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Investigation on the Equilibrium Phase Diagram of the Ternary System $TmCl_3-CdCl_2-H_2O$ at 298.15 K and Standard Molar Enthalpy of Formation of $Cd_3TmCl_9\cdot 15H_2O$

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Equilibrium phase relation and solubility data for the rare earth trichloride $TmCl_3\cdot 6H_2O$ and cadmium chloride in aqueous media were investigated. The corresponding equilibrium phase diagram in the ternary system $TmCl_3-CdCl_2-H_2O$ at 298.15 K was constructed. The results showed that the system was complicated and consisted of four stable equilibrium solid phases [$CdCl_2\cdot 2.5H_2O$, $CdCl_2\cdot H_2O$, $Cd_3TmCl_9\cdot 15H_2O$ (3:1 type), $TmCl_3\cdot 6H_2O$]. The new compound $Cd_3TmCl_9\cdot 15H_2O$ was found to be congruently soluble in the system. The 3:1 type compound obtained was identified and characterized by the method of X-ray diffraction, X-ray diffraction single-crystal structure analysis, thermogravimetry, and differential thermogravimetry (TG, DTG). It belongs to a monoclinic system, with space group $P2(1)/n$, $a = 1.2267(4)$ nm, $b = 2.0034(7)$ nm, $c = 1.2321(4)$ nm, $\beta = 113.793(5)°$, $V = 2.7706(17)$ nm^3, Dc $= 2.554$ g$\cdot$cm^{-3}, $Z = 4$. The standard molar enthalpy of solution of $Cd_3TmCl_9\cdot 15H_2O$ in deionized water was measured to be (29.73 ± 0.40) kJ$\cdot$mol^{-1} by heat conduction microcalorimetry. Its standard molar enthalpy of formation was calculated to be $-(6747.2 \pm 1.2)$ kJ$\cdot$mol^{-1}.

Introduction

As a part of the systematic investigation on the phase diagrams of ternary systems of rare earth chlorides, the equilibrium phase diagrams of the ternary systems $CdCl_2-RECl_3-H_2O$ (RE = La, Ce, Pr, Nd, Sm, Eu, Dy, Y) were investigated. The corresponding solubilities were determined in previous studies.[1−5] It is highly valuable and important for us to understand the phase relations and interactions of $CdCl_2$ and $RECl_3$ in aqueous media. For the $CdCl_2-RECl_3-H_2O$ (RE = La, Pr, Nd, Sm, Eu) system,[1,2] five equilibrium solid-phase regions, $CdCl_2\cdot 2.5H_2O$, $CdCl_2\cdot H_2O$, $Cd_8RECl_{19}\cdot nH_2O$ (RE =La, Nd, Sm, Eu, $n = 16$; RE = Pr, $n = 20$), $Cd_4RECl_{11}\cdot nH_2O$ (RE = La, Pr, Nd, Sm, $n = 12$; RE = Eu, $n = 14$), and $RECl_3\cdot nH_2O$ (RE = La, Pr, $n = 7$; RE = Nd, Sm, Eu, $n = 6$) were observed. In these ternary systems, the new compounds $Cd_4RECl_{11}\cdot nH_2O$ (4:1 type) were stable, and $Cd_8RECl_{19}\cdot nH_2O$ (8:1 type) were metastable complexes. Both are incongruently soluble in the aqueous systems. These results showed that phase chemical reactions of the five ternary systems are very similar. We reported the presence of five equilibrium solid-phase regions ($CdCl_2\cdot 2.5H_2O$, $CdCl_2\cdot H_2O$, $Cd_6CeCl_{15}\cdot 14H_2O$, $Cd_4CeCl_{11}\cdot 12H_2O$, and $CeCl_3\cdot 7H_2O$) in the $CeCl_3-CdCl_2-H_2O$ ternary system,[3] of which the $Cd_4CeCl_{11}\cdot 12H_2O$ (4:1 type) was a stable and $Cd_6CeCl_{15}\cdot 14H_2O$ (6:1 type) was a metastable complex. We re-examined the $YCl_3-CdCl_2-H_2O$[4] and $DyCl_3-CdCl_2-H_2O$[5] systems and confirmed the presence of four stable complexes ($CdCl_2\cdot 2.5H_2O$, $CdCl_2\cdot H_2O$, $Cd_4YCl_{11}\cdot 13H_2O$, and $Cd_5Y_2Cl_{16}\cdot 26H_2O$) and one metastable complex ($Cd_8YCl_{19}\cdot 15H_2O$) in the $CdCl_2-YCl_3-H_2O$ ternary system. At the same time, we affirmed that the $DyCl_3-CdCl_2-H_2O$ system is composed of four stable equilibrium solid phases: $CdCl_2\cdot 2.5H_2O$, $CdCl_2\cdot H_2O$, $Cd_9Dy_2Cl_{24}\cdot 29H_2O$, and $DyCl_3\cdot 6H_2O$, respectively. Comparing the reported ternary systems,[1−5] we find that the light rare-earth element trichlorides have similarity, but the heavy rare-earth element trichlorides have differences in phase chemical behavior in aqueous salt systems with $CdCl_2$. The present paper is concerned with the solubility and phase equilibrium relations of the $TmCl_3-CdCl_2-H_2O$ system at 298.15 K and related measurement of properties of a new solid-phase compound established in the system. The aim is to find more phase equilibria information on the $RECl_3-CdCl_2-H_2O$ ternary systems.

Experimental Section

Preparing Samples. All chemicals ($CdCl_2\cdot 2.5H_2O$) and solvents (H_2O) were analytically pure and commercially available. $TmCl_3\cdot 6H_2O$ was prepared by the reaction of Tm_2O_3 (99.99 %) with hydrochloric acid (37 % HCl). The composition of $TmCl_3\cdot 6H_2O$ was confirmed by analyzing the Cl^- content by titration with a normal solution of silver nitrate and the Tm^{3+} content by titration with EDTA. The purity reached in this way was found to be 99.9 %. The analysis errors for other ions were relative and found to be better than ± 0.20 %.

Investigations on the System at 298.15 K and Analysis Methods. The method of investigation of the solubility of the $TmCl_3-CdCl_2-H_2O$ ternary system has been previously reported.[1] All sealed samples were put in a big water tank with a thermostat fixed at 298.15 K and an electrical stirrer. The

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precision of the temperature was 0.1 K. The solid−liquid phase equilibrium was established for these samples after (7 to 10) days.

The saturated solutions and the corresponding wet solid phases (wet residues) of the samples were separated, taken out, and analyzed. For the analysis methods, see ref 2. The composition of the new compounds in the system was determined by the well-known wet residue method of Schreinemaker[6] and checked by chemical analysis. The new solid-phase compound was further demonstrated by XRD and single-crystal X-ray diffractometry, and its crystal water content 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. The diffraction data of the structure analysis were collected by a Bruker Smart Apex-II CCD diffractometer using graphite monochromatized Mo Kα radiation ($\lambda = 0.071\,073$ nm), at room temperature.

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.[7,8]

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) $\mu V\cdot mW^{-1}$. The reliability of the calorimeter was verified by measuring the enthalpy of solution of KCl(s) in deionized water. The average experimental value of $\Delta_{sol}H_m$(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.[9] 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 six 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 complete dissolution was about 0.1 h.

Results and Discussion

$TmCl_3-CdCl_2-H_2O$ System at 298.15 K. The solubility data of the $TmCl_3-CdCl_2-H_2O$ system at 298.15 K are listed in Table 1. Figure 1 depicts the corresponding phase equilibrium diagram.

As can be seen in Figure 1, the curves of solubility consist of four branches in the ternary system $TmCl_3-CdCl_2-H_2O$, which correspond to the equilibrium solid phases $CdCl_2\cdot 2.5H_2O$ (A), $CdCl_2\cdot H_2O$ (A1), $Cd_3TmCl_9\cdot 15H_2O$ (3:1 type) (B), and $TmCl_3\cdot 6H_2O$ (C), respectively. This indicates that the phase regions of two new compounds $CdCl_2\cdot H_2O$ (A1) and $Cd_3TmCl_9\cdot 15H_2O$ (B) are formed in this system except for initial compounds A and C, of which compound $CdCl_2\cdot H_2O$ (A1) is incongruently soluble, while the $Cd_3TmCl_9\cdot 15H_2O$ (B) (3:1 type) is congruently soluble in the aqueous system. The presence of $CdCl_2\cdot H_2O$ (A1) in the $TmCl_3-CdCl_2-H_2O$ system implies that $TmCl_3$ can dehydrate crystal water from $CdCl_2\cdot 2.5H_2O$. The compound $Cd_3TmCl_9\cdot 15H_2O$ is a new type of compound in the ternary systems $CdCl_2-RECl_3-H_2O$ and has not been synthesized and reported in the literature so far. The new compound $Cd_3TmCl_9\cdot 15H_2O$ obtained from the system was analyzed by a titration method. Its composition by mass is Cd (30.70 %), Tm (15.47 %), and Cl (29.20 %) in $Cd_3TmCl_9\cdot 15H_2O$. The value is in agreement with theoretical data (30.78 % Cd, 15.42 % Tm, and 29.13 % Cl).

Table 1. Solubility Data of the Ternary System $TmCl_3-CdCl_2-H_2O$ at 298.15 K

	composition of saturated solution (%)[a]		composition of wet residue (%)		
no.	$TmCl_3$	$CdCl_2$	$TmCl_3$	$CdCl_2$	solid phase[b]
1	0.00	54.61	0.00	80.26	A
2	3.75	51.38	1.24	73.84	A
3	8.58	47.87	2.19	72.85	A
4	11.86	45.93	2.87	72.01	A
5	13.71	44.62	2.93	73.07	A
6	16.71	43.92	4.31	71.33	A
7	16.80	43.90	5.28	72.14	A + A1
8	18.12	43.05	6.33	73.75	A1
9	19.20	42.71	7.76	71.42	A1
10	19.72	42.61	15.86	56.77	A1 + B
11	19.81	42.56	18.22	51.91	A1 + B
12	19.85	42.44	18.71	50.23	A1 + B
13	20.33	41.83	24.10	47.68	B
14	22.96	37.59	24.35	45.02	B
15	32.68	26.54	26.13	46.87	B
16	31.51	27.28	26.36	45.46	B
17	37.74	22.92	27.67	44.13	B
18	38.94	22.38	29.77	41.77	B
19	40.36	21.96	30.35	44.00	B + C
20	40.51	22.11	33.19	39.58	B + C
21	43.08	18.26	63.70	4.93	C
22	46.05	12.07	63.60	3.24	C
23	48.41	5.97	68.53	1.23	C
24	51.64	0.00	71.77	0.00	C

[a] Double saturation point (average). E_1: $CdCl_2$, 43.90 %; $TmCl_3$, 16.80 %. E_2: $CdCl_2$, 42.54 %; $TmCl_3$, 19.79 %. E_3: $CdCl_2$, 22.03 %; $TmCl_3$, 40.43 %. [b] Complexes: A, $CdCl_2\cdot 2.5H_2O$; A1, $CdCl_2\cdot H_2O$; B, $Cd_3TmCl_9\cdot 15H_2O$; C, $TmCl_3\cdot 6H_2O$.

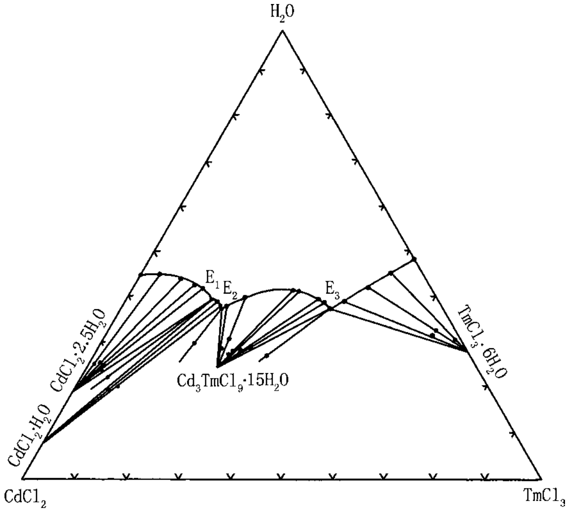

Figure 1. Isothermal solubility diagram of the system $TmCl_3-CdCl_2-H_2O$ at 298.15 K.

Characterization of $Cd_3TmCl_9\cdot 15H_2O$. The X-ray powder diffraction pattern of the $Cd_3TmCl_9\cdot 15H_2O$ compound obtained is shown in Figure 2. It is neither the same as $CdCl_2\cdot 2.5H_2O$ and $TmCl_3\cdot 6H_2O$ nor the simple superposition of $CdCl_2\cdot 2.5H_2O$

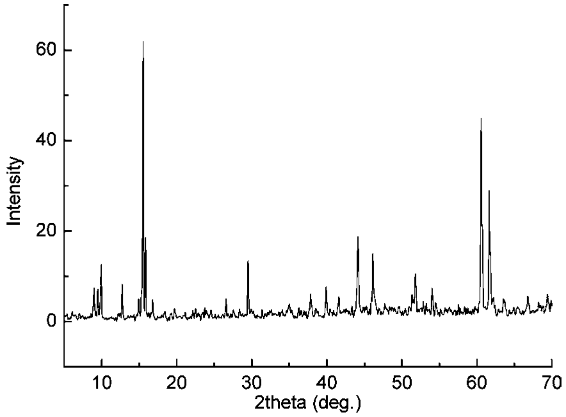

Figure 2. X-ray powder diffraction spectrum of $Cd_3TmCl_9 \cdot 15H_2O$.

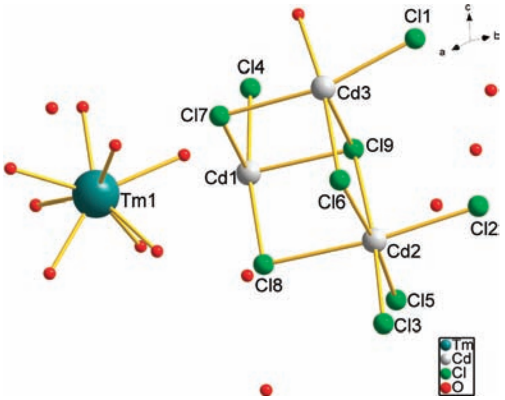

Figure 3. Asymmetric unit structure of $Cd_3TmCl_9 \cdot 15H_2O$.

and $TmCl_3 \cdot 6H_2O$. This demonstrates that $Cd_3TmCl_9 \cdot 15H_2O$ is formed from a reaction between $CdCl_2 \cdot 2.5H_2O$ and $TmCl_3 \cdot 6H_2O$.

A single crystal of $Cd_3TmCl_9 \cdot 15H_2O$ with approximate dimension of 0.32 mm × 0.28 mm × 0.24 mm was selected for the structure analysis. The diffraction data were collected on a Bruker Smart Apex-II CCD diffractometer. The compound $Cd_3TmCl_9 \cdot 15H_2O$ belongs to a monoclinic system, with space group $P2(1)/n$, $a = 1.2267(4)$ nm, $b = 2.0034(7)$ nm, $c = 1.2321(4)$ nm, $\beta = 113.793(5)°$, $V = 2.7706(17)$ nm^3, Dc = 2.554 g·cm^{-3}, $Z = 4$. The asymmetric unit structure of the compound is shown in Figure 3. This demonstrates that the composition of $Cd_3TmCl_9 \cdot 15H_2O$ is in accordance with the composition determined by Schreinemaker's method and further confirms that the compound $Cd_3TmCl_9 \cdot 15H_2O$ is new.

TG-DTG data for the compound are presented in Figure 4. The curve for the compound $Cd_3TmCl_9 \cdot 15H_2O$ shows that there are two obvious mass-loss steps in the temperature range (310.6 to 486.1) K. They arise from the loss of crystal water from the hydrated compound. The mass-loss values are 11.50 % (theory 11.51 %, 7 crystal water) and 13.02 % (theory 13.15 %, 8 crystal water), respectively. The total mass-loss value is 24.52 %, which corresponds to the theoretical dehydration value of 24.66 %. It should be noted that the total mass-loss value is in accordance with data of water determined by the Schreinemaker method and analyzed by a titration method.

Enthalpies of Solution. The molar enthalpy of solution of $Cd_3TmCl_9 \cdot 15H_2O$ in water is (29.73 ± 0.40) kJ·mol^{-1} at 298.15 K. The values are listed in Table 2, in which m is the mass of 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, namely

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

in which n is the number of experimental measurements ($n = 6$); 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 $Cd_3TmCl_9 \cdot 15H_2O$ can be calculated as shown in the following equation

$$\Delta_f H_m^{\ominus}(s) = 3\Delta_f H_m^{\ominus}(Cd^{2+})(aq) + \Delta_f H_m^{\ominus}(Tm^{3+})(aq) + 9\Delta_f H_m^{\ominus}(Cl^{-})(aq) + 15\Delta_f H_m^{\ominus}(H_2O)(l) - \Delta_{sol} H_m^{\ominus}(Cd_3TmCl_9 \cdot 15H_2O)(s)$$

The standard molar enthalpies of formation of Cd^{2+}, Cl^-, and H_2O were taken from the CODATA Key Values,[10] 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. Tm^{3+} was taken from the NBS table,[11] −(697.9 ± 0.20) kJ·mol^{-1}. Using these schemes and data, the standard molar enthalpy of formation of $Cd_3TmCl_9 \cdot 15H_2O$ was calculated to be −(6747.2 ± 1.2) kJ·mol^{-1}.

Conclusion

The solubility of the ternary system $TmCl_3-CdCl_2-H_2O$ at 298.15 K was measured, and the corresponding phase diagram was prepared to search for new compounds and obtain equilibrium data for cadmium chloride/thulium chloride in aqueous solution. One kind of a new compound ($CdCl_2$:$TmCl_3$) of 3:1 type was found to exist in the above system besides the earlier reported systems $CdCl_2-RECl_3-H_2O$ (RE = La, Ce, Pr, Nd, Sm, Eu, Dy, Y). The composition of a new solid phase was determined by the Schrienemaker method and confirmed by

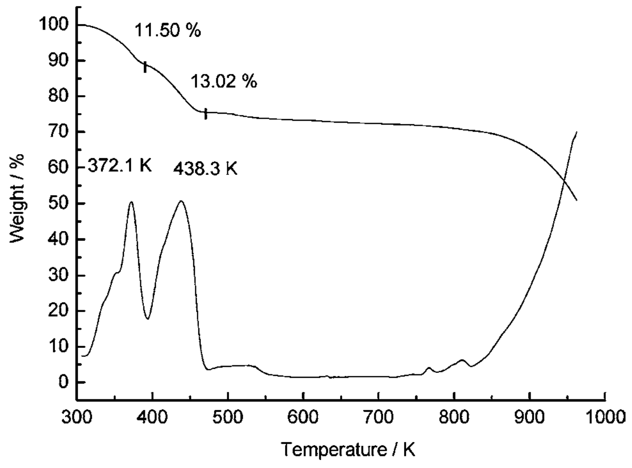

Figure 4. Thermogravimetric curve of $Cd_3TmCl_9 \cdot 15H_2O$.

Table 2. Molar Enthalpies of Solution of $Cd_3TmCl_9 \cdot 15H_2O$ in Deionized Water at 298.15 K[a]

no.	m g	Q_s mJ	$\Delta_{sol}H^{\ominus}_m$ (kJ·mol^{-1})
1	0.06080	1640.7	29.561
2	0.06067	1644.8	29.699
3	0.06050	1606.4	29.087
4	0.06034	1645.6	29.876
5	0.06051	1634.3	29.587
6	0.06052	1689.1	30.574
Mean[b]		$\Delta_{sol}H^{\ominus}_m$ = (29.73 ± 0.40) kJ·mol^{-1}	

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

chemical analysis. The compound $Cd_3TmCl_9 \cdot 15H_2O$ is congruently soluble. Through measuring the standard molar enthalpy of solution, the standard molar enthalpy of formation of the new compound $Cd_3TmCl_9 \cdot 15H_2O$ was calculated.

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