Phase Equilibrium System of $RbCl-LaCl_3-HCl$(12.60 Mass %)$-H_2O$ at 298.15 K and Standard Molar Enthalpy of Formation of $RbLaCl_4 \cdot 4H_2O$

Zhan-Ping Qiao,* Ru-Zhong Sun, Xin Chen, Shuai Zhang, and Mei-Li Wang

College of Chemistry and Pharmacy Engineering, Nanyang Normal University, Nanyang 473061, People's Republic of China

Solubilities of the quaternary system $RbCl-LaCl_3-HCl-H_2O$ were determined at 298.15 K, and the corresponding equilibrium diagram was constructed in this paper. There are three equilibrium solid phases, RbCl, $RbLaCl_4 \cdot 4H_2O$ (1:1 type), and $LaCl_3 \cdot 7H_2O$ in the quaternary system. The new compound $RbLaCl_4 \cdot 4H_2O$ was found to be congruently soluble in the system. The compound $RbLaCl_4 \cdot 4H_2O$ was characterized by the methods of X-ray diffraction, thermogravimetry, and differential thermogravimetry. The compound loses its crystal water by one step at (358 to 449) K. The standard molar enthalpy of solution of $RbLaCl_4 \cdot 4H_2O$ in deionized water was measured to be $(-19.61 \pm 0.24)\ \mathrm{kJ \cdot mol^{-1}}$ by heat conduction microcalorimetry. Its standard molar enthalpy of formation was calculated to be $(-2750.4 \pm 1.1)\ \mathrm{kJ \cdot mol^{-1}}$.

Introduction

Phase equilibria of quaternary systems of $CsCl-RECl_3-HCl$ (13 %)$-H_2O$ (RE = La, Pr, Nd, Sm, Y, Ce, Eu, Gd, Tm, Lu) at 298.15 K have been reported.[1–9] It is highly valuable and important for us to understand the phase relations and interactions of CsCl and $RECl_3$ in aqueous media. Nineteen new compounds were obtained from the systems, and they are $CsRECl_4 \cdot nH_2O$ (RE = La, Ce, Pr, Nd,), $Cs_2RECl_5 \cdot nH_2O$ (RE = Sm, Nd, Eu, Gd, Lu), $Cs_3RECl_6 \cdot nH_2O$ (RE = La, Ce, Pr), $Cs_3RE_2Cl_9 \cdot nH_2O$ (RE = Tm, Y), $Cs_4RECl_7 \cdot nH_2O$ (RE = Gd, Y, Lu), $Cs_5EuCl_8 \cdot 14H_2O$, and $Cs_9Lu_5Cl_{24} \cdot 29H_2O$. Moreover, the research results on these systems showed that the rare earth trichlorides have both comparabilities and dissimilarities, thus confirming that lanthanide rare earth elements are showing "the effect of two groups" before and after Gd in the aqueous phase equilibrium of the quaternary system.[5,6]

As a part of the systematic investigation on the quaternary systems of rare earth chlorides, phase equilibria of the $MCl-GdCl_3-HCl$(13.26 %, 21.65 %)$-H_2O$ (M = K, Rb) at 293.15 K and $RbCl-CeCl_3-HCl$(13.05 %)$-H_2O$ at 298.15 K have been reported.[10,11] Two new compounds were obtained from the systems, and they are $RbRECl_4 \cdot 4H_2O$ (RE = Ce, Gd). Comparison of the quaternary systems finds that the quaternary system $KCl-RECl_3-HCl-H_2O$ is simple. However, the quaternary system $RbCl-GdCl_3-HCl-H_2O$ is simple when the concentration of HCl is below 21.65 % and complicated when HCl is over 21.65 %. The compound $RbGdCl_4 \cdot 4H_2O$ is uncongruently soluble, and its phase region (crystallization field) is very small in the system. The quaternary system $RbCl-CeCl_3-HCl-H_2O$ is complicated when the concentration of HCl is 13.03 %. The compound $RbCeCl_4 \cdot 4H_2O$ is congruently soluble, and its phase region is big in the system. This indicates differences in behavior of Ce and Gd trichlorides in aqueous salt systems with RbCl. To further contrast the difference of the phase chemical relationship of rare alkali metal and rare-earth chloride in aqueous salt systems and find more phase equilibrium information on the $RbCl-RECl_3-HCl-H_2O$ quaternary systems, it is necessary for us to further study the phase equilibria systematically. The present paper is concerned with the solubility and phase equilibrium relation of the $RbCl-LaCl_3-HCl$(12.60 %)$-H_2O$ system at 298.15 K. In this system, a new solid-phase compound was found, and related measurement of its properties was also performed.

Experimental Section

Preparing Samples. All chemicals (RbCl) and solvents [H_2O and HCl (37 mass %)] were analytically pure and commercially available and used without further purification. $LaCl_3 \cdot 7H_2O$ was prepared by the reaction of La_2O_3 (99.99 mass %) with hydrochloric acid (37 mass % HCl). The composition of $LaCl_3 \cdot 7H_2O$ was confirmed by analyzing the Cl^- content by titration with a normal solution of silver nitrate and the La^{3+} content by titration with EDTA. The purity reached in this way was found to be 99.9 mass %.

Investigations on the System at 298.15 K and Analysis Methods. The method of the investigation of the solubility of the $RbCl-LaCl_3-HCl$(12.60 %)$-H_2O$ quaternary system has been previously reported.[9] All sealed samples were put in a big water tank with a thermostat fixed at 298.15 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 (8 to 9) days.

The methods used for analyzing the saturated solutions and the corresponding wet solid phases (wet residues) of the samples and determining the composition of the solid phase are given in the literature.[9–12]

Equipment and Conditions. Thermal characterization of the new compound was undertaken with an SDT Q600 V8.0 thermal analysis apparatus (TG-DTG) that worked with a heating rate of $10\ \mathrm{K \cdot min^{-1}}$ under an N_2 atmosphere with a flow rate of $100\ \mathrm{cm^3 \cdot min^{-1}}$. X-ray diffraction (XRD) measurement was performed by a D/Max-3C diffractometer using Cu Kα radiation, 50 kV and 80 mA, at room temperature, in air.

The enthalpies of solution were measured using an RD496-III-2000 heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China), which is a totally automatic

---

* Corresponding author. Tel.: +86-0377-63513735. Fax: +86-0377-63513540. E-mail: nyqiaozp@yahoo.com.cn.

10.1021/je700756f CCC: $40.75

Table 1. Solubility Data of the Saturated Solution of the Quaternary System RbCl−LaCl$_3$−HCl(12.60 mass %)−H$_2$O at (298.15 ± 0.1) K and Central Projection Data on the Trigonal Basal Face of RbCl−LaCl$_3$−H$_2$O

	composition of solution (% mass weight)					composition of residue (% mass weight)					
	composition in the tetrahedral			composition in the trigonal basal face[a]		composition in the tetrahedral			composition in the trigonal basal face		
no.	HCl	LaCl$_3$	RbCl	LaCl$_3$	RbCl	HCl	LaCl$_3$	RbCl	LaCl$_3$	RbCl	solid phase[b]
				w(HCl) = 12.60 %							
1	12.10	0.00	24.29	0.00	27.63	—	—	—	—	—	A
2	13.02	3.47	22.15	3.99	25.47	2.65	0.78	84.90	0.80	87.21	A
3	12.44	7.50	20.77	8.57	23.72	2.43	1.49	84.75	1.53	86.86	A
4	12.72	10.67	19.02	12.23	21.79	1.72	1.40	89.00	1.42	90.56	A
5	12.29	13.58	18.62	15.48	21.23	2.04	2.26	89.48	2.31	91.34	A
6	12.55	14.91	17.43	17.05	19.93	3.25	12.87	67.68	13.30	69.95	A + B
7	12.79	14.52	18.46	16.65	21.17	2.78	26.12	51.70	26.87	53.18	A + B
8	12.56	14.86	18.24	16.99	20.80	3.39	35.63	36.18	36.88	37.45	A + B
9	12.67	14.80	18.00	16.94	20.60	5.28	38.87	23.45	41.04	24.76	B
10	12.40	17.79	13.17	20.31	15.03	5.21	39.91	21.53	42.14	22.71	B
11	13.05	18.71	10.08	21.52	11.60	4.05	44.20	22.11	46.07	23.04	B
12	12.85	21.54	7.00	24.72	8.03	4.01	44.36	20.14	46.21	20.98	B
13	12.30	27.01	2.58	30.80	2.94	4.32	46.12	17.54	48.20	18.33	B + C
14	12.61	26.31	2.79	30.11	3.19	2.96	53.00	10.03	54.62	10.34	B + C
15	13.26	25.37	2.26	29.25	2.61	0.98	58.01	6.63	58.58	6.70	B + C
16	11.97	28.08	0.00	31.90	0.00	—	—	—	—	—	C

[a] Double saturation point (average). E$_1$: LaCl$_3$ 16.90 %, RbCl 20.63 %. E$_2$: LaCl$_3$ 30.05 %, RbCl 2.91 %. [b] Compounds: A, RbCl; B, RbLaCl$_4$·4H$_2$O; C, LaCl$_3$·7H$_2$O.

instrument utilizing computer control. The microcalorimeter is described in the literature.[9,13]

To check the performance of the RD496-III-2000 heat conduction microcalorimeter, the calorimetric constant was determined at 298.15 K by the Joule effect before the experiments. The Joule cell was supplied with 100 mW electric power for 100 s. The calorimetric constant obtained in this way was (59.31 ± 0.04) μV·mW^{-1}. The reliability of the calorimeter was verified by measuring the enthalpy of solution of KCl(s) in deionized water. The average experimental value of $\Delta_{\text{sol}}H_{\text{m}}$(KCl) was determined to be (17.31 ± 0.06) kJ·mol^{-1} ($n = 6$), which is in excellent agreement with that of 17.234 kJ·mol^{-1} reported in the literature.[14] The relative error between the literature and the measured value was 0.45 %. This shows that the device used for measuring the enthalpy of solution in this work is reliable.

Each calorimetric experiment was performed five times. The temperature of the calorimetric experiment was (298.15 ± 0.01) K. Water was put in the 15 cm^3 stainless steel sample cell and reference cell of the calorimeter. After thermal equilibration for at least 2 h, the solid sample was dissolved in deionized water. The thermal effect was then recorded automatically on a computer. The total time required for the complete dissolution was about 0.3 h.

Results and Discussion

RbCl−LaCl$_3$−HCl(12.60 mass %)−H$_2$O Quaternary System at 298.15 K. The solubility data of the RbCl−LaCl$_3$−HCl(12.60 mass %)−H$_2$O quaternary system and the central projection data on the trigonal basal face of the RbCl−LaCl$_3$−H$_2$O at 298.15 K are listed in Table 1 and plotted in Figure 1. It can be seen that the phase diagram of the RbCl−LaCl$_3$−HCl−H$_2$O quaternary system consists of three solubility curves which correspond to the equilibrium solid phases RbCl (A), RbLaCl$_4$·4H$_2$O (B) (1:1 type), and LaCl$_3$·7H$_2$O (C), respectively. The solid compound RbLaCl$_4$·4H$_2$O is congruently soluble in the medium of ~12.60 mass % HCl. The new compound RbLaCl$_4$·4H$_2$O obtained from this system was analyzed by a titration method. Its composition is 27.48 % RbCl and 56.04 % LaCl$_3$ in RbLaCl$_4$·4H$_2$O. The value is in agreement with theoretical data (27.59 % RbCl and 55.97 % LaCl$_3$). This indicates that the formation of the solid compound determined by Schreinemaker's method is reliable. It should be noted that the compound has not been reported up to now in the literature.

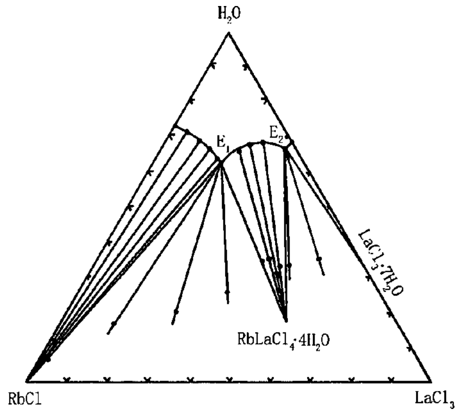

Figure 1. Solubility diagram of the quaternary system RbCl−LaCl$_3$−HCl(12.60 mass %)−H$_2$O projected on RbCl−LaCl$_3$−H$_2$O at (298.15 ± 0.1) K.

Comparing the reported quaternary systems[10,11] with the present quaternary system, for the two quaternary systems RbCl−RECl$_3$−HCl(~13 %)−H$_2$O (RE = La, Ce), their phase chemical reactions are very similar because they both have a 1:1 type compound. The new solid compounds are also congruently soluble, and the phase region is big. But the phase behavior for La and Ce chloride differs from Gd (see Table 2 and Figure 2, quotations from ref 10). This indicates differences in behavior of the light and middle rare earth element trichlorides in aqueous salt systems with RbCl.

Characterization of RbLaCl$_4$·4H$_2$O. The X-ray powder diffraction pattern of the RbLaCl$_4$·4H$_2$O compound obtained is shown in Figure 3. The important X-ray data of the compound are d (nm) = 0.5647 (99), 0.4454 (38), 0.2980 (50), and 0.2875 (21). They are obviously different from the literature XRD data of the two starting salts: RbCl, d (nm) = 0.3800 (30), 0.3291 (100), 0.2327 (65), 0.1900 (20), 0.1472 (20) and LaCl$_3$·7H$_2$O, d (nm) = 0.6600 (70), 0.2630 (100), 0.2474 (100), 0.2360 (80),

Table 2. Solubility Data of the Saturated Solution of the Quaternary System RbCl−$GdCl_3$−HCl(13.26, 21.65 mass %)−H_2O at 293.15 K and Central Projection Data on the Trigonal Basal Face RbCl−$GdCl_3$−H_2O

	composition of solution (% mass weight)					composition of residue (% mass weight)					
	composition in the tetrahedral			composition in the trigonal basal face[a]		composition in the tetrahedral			composition in the trigonal basal face		
no.	HCl	RbCl	$GdCl_3$	RbCl	$GdCl_3$	HCl	RbCl	$GdCl_3$	RbCl	$GdCl_3$	solid phase[b]
					w(HCl) = 13.26 mass %						
1	12.09	24.31	0.00	27.65	0.00	—	—	—	—	—	A
2	12.66	20.05	6.13	22.96	7.02	4.36	69.78	2.37	72.96	2.48	A
3	12.52	16.10	12.65	18.40	14.46	4.72	68.36	4.75	71.75	4.98	A
4	12.49	15.31	14.51	17.49	16.58	4.24	71.38	5.02	74.54	5.24	A
5	12.23	14.61	18.37	16.64	20.89	4.73	67.12	7.07	70.45	7.42	A
6	13.61	13.67	18.60	15.82	21.53	5.47	51.42	17.66	54.39	18.68	A + C
7	13.74	13.90	18.41	16.11	21.34	5.08	18.84	41.36	19.85	43.57	A + C
8	14.30	10.50	19.24	12.25	22.45	4.76	3.19	53.34	3.35	56.00	C
9	14.40	4.22	21.09	4.93	24.64	5.36	1.19	51.93	1.26	54.87	C
10	14.58	0.00	22.44	0.00	26.27	—	—	—	—	—	C
					w(HCl) = 21.65 mass %						
1	19.32	15.47	0.00	19.17	0.00	—	—	—	—	—	A
2	21.54	13.36	3.82	17.03	4.87	8.63	64.71	1.67	70.82	1.83	A
3	21.05	13.01	6.43	16.48	8.14	6.89	70.61	2.29	75.83	2.46	A
4	21.24	13.32	7.51	16.91	9.53	9.09	43.57	16.88	47.93	18.57	A + B
5	21.61	13.23	7.38	16.88	9.41	7.97	24.61	33.10	26.74	35.97	A + B
6	21.53	13.18	7.33	16.80	9.34	9.54	19.98	31.71	22.09	35.05	B
7	21.86	13.02	7.14	16.66	9.14	15.36	16.37	20.67	19.34	24.42	B
8	21.34	12.99	7.62	16.51	9.69	8.09	12.14	42.25	13.21	45.97	B + C
9	21.76	12.86	7.08	16.44	9.05	8.41	9.65	42.77	10.54	46.71	B + C
10	22.19	12.39	7.08	15.92	9.10	7.50	4.86	48.36	5.25	52.28	C
11	22.92	8.32	6.97	10.79	8.96	5.52	1.81	55.42	1.91	58.66	C
12	22.63	4.65	7.81	6.01	10.09	8.07	1.53	49.00	1.66	53.30	C
13	22.50	0.00	10.40	0.00	13.42	—	—	—	—	—	C

[a] Double saturation point (average): HCl = 13.26 mass %. E: RbCl 15.96 %, $GdCl_3$ 21.43 %. HCl = 21.65 mass %. E_1: RbCl 16.89 %, $GdCl_3$ 9.47 %. E_2: RbCl 16.47 %, $GdCl_3$ 9.37 %. [b] Compounds: A, RbCl; B, $RbGdCl_4 \cdot 4H_2O$; C, $GdCl_3 \cdot 6H_2O$.

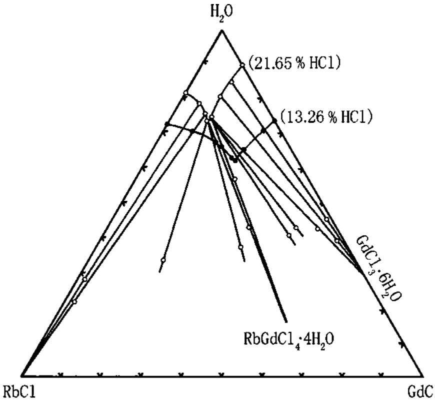

Figure 2. Solubility diagram of the quaternary system RbCl−$GdCl_3$−HCl(13.26, 21.65 mass %)−H_2O projected on RbCl−$GdCl_3$−H_2O at 293.15 K.

0.2210 (100) (d is crystal plane distance, and numbers in parentheses are relative intensities of the diffraction peak). This demonstrates that the compound is new.

TG-DTG data for the compound are presented in Figure 4. The curve for the compound $RbLaCl_4 \cdot 4H_2O$ shows that there is one obvious mass-loss step in the temperature range (358 to 449) K (395.8 K denotes temperature at which weight loss is most), and the mass-loss value (16.33 mass %) is in agreement with theoretical dehydration data (16.44 mass %). This indicates that the compound loses its crystal water by one step at (358 to 449) K. It should be noted that the total mass-loss value is in accordance with data of water determined by Schreinemakers method and analyzed by a titration method.

Enthalpies of Solution. The molar enthalpy of solution of $RbLaCl_4 \cdot 4H_2O$ in water is (-19.61 ± 0.24) kJ·mol^{-1} at 298.15 K. The values are listed in Table 3, in which m is the mass of the sample and $\Delta_{sol}H_m$ is the molar enthalpy of solution of the sample. The uncertainty is estimated as twice the standard deviation of the mean,[15] namely

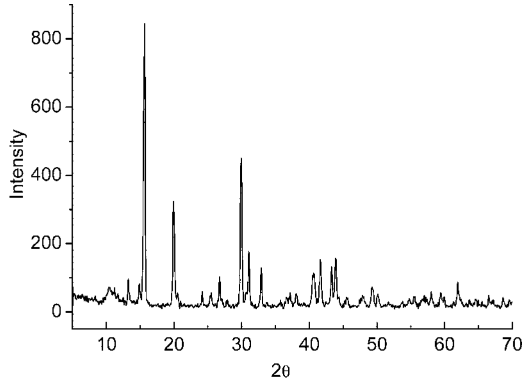

Figure 3. X-ray powder diffraction spectrum of $RbLaCl_4 \cdot 4H_2O$.

$$\delta = 2\sqrt{\sum (x_i - \bar{x})^2 / n(n-1)}$$

in which n is the number of experimental measurements (n = 5); x_i is the experimental value of each repeated measurement; and $\bar{x}$ is the mean value.

Standard Molar Enthalpy of Formation. The molar enthalpy of formation of $RbLaCl_4 \cdot 4H_2O$ can be calculated as shown in the following equation

$$\Delta_f H_m^{\ominus}(s) = \Delta_f H_m^{\ominus}(Rb^+)(aq) + \Delta_f H_m^{\ominus}(La^{3+})(aq) + 4\Delta_f H_m^{\ominus}(Cl^-)(aq) + 4\Delta_f H_m^{\ominus}(H_2O)(l) - \Delta_{sol} H_m^{\ominus}(RbLaCl_4 \cdot 4H_2O)(s) \quad (1)$$

The standard molar enthalpies of formation of Rb^+, La^{3+}, Cl^-, and H_2O were taken from the NBS table,[16] namely, (−251.17

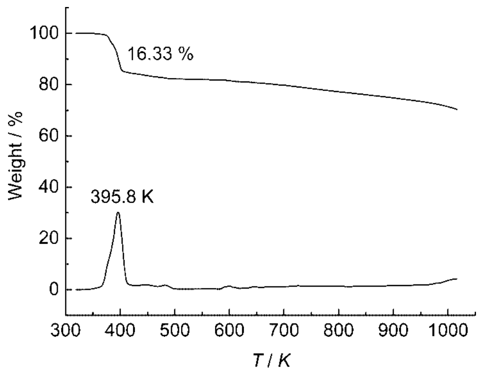

Figure 4. Thermogravimetric curve of $RbLaCl_4 \cdot 4H_2O$.

Table 3. Molar Enthalpies of Solution of $RbLaCl_4 \cdot 4H_2O$ in Deionized Water at 298.15 K[a]

	m	Q_s	$\Delta_{sol}H^{\ominus}_m$
no.	g	mJ	$kJ \cdot mol^{-1}$
1	0.04852	−2196.6	−19.840
2	0.04919	−2214.5	−19.729
3	0.04912	−2198.0	−19.611
4	0.04919	−2213.8	−19.723
5	0.04854	−2119.9	−19.139
mean[b]	$\Delta_{sol}H^{\ominus}_m$= (−19.61 ± 0.24) $kJ \cdot mol^{-1}$		

[a] In each experiment, 8.0 cm^3 water was used. [b] Uncertainty is twice the standard deviation of the mean.

± 0.56) $kJ \cdot mol^{-1}$, (−707.1 ± 0.80) $kJ \cdot mol^{-1}$, (−167.159 ± 0.1) $kJ \cdot mol^{-1}$, and (−285.83 ± 0.042) $kJ \cdot mol^{-1}$ for Rb^+, La^{3+}, Cl^-, and H_2O, respectively. Using these schemes and data, the standard molar enthalpy of formation of $RbLaCl_4 \cdot 4H_2O$ was calculated to be (−2750.4 ± 1.1) $kJ \cdot mol^{-1}$.

Conclusion

The solubilities of the quaternary system $RbCl-LaCl_3-HCl(12.60\ \%)-H_2O$ at 298.15 K were measured, and the corresponding phase diagram was prepared to search for new compounds and obtain the equilibrium data for rubidium chloride/lanthanum chloride in aqueous solution. The composition of a new solid phase was determined by Schrienemaker's method and confirmed by chemical analysis. The compound $RbLaCl_4 \cdot 4H_2O$ is congruently soluble in the quaternary system. Through measuring the standard molar enthalpy of solution, the standard molar enthalpy of formation of the new compound was calculated.

Comparing the reported quaternary systems $RbCl-RECl_3-HCl(\sim 13\ \%)-H_2O$ (RE = Ce, Gd) with the present quaternary system, the phase behavior for La chloride differs from Gd chloride, but the phase behaviors for La and Ce are similar.

Literature Cited

(1) Li, Y. H.; Ran, X. Q.; Chen, P. H. Studies on Solvent System of Cesium Chloride and Lanthanum Chloride and Synthesization of Four Types of New Compounds. *J. Rare Earths* **1997**, *15* (2), 113–116.
(2) Li, Y. H.; Ran, X. Q.; Chen, P. H. Studies on Quaternary Systems $CsCl-PrCl_3-13\%\ HCl-H_2O$ (298 K) and $CsCl-PrCl_3-42\%\ HAc-H_2O$ (303 K). *Chem. J. Chin. U.* **1997**, *18* (3), 353–356.
(3) Jiao, H.; Wang, H.; Ran, X. Q.; Chen, P. H. Study on the Quaternary System of $CsCl-NdCl_3-13\%HCl-$ (42%HOAc) $-H_2O$. *Acta Chim. Sin.* **1998**, *56*, 854–858.
(4) Li, Y. H.; Ran, X. Q.; Chen, P. H. Phase Behavior of Hydrochloric Aqueous Solution Containing Cesium and Samarium Chloride and Two Sub-Group Effect of The Light Rare Earth Element. *Zh. Neorg. Khim.* **1999**, *44* (7), 1207–1209.
(5) Wang, H.; Duan, J. X.; Ran, X. Q.; Gao, S. Y. Study on the Phase Diagram of $CsCl-CeCl_3-HCl(11\%)\ -H_2O$ System at 298.15 K. and the Fluorescence Properties of its Compounds. *Chin. J. Chem.* **2002**, *20* (9), 904–908.
(6) Wang, H.; Duan, J. X.; Ran, X. Q.; Gao, S. Y. Study on the Phase Diagram of $CsCl-EuCl_3-0.11HCl-H_2O$ Quaternary System at T = 298.15 K and the Fluorescence Spectra of Its Compounds. *J. Chem. Thermodyn.* **2002**, *34* (9), 1495–1506.
(7) Wang, H.; Duan, J. X.; Ran, X. Q.; Gao, S. Y. Phase Equilibrium System of $CsCl-YCl_3-(9.5\%)HCl-H_2O$ at T = 298.15 K and Its Compounds. *Chin. J. Chem.* **2004**, *22* (10), 1129–1132.
(8) Qiao, Z. P.; Zhuo, L. H.; Zhang, S. S.; Wang, H. $CsCl-TmCl_3-HCl-H_2O$ at 298 K: Phase Equilibrium and New Solid Phase Compound. *Chin. Inorg. Chem* **2006**, *22* (8), 1545–1549.
(9) Qiao, Z.-P.; Xie, H.-Q.; Zhuo, L.-H.; Chen, X. Study on Phase Equilibrium in the Quaternary System $CsCl-LuCl_3-HCl(10.06\ \%)-H_2O$ at 298.15 ± 0.1 K and New Solid-Phase Compounds. *J. Chem. Eng. Data* **2007**, *52* (5), 1681–1685.
(10) Wang, H.; Ran, X. Q.; Chen, P. H. A Study on Quaternary Systems $MCl-GdCl_3-HCl-H_2O$ (M = K, Rb, Cs; 293 K). *Acta Chim. Sin.* **1994**, *52*, 789–796.
(11) Qiao, Z. P.; Zhuo, L. H.; Guo, Y. C.; Wang, H. Phase Equilibrium of the $RbCl-CeCl_3-HCl-H_2O$ System at 298 K and New Solid Phase Compound. *J. Chin. Rare Earth* **2007**, *25* (6), 651–655.
(12) Chen, Y. S. *Analysis of Physical Chemistry*; Higher Education Press: Beijing, 1988; pp 505−506.
(13) Ji, M.; Liu, M. Y.; Gao, S. L. A New Microcalorimeter for Measuring Thermal Effects. *J. Instrum. Sci. Technol.* **2001**, *29*, 53–57.
(14) Weast, R. C. *CRC Handbook of Chemistry and Physics*, 70th ed.; CRC Press: Boca Raton, FL, 1989.
(15) Liu, Z. H.; Li, P.; Zhang, C. F. Standard Molar Enthalpies of Formation for the Two Hydrated Calcium Borates $xCaO \cdot 5B_2O_3 \cdot yH_2O$ (x = 2 and 4, y = 5 and 7). *J. Chem. Eng. Data* **2006**, *51*, 272–275.
(16) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow,I.; Bailey, S. M.; Chumey, K. L.; Nuttal, R. L. The NBS Tables of Chemical Thermodynamic Properties. *J. Phys. Chem. Data* **1982**, *11* (suppl. 2).

Received for review December 22, 2007. Accepted February 23, 2008. Acknowledgement is expressed for the financial support from the STP Foundation of Nanyang Normal University.

JE700756F