37.13	A + B
12	13.37	51.03	38.18	40.20	B
13	11.48	52.88	37.59	40.40	B
14	8.44	56.53	35.76	41.75	B
15	7.60	57.72	33.92	43.03	B
16	7.54	57.91	34.70	42.70	B
17	5.82	60.88	30.45	48.57	B + C
18	5.99	60.84	19.04	57.33	B + C
19	6.00	60.87	12.01	63.25	B + C
20	5.88	61.04	7.38	66.43	B + C
21	3.70	62.18	1.26	70.93	C
22	0.00	64.09			C

[a] Standard uncertainties $u(w)$ for CsBr and $PrBr_3$ are 0.0041 and 0.0020, respectively (0.95 level of confidence).
[b] Double saturation point (average): E_1: CsBr, 17.32%; $PrBr_3$, 47.37%. E_2: CsBr, 5.92%; $PrBr_3$, 60.91%.
[c] Compounds: A, CsBr; B, $Cs_2PrBr_5·10H_2O$; C, $PrBr_3·7H_2O$.

TABLE 3
Solubility data, in mass fraction, for the ternary system ($CsBr + NdBr_3 + H_2O$) at T = 298.2 ± 0.1 K and p = 0.1 ± 0.005 MPa.[a]

Composition of saturated solution/100·w[b]			Composition of wet residue/100·w		Solid phase[c]
No.	CsBr	$NdBr_3$	CsBr	$NdBr_3$	
1	55.51	0.00			A
2	47.23	7.35	92.66	1.26	A
3	39.38	15.11	94.48	1.41	A
4	32.68	22.34	94.23	2.09	A
5	26.90	28.95	87.52	5.06	A
6	23.52	33.77	88.92	5.25	A
7	19.73	39.30	84.80	7.68	A
8	18.23	43.30	90.05	5.46	A
9	17.15	47.40	70.45	18.42	A + B
10	17.26	47.31	44.58	35.54	A + B
11	11.66	52.65	38.46	40.10	B
12	9.50	55.52	37.42	41.67	B
13	7.03	58.50	33.90	43.34	B
14	5.52	60.85	35.37	43.01	B
15	5.64	61.89	41.37	41.79	B + C
16	5.87	61.65	35.88	46.39	B + C
17	5.74	61.63	21.48	57.56	B + C
18	5.71	61.33	14.37	64.29	B + C
19	4.02	62.56	1.05	73.92	C
20	0.00	64.73			C

[a] Standard uncertainties $u(w)$ for CsBr and $NdBr_3$ are 0.0041 and 0.0020, respectively (0.95 level of confidence).
[b] Double saturation point (average): E_1: CsBr, 17.20%; $NdBr_3$, 47.35%. E_2: CsBr, 5.74%; $NdBr_3$, 61.62%.
[c] Compounds: A, CsBr; B, $Cs_2NdBr_5·10H_2O$; C, $NdBr_3·6H_2O$.

TABLE 1
Reagents used in this study.

Reagent	Source	State	Initial mass fraction
CsBr	Sinopharm Chemical Reagent Co., Ltd.	Solid	0.995
Pr_2O_3, Nd_2O_3, Sm_2O_3	National Engineering Research Centre of Rare Earth Metallurgy and Function Materials	Solid	0.9999
Hydrobromic acid	Sinopharm Chemical Reagent Co., Ltd.	Liquid	HBr ⩾ 0.40 (analytical reagent)