Phase Equilibrium System of $HoCl_3-CdCl_2-HCl(7.52\ \%)-H_2O$ at 298.15 K and Standard Molar Enthalpy of Formation of $Cd_4HoCl_{11}\cdot 14H_2O$

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The equilibrium solubility of the quaternary system $HoCl_3-CdCl_2-HCl-H_2O$ was determined at 298.15 K, and the corresponding equilibrium diagram was constructed. The quaternary system is complicated with three equilibrium solid phases, $CdCl_2\cdot H_2O$, $Cd_4HoCl_{11}\cdot 14H_2O$ (4:1 type), and $HoCl_3\cdot 6H_2O$, of which the new compound $Cd_4HoCl_{11}\cdot 14H_2O$ was found to be congruently soluble in the system. The new compound obtained was identified and characterized by the methods of X-ray diffraction, thermogravimetry, and differential thermogravimetry. The standard molar enthalpy of solution of $Cd_4HoCl_{11}\cdot 14H_2O$ in deionized water was measured to be $(15.74 \pm 0.18)\ kJ\cdot mol^{-1}$ by heat conduction microcalorimetry. Its standard molar enthalpy of formation was calculated to be $(-6864.7 \pm 1.3)\ kJ\cdot mol^{-1}$. The standard molar enthalpy of formation, the solubility data, and the phase diagram of the quaternary system could provide the fundamental basis and serve as a guide for the preparation of $Cd_4HoCl_{11}\cdot 14H_2O$.

Introduction

Phase equilibria of quaternary systems of $RECl_3-CdCl_2-HCl(\sim 8\ \%)-H_2O$ (RE = La, Ce, Pr, Nd, Eu, Tb, Dy, Y, Er, Lu) at 298.15 K have been previously reported.[1−10] It is highly valuable and important for us to understand the phase relations and interactions of $RECl_3$ and $CdCl_2$ in aqueous media. Li et al. and Wang et al.[1,3] reported the presence of four equilibrium solid−phase regions ($CdCl_2\cdot H_2O$, $Cd_8RECl_{19}\cdot nH_2O$, $Cd_4RECl_{11}\cdot 12H_2O$, and $RECl_3\cdot 7H_2O$) (RE = La, Pr, n = 16, 20) in the $LaCl_3-CdCl_2-HCl-H_2O$ and $CdCl_2-PrCl_3-HCl-H_2O$ quaternary systems. For the $CeCl_3-CdCl_2-HCl-H_2O$ system,[2] five equilibrium solid phases ($CdCl_2\cdot H_2O$, $Cd_9CeCl_{21}\cdot 19H_2O$, $Cd_6CeCl_{15}\cdot 14H_2O$, $Cd_4CeCl_{11}\cdot 12H_2O$, and $CeCl_3\cdot 7H_2O$) were observed. We carried out the $NdCl_3-CdCl_2-HCl\text{-}H_2O$,[4] $EuCl_3-CdCl_2-HCl-H_2O$,[5] $TbCl_3-CdCl_2-HCl-H_2O$,[6] and $DyCl_3-CdCl_2-HCl-H_2O$[7] systems and confirmed the presence of four equilibrium solid phases ($CdCl_2\cdot H_2O$, $Cd_9NdCl_{21}\cdot 20H_2O$, $Cd_5NdCl_{13}\cdot 13H_2O$, and $NdCl_3\cdot 6H_2O$) in the $NdCl_3-CdCl_2-HCl-H_2O$ quaternary system and four equilibrium solid phases ($CdCl_2\cdot H_2O$, $Cd_9EuCl_{21}\cdot 22H_2O$, $Cd_4EuCl_{11}\cdot 14H_2O$, and $EuCl_3\cdot 6H_2O$) in the $EuCl_3-CdCl_2-HCl-H_2O$ quaternary system. But for the quaternary systems $TbCl_3-CdCl_2-HCl-H_2O$ and $DyCl_3-CdCl_2-HCl-H_2O$, there are only three equilibrium solid phases ($CdCl_2\cdot H_2O$, $Cd_4TbCl_{11}\cdot 14H_2O$, and $TbCl_3\cdot 6H_2O$) and ($CdCl_2\cdot H_2O$, $Cd_9Dy_2Cl_{24}\cdot 29H_2O$, and $DyCl_3\cdot 6H_2O$). We reexamined the $YCl_3-CdCl_2-HCl-H_2O$,[8] $ErCl_3-CdCl_2-HCl-H_2O$,[9] and $LuCl_3-CdCl_2-HCl-H_2O$[10] systems and confirmed that the $YCl_3-CdCl_2-HCl-H_2O$ system is composed of four equilibrium solid phases: $CdCl_2\cdot H_2O$, $Cd_4YCl_{11}\cdot 13H_2O$, $Cd_5Y_2Cl_{16}\cdot 26H_2O$, and $YCl_3\cdot 6H_2O$, respectively. For the $ErCl_3-CdCl_2-HCl-H_2O$ system, four equilibrium solid phases ($CdCl_2\cdot H_2O$, $Cd_9Er_2Cl_{24}\cdot 29H_2O$, $CdEr_7Cl_{23}\cdot 42H_2O$, and $ErCl_3\cdot 6H_2O$) were observed. At the same time, four equilibrium solid phases ($CdCl_2\cdot H_2O$, $Cd_3LuCl_9\cdot 14H_2O$, $CdLuCl_5\cdot 9H_2O$, and $LuCl_3\cdot 6H_2O$) were observed in the $LuCl_3-CdCl_2-HCl-H_2O$ system.

As was stated above, in addition to the initial components $CdCl_2\cdot H_2O$ and $RECl_3\cdot nH_2O$ (n = 6, 7), 19 new compounds were obtained from those systems, and they are $Cd_9RECl_{21}\cdot nH_2O$ (RE = Ce, Nd, Eu), $Cd_9RE_2Cl_{24}\cdot nH_2O$ (RE = Dy, Er), $Cd_8RECl_{19}\cdot nH_2O$ (RE = La, Pr), $Cd_6CeCl_{15}\cdot 14H_2O$, $Cd_5NdCl_{13}\cdot 14H_2O$, $Cd_5Y_2Cl_{16}\cdot 26H_2O$, $Cd_4RECl_{11}\cdot nH_2O$ (RE =La, Ce, Pr, Eu, Tb, Y), $Cd_3LuCl_9\cdot 14H_2O$, $CdLuCl_5\cdot 9H_2O$, and $CdEr_7Cl_{23}\cdot 42H_2O$. Comparison of phase chemical behavior of the quaternary systems finds that phase chemical reactions of the two quaternary systems $RECl_3-CdCl_2-HCl-H_2O$ (RE = La, Pr) are very similar because they all have the 8:1 type and 4:1 type compounds, while for the three quaternary systems $RECl_3-CdCl_2-HCl-H_2O$ (RE = Ce, Eu, Nd), their phase chemical reactions have both similarities (all having a 9:1 type compound) and dissimilarities (all having various types of compounds). The quaternary system $YCl_3-CdCl_2-HCl-H_2O$ and the five quaternary systems $RECl_3-CdCl_2-HCl-H_2O$ (RE = La, Ce, Pr, Eu, Tb) were compared further, where it was found that their phase chemical reactions also have both similarities (all having a 4:1 type compound) and dissimilarities. Similarly, the quaternary systems $RECl_3-CdCl_2-HCl-H_2O$ (Dy, Er) have both similarities and dissimilarities. But the quaternary system $LuCl_3-CdCl_2-HCl-H_2O$ is different from the others, as it has 3:1 and 1:1 type compounds.

As a part of the systematic investigation on the rare-earth and cadmium chloride in an aqueous salt system, the present paper is concerned with the solubility and phase equilibrium relation of the $HoCl_3-CdCl_2-HCl(7.52\ \%)-H_2O$ system at 298.15 K. It is very useful for us to contrast the difference of the phase chemical relationship in the $HoCl_3-CdCl_2-HCl-H_2O$ with the $RECl_3-CdCl_2-HCl-H_2O$ (RE = La, Ce, Pr, Nd, Eu, Dy, Tb,Y, Er, Lu) systems and to find more phase equilibrium information on the $RECl_3-CdCl_2-HCl-H_2O$ quaternary systems.

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Table 1. Solubility Data of the Saturated Solution of the Quaternary System $HoCl_3-CdCl_2-HCl(7.52$ mass %$)-H_2O$ at (298 ± 0.1) K and Central Projection Data on the Trigonal Basal Face $HoCl_3-CdCl_2-H_2O$

	composition of solution/(% mass fraction)					composition of residue/(% mass fraction)					
	composition in the tetrahedral			composition in the trigonal basal face[a]		composition in the tetrahedral			composition in the trigonal basal face		
no.	HCl	$CdCl_2$	$HoCl_3$	$CdCl_2$	$HoCl_3$	HCl	$CdCl_2$	$HoCl_3$	$CdCl_2$	$HoCl_3$	solid phase[b]
						$W(HCl) = 7.52$ %					
1	8.71	47.62	0.00	52.16	0.00	---	---	---	---	---	A
2	8.28	48.71	2.32	53.11	2.53	4.64	65.74	1.22	68.94	1.28	A
3	7.78	16.57	4.81	50.50	5.22	4.55	64.84	2.82	67.93	2.95	A
4	7.22	46.55	7.17	50.17	7.73	3.74	67.91	3.69	70.55	3.83	A
5	6.96	47.32	7.61	50.86	8.18	3.83	65.61	4.41	68.22	5.59	A+B
6	7.52	45.97	8.20	49.71	8.87	3.45	52.21	15.36	54.08	15.91	B
7	7.02	43.48	10.48	46.76	11.27	4.39	49.90	14.88	52.19	15.56	B
8	6.80	37.23	12.39	44.43	13.29	4.61	47.73	15.56	50.04	16.31	B
9	7.81	38.31	13.92	41.56	15.10	5.42	46.50	16.91	49.17	17.88	B
10	8.04	37.23	14.70	40.48	15.98	5.73	45.52	17.26	48.29	18.31	B
11	7.99	36.83	15.26	40.03	16.58	5.23	46.67	17.50	49.24	18.46	B
12	7.77	36.64	16.00	39.73	17.35	5.22	44.25	18.12	46.69	19.12	B
13	7.24	34.38	18.99	37.06	20.47	4.18	45.15	20.38	47.12	21.27	B
14	6.64	33.79	20.73	36.19	22.20	4.11	43.60	21.42	45.47	22.34	B
15	7.33	31.24	23.06	33.71	24.88	1.61	44.62	27.21	45.35	27.66	B+C
16	7.28	31.30	23.43	33.76	25.27	2.56	21.33	46.05	21.89	47.26	B+C
17	7.48	27.76	24.44	30.00	26.42	1.45	5.46	61.88	5.54	62.79	C
18	7.65	24.14	25.76	26.14	27.89	1.11	3.29	64.68	3.33	65.41	C
19	7.38	19.27	28.40	20.81	30.66	1.22	3.27	64.42	3.31	65.22	C
20	7.53	12.75	31.00	13.79	33.52	1.26	2.41	64.46	2.44	65.28	C
21	7.69	6.63	33.53	7.18	36.32	1.26	0.85	65.54	0.86	66.38	C
22	7.30	0.00	37.04	0.00	39.96	---	---	---	---	---	C

[a] Double saturation point (average). E_1: $CdCl_2$ 50.86 %, $HoCl_3$ 8.18 %. E_2: $CdCl_2$ 33.74 %, $HoCl_3$ 25.08 %. [b] Compounds: A, $CdCl_2 \cdot H_2O$; B, $Cd_4HoCl_{11} \cdot 14H_2O$; C, $HoCl_3 \cdot 6H_2O$.

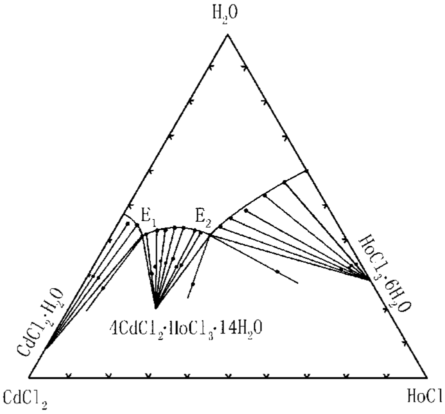

Figure 1. Solubility diagram of the quaternary system $HoCl_3-CdCl_2-HCl$ (7.52 mass %)$-H_2O$ on the $HoCl_3-CdCl_2-H_2O$ trigonal basal face at 298.15 K.

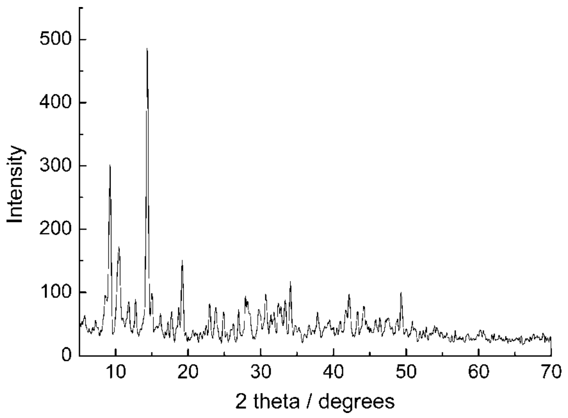

Figure 2. X-ray powder diffraction spectrum of $Cd_4HoCl_{11} \cdot 14H_2O$.

Experimental Section

Preparing Samples. All chemicals ($CdCl_2$) and solvents [H_2O and HCl (37 mass %)] were analytically pure and purchased from the market. $HoCl_3 \cdot 6H_2O$ was prepared by the reaction of Ho_2O_3 (99.99 mass %) with hydrochloric acid (37 mass % HCl). For detailed information on the preparation of $HoCl_3 \cdot 6H_2O$, see ref 11. The composition of $HoCl_3 \cdot 6H_2O$ was confirmed by analyzing the Cl^- content by titration with a normal solution of silver nitrate and the Ho^{3+} content by titration with EDTA. The purity reached in this way was found to be 99.9 mass %. The analysis errors for those ions were relative and found to be better than ± 0.21 %.

Investigations on the System at 298.15 K and Analysis Methods. The method of the investigation of the solubility of the $HoCl_3-CdCl_2-HCl(7.52$ %$)-H_2O$ quaternary system has been previously reported.[12] 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 (13 to 15) days.

The saturated solutions and the corresponding wet solid phases (wet residues) of the samples were separated, taken out, and analyzed. The analysis methods were as follows: (1) the concentration of protons was analyzed by titration with a solution of sodium hydroxide; (2) the total amount of Ho^{3+} and Cd^{2+} by titration with a normal solution of EDTA; (3) the individual concentrations of Ho^{3+} and Cd^{2+} were determined by titration with a normal solution of EDTA after Cd^{2+} was blanketed with a screening agent of 1,10-phenanthroline; and (4) the concentration of Cl^- by titration with a normal solution of silver nitrate. The compositions of the saturated solution and the corresponding wet solid-phase points were determined by calculating the individual contents of HCl, $HoCl_3$, and $CdCl_2$ according to the analysis results of the H^+, Ho^{3+}, and Cd^{2+} ions. The solid-phase compositions in the system were determined graphically by the well-known wet residue method of Schreinemakers[13] and checked by chemical analysis. The new solid-phase compound was further demonstrated by XRD, and its amount of crystal water was further determined by thermogravimetry.

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 K$\cdot$min^{-1} under an N_2 atmosphere with a flow rate of 100 cm$^3\cdot$min^{-1}. X-ray diffraction (XRD) measurements were performed by a D/Max-3C diffractometer using Cu Kα radiation, 50 kV and 80 mA, at room temperature, in air.

All 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 instrument utilizing computer control. The microcalorimeter is described in the literature.[12,14,15]

To check the performance of the RD496-3-2000 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$\cdot$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$\cdot$mol^{-1} ($n = 6$), which is in excellent agreement with that of 17.234 kJ$\cdot$mol^{-1} reported in the literature.[16] 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 0.4 h. There were no solid residues observed after the dissolution in each calorimetric experiment.

Results and Discussion

$HoCl_3-CdCl_2-HCl$(7.52 %)$-H_2O$ Quaternary System at 298.15 K. The solubility data of the $HoCl_3-CdCl_2-HCl$(7.52 %)$-H_2O$ quaternary system and the central projection data on the trigonal basal face of the $HoCl_3-CdCl_2-H_2O$ at 298.15 K are listed in Table 1 and plotted in Figure 1. It can be seen that the phase diagram of the $HoCl_3-CdCl_2-HCl-H_2O$ quaternary system consists of three solubility curves which correspond to the equilibrium solid phases $CdCl_2\cdot H_2O$ (A), $Cd_4HoCl_{11}\cdot 14H_2O$ (B), and $HoCl_3\cdot 6H_2O$ (C), respectively. The solid compound $Cd_4HoCl_{11}\cdot 14H_2O$ (4:1 type) is congruently soluble in the medium of ~7.52 mass % HCl. The new compound $Cd_4HoCl_{11}\cdot 14H_2O$ obtained from this system was analyzed by a titration method. Its compositions are Cd 35.61 %, Ho 13.11 %, and Cl 31.10 % in $Cd_4HoCl_{11}\cdot 14H_2O$. The value is in agreement with theoretical data (35.77 % Cd, 13.12 % Ho, and 31.03 % Cl). It should be noted that the compound has not been reported up to now in the present system.

Comparing the reported quaternary systems 1 to 10 with the present quaternary system, for the two quaternary systems $RECl_3-CdCl_2-HCl$(~8 %)$-H_2O$ (RE = Tb, Ho), their phase chemical reactions are very similar because they both only have a 4:1 type compound and the new solid compounds are also congruently soluble.

Characterization of $Cd_4HoCl_{11}\cdot 14H_2O$. The X-ray powder diffraction pattern of the $Cd_4HoCl_{11}\cdot 14H_2O$ compound obtained is shown in Figure 2. The important X-ray data of the compound are d (nm) = 0.9502(62), 0.8434(35), 0.6146(99), and 0.4614(30). They are obviously different from the XRD data of the two starting salts: $CdCl_2$, d (nm) = 0.5850(100), 0.3270(70), 0.2648(90), 0.2412(30), 0.1826(55), and 0.1922(30) and $HoCl_3\cdot 6H_2O$, d (nm) = 0.4787(100), 0.3081(26), and 0.2400(30), and these diffraction peaks are also not the simple overlapping peaks assigned to the two starting salts. All these demonstrate that the compound is a new one.

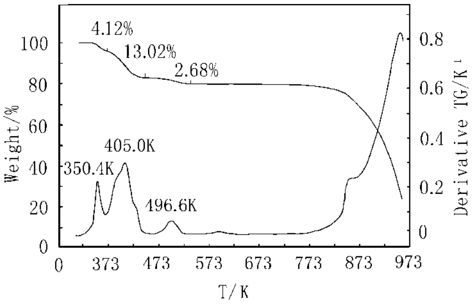

Figure 3. Thermogravimetric curves of $Cd_4HoCl_{11}\cdot 14H_2O$.

Table 2. Molar Enthalpies of Solution of $Cd_4HoCl_{11}\cdot 14H_2O$ in Deionized Water at 298.15 K[a]

no.	m/g	Q_s/mJ	$\Delta_{\text{sol}}H^{\ominus}_{\text{m}}$ (kJ$\cdot$mol^{-1})
1	0.04177	528.1	15.889
2	0.04098	515.1	15.796
3	0.04127	507.1	15.441
4	0.04104	511.2	15.654
5	0.04187	530.9	15.935
mean[b]	$\Delta_{\text{sol}}H^{\ominus}_{\text{m}}$ = (15.74 ± 0.18) kJ$\cdot$mol^{-1}		

[a] In each experiment, 4.0 cm^3 water was used. [b] Uncertainty is twice the standard deviation of the mean

TG-DTG data for the compound are presented in Figure 3. The curve for the compound $Cd_4HoCl_{11}\cdot 14H_2O$ shows that there are three obvious mass-loss steps in the temperature range (340 to 528) K. They arise from the loss of crystal water from the hydrated compound. The total mass-loss value (19.82 mass %) is in agreement with theoretical dehydration data (20.06 mass %). 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. On the basis of these results, we suggest that the dehydration equation for the compound is as follows

$$Cd_4HoCl_{11}\cdot 14H_2O \xrightarrow[-3H_2O]{340\sim 367\text{ K}} Cd_4HoCl_{11}\cdot 11H_2O \xrightarrow[-9H_2O]{367\sim 442\text{ K}}$$

$$Cd_4HoCl_{11}\cdot 2H_2O \xrightarrow[-2H_2O]{473\sim 528\text{ K}} Cd_4HoCl_{11}$$

Enthalpy of Solution. The molar enthalpy of solution of $Cd_4HoCl_{11}\cdot 14H_2O$ in water is (15.74 ± 0.18) kJ$\cdot$mol^{-1} at 298.15 K. The values are listed in Table 2, in which m is the mass of sample and $\Delta_{\text{sol}}H_{\text{m}}$ is the molar enthalpy of solution of the sample. The uncertainty is estimated as twice the standard deviation of the mean,[14] namely

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

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 $Cd_4HoCl_{11}\cdot 14H_2O$ can be calculated as shown in following equation

$$\Delta_f H_m^{\ominus} = 4\Delta_f H_m^{\ominus}(\mathrm{Cd}^{2+})(\mathrm{aq}) + \Delta_f H_m^{\ominus}(\mathrm{Ho}^{3+})(\mathrm{aq}) + 11\Delta_f H_m^{\ominus}(\mathrm{Cl}^-)(\mathrm{aq}) + 14\Delta_f H_m^{\ominus}(\mathrm{H_2O})(\mathrm{l}) - \Delta_{sol} H_m^{\ominus}$$

The standard molar enthalpies of formation of Cd^{2+}, Cl^-, and H_2O were taken from the CODATA Key Values,[17] namely, (−75.90 ± 0.10) kJ·mol^{-1}, (−167.159 ± 0.10) kJ·mol^{-1}, and (−285.830 ± 0.042) kJ·mol^{-1} for Cd^{2+}, Cl^-, and H_2O, respectively. Ho^{3+} was taken from the NBS table,[18] (−705.0 ± 0.20) kJ·mol^{-1}. Using these schemes and data, the standard molar enthalpy of formation of $Cd_4HoCl_{11}\cdot 14H_2O$ was calculated to be (−6864.7 ± 1.3) kJ·mol^{-1}.

Conclusion

The solubilities of the quaternary system $HoCl_3-CdCl_2-HCl$(7.52 mass %)$-H_2O$ at 298.15 K were measured, and the corresponding phase diagram was prepared to search for new compounds and obtain the equilibrium data for cadmium chloride/rare earth metal chloride in aqueous solution. The compositions of the solid phases were determined by Schrienemakers method and confirmed by chemical analysis. The compound $Cd_4HoCl_{11}\cdot 14H_2O$ (1:1 type) 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. The standard molar enthalpy of formation, the solubility data, and the phase diagram of the quaternary system could provide the fundamental basis and serve as a guide for the preparation of $Cd_4HoCl_{11}\cdot 14H_2O$.

Literature Cited

(1) LI, L.; Wang, H.; Xia, S. P.; Hu, M. C.; Gao, S. Y. A Study on the phase diagram of the $LaCl_3$-$CdCl_2$-(9.7%)HCl-H_2O system at 298 K and its compounds characterized. *Chin. Inorg. Chem.* **2003**, *19* (2), 201–205, in Chinese.

(2) Zhuo, L. H.; Qiao, Z. P.; Guo, Y. C.; Wang, H. Phase equilibrium of the $CeCl_3$-$CdCl_2$-H_2O and $CeCl_3$-$CdCl_2$-HCl-H_2O. *Acta Chim. Sinica* **2005**, *21* (2), 128–133, in Chinese.

(3) Wang, H.; LI, L.; Ran, X. Q.; Wang, X. F.; Gao, S. Y. Study on the phase equilibrium $CdCl_2$-$PrCl_3$-HCl(8.3%)-H_2O and $CdCl_2$-$PrCl_3$-H_2O at 298 ± 1 K. *J. Chem. Eng. Data* **2006**, *51*, 1541–1545.

(4) Qiao, Z. P.; Zhuo, L. H.; Guo, Y. C.; Wang, H. Phase equilibrium of the $NdCl_3$-$CdCl_2$-HCl-H_2O system at 298.15 K and characterization of new compounds. *Acta Chim. Sinica* **2005**, *21* (11), 1249–1253, in Chinese.

(5) Qiao, Z. P.; Zhuo, L. H.; Chen, X.; Wang, H. Phase equilibrium of the system $EuCl_3$-$CdCl_2$-HCl-H_2O at 298 K and characterization of new compounds. *Chin. Inorg. Chem.* **2006**, *22* (5), 854–860, in Chinese.

(6) Qiao, Z. P.; Zhuo, L. H.; Chen, X.; Wang, H. Phase equilibrium of the system $TbCl_3$-$CdCl_2$-HCl(7.92 wt %)−H_2O at 298.15 ± 0.1 K. *Russ. Inorg. Chem.* **2008**, *53* (3), 446–449.

(7) Qiao, Z. P.; Zhuo, L. H.; Guo, Y. C.; Wang, H. Phase equilibrium of the $DyCl_3$-$CdCl_2$-H_2O and $DyCl_3$-$CdCl_2$-HCl(8%)-H_2O at 298 K and characterization of new compound. *Chin. Inorg. Chem.* **2005**, *21* (11), 1667–1671, in Chinese.

(8) Qiao, Z. P.; Zhuo, L. H.; Wang, H. A study on the phase diagram of YCl_3-$CdCl_2$-H_2O and YCl_3-$CdCl_2$-HCl(8.8%)-H_2O at 298 K and their compounds characterization. *Chin. Inorg. Chem.* **2004**, *20* (8), 929–934, in Chinese.

(9) Zhuo, L. H.; Qiao, Z. P.; Guo, Y. C.; Wang, H. Phase equilibrium of the $ErCl_3$-$CdCl_2$-HCl-H_2O at 298 K and characterization of the new compounds. *Acta Chim. Sinica* **2006**, *22* (5), 616–621.

(10) Qiao, Z. P.; Zhuo, L. H.; Guo, Y. C.; Zhang, S. S. Phase equilibrium system of $LuCl_3$-$CdCl_2$-HCl(7.47%)-H_2O at 298.15 K and standard molar enthalpies of formation of new solid-phase compounds. *J. Chem. Eng. Data* **2008**, *53*, 471–474.

(11) Meyer, G.; Volkmar, V. Synthesis and structures of A_2REX_5-type halides (RE = rare earth). *J. Less-Common Met.* **1983**, *93* (2), 452.

(12) Qiao, Z. P.; Xie, H. Q.; Zhuo, L. H.; Chen, X. Study on phase equilibrium in the quaternary 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*, 1681–1685.

(13) Chen, Y. S. *Analysis of Physical Chemistry*; Higher Education Press: Beijing, 1988; pp 505−506 (in Chinese).

(14) Liu, Z. H.; Li, P.; Zhang, C. F. Standard molar enthalpies of formation for the two hydrated calcium borates xCaO·5B_2O_3·$y$$H_2O$ (x = 2 and 4, y = 5 and 7). *J. Chem. Eng. Data* **2006**, *51*, 272–275.

(15) Chen, S. P.; Meng, X. X.; Xia, G.; Gao, S. L.; Shi, Q. Z. Thermochemistry of the ternary solid complex $Er(C_5H_8NS_2)_3(C_{12}H_8N_2)$. *J. Chem. Eng. Data* **2005**, *50*, 1204–1211.

(16) Weast, R. C. *CRC Handbook of Chemistry and Physics*, 70th ed.; CRC Press: Boca Raton, FL,1989.

(17) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.

(18) 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**, (suppl.2), 11.

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