Studies on Phase Equilibria in the Systems $CdCl_2$−$PrCl_3$−HCl (8.3 %)−H_2O and $CdCl_2$−$PrCl_3$−H_2O at 298 ± 1 K

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The equilibrium solubility of the quaternary system $CdCl_2$−$PrCl_3$−HCl (8.3 mass %)−H_2O and the ternary system $CdCl_2$−$PrCl_3$−H_2O at 298 K was investigated, and the corresponding phase diagrams were plotted. The results showed that the quaternary system was a complicated one consisting of four stable equilibrium solid phases $CdCl_2 \cdot H_2O$, $Cd_8PrCl_{19} \cdot 20H_2O$ (8:1 type), $Cd_4PrCl_{11} \cdot 12H_2O$ (4:1 type), and $PrCl_3 \cdot 7H_2O$, of which two new compounds $Cd_8PrCl_{19} \cdot 20H_2O$ and $Cd_4PrCl_{11} \cdot 12H_2O$ were found to be congruently soluble in the system. The ternary system consisted of four stable equilibrium solid phases ($CdCl_2 \cdot 2.5H_2O$, $CdCl_2 \cdot H_2O$, $Cd_4PrCl_{11} \cdot 12H_2O$, and $PrCl_3 \cdot 7H_2O$) and a metastable phase ($Cd_8PrCl_{19} \cdot 20H_2O$). Two new compounds of the 8:1 type and 4:1 type were found to be incongruently soluble in the system. Both of the 8:1 type and 4:1 type compounds obtained were identified and characterized by the method of X-ray diffraction and the thermal analysis methods of thermogravimetry-differential thermogravimetry (TG-DTG).

Introduction

Studies on the equilibrium solubility of several quaternary systems of CsX-REX_3−HX−H_2O (X = Cl, Br; RE = La, Ce, Pr, Nd, Sm, Gd, Dy) have been determined.[1−9] The crystallization of a 1:1 type $CsRECl_4 \cdot nH_2O$ (RE = La, Ce, Pr, Nd) and $RbGdCl_4 \cdot 4H_2O$, a 4:1 type $Cs_4GdCl_7 \cdot H_2O$, a 5:3 type $Cs_5Dy_3Br_{14} \cdot 24H_2O$, and a 5:2 type $Cs_5RE_2Br_{11} \cdot 22H_2O$ (RE = La, Pr, Nd, Sm) were established in the systems. Some of these compounds show behavior of up-conversion fluorescence when excited in the near-infrared or visible region.[10,11] Therefore, it is appropriate to search for new compounds by carrying out research on new equilibrium systems of this kind. Moreover, solubility and equilibrium data in the aqueous quaternary and ternary equilibrium systems of aqueous rare earth halides could also be interesting to scientists and engineers using corresponding phase diagrams.

To compare the phase relations between aqueous alkali metal halide/rare earth metal halide and transition metal halide/rare earth metal halide systems and to establish the formation of new compounds, a series of investigations on $CdCl_2$−$RECl_3$−HCl (8−12 mass %)−H_2O (RE = La, Ce, Pr, Nd, Sm, Eu, Dy, Gd or Y) quaternary systems and the $CdCl_2$−$RECl_3$−H_2O ternary system at 298 K have been done in this laboratory.[12−15] This is very important for understanding the interactions between $CdCl_2$ and $RECl_3$ in the HCl (8−13 mass %)−H_2O medium. The present paper is concerned with the solubility and phase equilibrium relations of the $CdCl_2$−$PrCl_3$−HCl (8.3 %)−H_2O and the $CdCl_2$−$PrCl_3$−H_2O systems at 298 K and related measurements of properties of two new solid-phase compounds established in the systems.

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Experimental Section

Preparing Samples. All chemicals ($CdCl_2 \cdot 2.5H_2O$) and solvents (H_2O and 37 mass %) were analytically pure and purchased from the market. $PrCl_3 \cdot 7H_2O$ was prepared by the reaction of Pr_2O_3 with hydrochloric acid (37 mass % HCl). The composition of $PrCl_3 \cdot 7H_2O$ was confirmed by analyzing the Cl^- content by titration with a normal solution of silver nitrate and the Pr^{3+} content by titration with EDTA (0.02247 mol·L^{-1}). The purity reached this way was found to be 99.9 %. The analysis errors for those ions were relative ones and better than ±0.2 %.

Investigations on the Systems at 298 K and Analysis Methods. For the investigation of the solubility of the $CdCl_2$−$PrCl_3$−H_2O ternary system, 34 samples were prepared for using $CdCl_2 \cdot 2.5H_2O$ and $PrCl_3 \cdot 7H_2O$. As far as the $CdCl_2$−$PrCl_3$−HCl (8.3 %)−H_2O quaternary system is concerned, one ternary section $CdCl_2$−$PrCl_3$−H_2O of the system was investigated. Different samples were first assigned on the phase diagram cross-section on which the HCl mass percentage of the liquid phase is 8 mass %. The different weight ratio of $CdCl_2$, $PrCl_3 \cdot 7H_2O$, 37 mass % hydrochloric acid, and H_2O were mixed for each sample (42 samples) according to the mass percentage of the different points of the quaternary system $CdCl_2$−$PrCl_3$−HCl−H_2O projected on the trigonal basal face $CdCl_2$−$PrCl_3$−H_2O. Each sample containing solid and liquid phases was sealed in a plastic container. A single sample was used to determine two points that were the saturated solution and the corresponding wet solid-phase points. The acidity of the liquid phase of every sample only for the quaternary system was kept at 8 mass % HCl. All the sealed samples were put in a big water tank with a thermostat fixed at 298 K and agitated by an electrical stirrer. The precision of the temperature was ±1 K. After 10−15 days, the solid−liquid-phase equilibrium was established for the

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Table 1. Solubility Data of the Saturated Solution of the Quaternary System $CdCl_2-PrCl_3-HCl$ (8.3 mass %)$-H_2O$ at 298 ± 1 K and Central Projection Data on the Trigonal Basal Face

	composition of solution (% mass weight)					composition of residue (% mass weight)					
	composition in the tetrahedra			composition in the trigonal basal face[a]		composition in the tetrahedra			composition in the trigonal basal face		
no.	HCl	$CdCl_2$	$PrCl_3$	$CdCl_2$	$PrCl_3$	HCl	$CdCl_2$	$PrCl_3$	$CdCl_2$	$PrCl_3$	solid phase[b]
1	9.23	50.06	0	55.14	0	0	0	0	91.07	0	A
2	7.94	46.80	0.60	50.84	0.65	4.86	63.95	1.14	67.22	1.19	A
3	9.30	47.15	1.58	51.98	1.74	4.71	68.62	1.31	72.02	1.37	A
4	7.90	47.59	1.96	51.68	2.13	4.49	67.17	1.17	70.33	1.23	A
5	8.24	46.40	2.32	50.57	2.53	5.74	58.91	2.03	62.50	2.15	A
6	8.12	46.74	2.68	50.87	2.92	6.14	58.39	2.39	62.21	2.54	A
7	8.42	46.08	2.31	50.31	2.52	5.15	62.53	2.38	65.92	2.51	A + B
8	8.03	47.76	3.18	51.93	3.46	4.39	68.35	2.50	71.49	2.62	A + B
9	7.80	47.98	3.25	52.04	3.52	7.05	51.80	3.97	55.73	4.27	A + B
10	8.13	46.39	3.38	50.50	3.68	7.66	48.72	4.24	52.77	4.59	B
11	7.70	47.21	4.67	51.14	5.06	6.59	51.52	6.20	55.15	6.64	B
12	7.15	46.53	4.95	50.11	5.33	6.54	50.22	6.23	53.74	6.67	B
13	8.19	45.05	5.01	49.07	5.46	6.95	48.62	6.48	52.25	6.96	B
14	10.21	43.55	3.54	48.51	3.94	9.58	46.47	5.10	51.39	5.65	B
15	7.45	45.58	6.63	49.25	7.16	6.90	48.46	7.05	52.05	7.57	B
16	6.98	46.19	6.65	49.66	7.15	6.58	47.45	6.99	50.79	7.48	B
17	9.71	41.87	6.68	46.37	7.40	8.55	46.24	7.97	50.56	8.71	B
18	7.19	43.15	8.05	46.49	8.68	6.41	48.27	8.13	51.58	8.69	B
19	7.69	42.89	9.14	46.46	9.91	6.67	47.50	9.49	50.89	10.17	B
20	8.63	42.11	9.13	46.09	9.99	4.86	50.58	13.24	53.16	13.92	C
21	7.82	41.87	8.67	45.42	9.41	6.79	45.39	9.93	48.70	10.65	C
22	9.43	41.67	7.42	46.01	8.20	5.47	49.24	14.06	52.09	14.87	C
23	7.74	41.12	9.43	44.57	10.22	4.81	48.35	13.58	50.79	14.27	C
24	7.82	40.32	10.41	43.75	11.30	6.75	41.98	12.04	45.02	12.91	C
25	7.42	38.48	12.80	41.56	13.83	7.20	38.80	13.19	41.81	14.21	C
26	7.10	38.42	13.98	41.36	15.05	4.34	46.58	16.34	48.69	17.08	C
27	9.72	35.55	13.04	39.38	14.44	2.94	56.15	18.65	57.85	19.22	C
28	8.37	36.49	14.91	39.83	16.27	4.13	48.87	17.37	50.97	18.12	C
29	8.63	33.97	17.07	37.18	18.68	8.09	37.11	17.40	40.38	18.93	C
30	7.85	33.72	17.65	36.59	19.16	6.97	36.86	17.61	39.62	18.92	C
31	6.07	36.06	17.63	38.39	18.77	5.49	39.58	17.70	41.87	18.73	C
32	8.57	29.96	21.10	32.77	23.07	3.14	47.83	22.22	49.38	22.94	C
33	8.45	29.54	21.63	32.27	23.63	3.19	39.01	28.80	40.30	29.74	C + D
34	9.33	30.21	20.82	33.31	22.96	3.26	35.64	30.54	36.84	31.57	C + D
35	8.64	30.09	21.43	32.94	23.46	3.86	30.38	33.05	31.59	34.38	C + D
36	8.22	30.09	22.50	32.78	24.52	4.26	27.91	33.72	29.15	35.23	C + D
37	8.78	29.75	21.37	32.61	23.43	4.84	24.49	35.83	25.74	37.65	C + D
38	8.09	23.56	25.09	25.63	27.30	3.42	10.36	48.48	10.73	50.20	D
39	9.08	21.07	24.93	23.17	27.42	3.10	7.91	50.81	8.16	52.44	D
40	9.34	25.05	22.70	27.64	25.04	3.99	11.19	46.37	11.66	48.30	D
41	10.20	6.06	28.91	6.75	32.19	3.59	2.74	51.73	2.85	53.66	D
42	8.34	0	34.14	0	37.24	0	0	0	0	66.90	D

[a] Double saturation point (average): E_1, $CdCl_2$ 51.13 %, $PrCl_3$ 3.22 %; E_2, $CdCl_2$ 46.00 %, $PrCl_3$ 9.38 %; E_3, $CdCl_2$ 32.78 %, $PrCl_3$ 23.51 %. [b] Compounds: A, $CdCl_2 \cdot H_2O$; B, $Cd_8PrCl_{19} \cdot 20H_2O$; C, $Cd_4PrCl_{11} \cdot 12H_2O$; D, $PrCl_3 \cdot 7H_2O$.

ternary system. The acidity (HCl mass %) of the liquid phase could deviate from 8 mass % in the first 5−6 days in the quaternary system due to the gradual establishment of equilibrium in the system. As a consequence, the liquid phase of the samples may vary from 8 mass % HCl and was subsequently adjusted to this concentration. This process was done repetitively until the HCl mass percentage was maintained at 8 mass %. The samples were sealed again and agitated continuously for another 6−8 days until a new equilibrium was attained. The composition of the saturated solutions and the corresponding solid (wet residue point) was established and not changed as time went on.

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) the concentration of protons (only for the quaternary system) was analyzed by titration with a solution of sodium hydroxide (0.06156 $mol \cdot L^{-1}$), (2) the total amount of Pr^{3+} and Cd^{2+} (both for the ternary and quaternary system) by titration with EDTA (0.02247 $mol \cdot L^{-1}$), and (3) the individual concentrations of Cd^{2+} and Pr^{3+} were determined by titration with EDTA after Pr^{3+} was blanketed with a screening agent of thiourea and sodium carbonate (pH = 5−6 and controlled by hydrofluoric acid). The composition of the saturated solution and the corresponding wet solid-phase points was determined by calculating the individual contents of $CdCl_2$, $PrCl_3$, and HCl according to the analysis results of the H^+, Cd^{2+}, and Pr^{3+} ions. The solid-phase compositions were determined graphically by the Schreinemarkers method.[16] The results of analyses of each sample for the quaternary and ternary systems are shown in Table 1 and Table 2. As shown in Table 1, the HCl mass percentage in the liquid phase of the quaternary system is an average of the acidity (8.3 %).

Equipment and Conditions. Thermal characterization of the new compounds was undertaken with a Parkin-Elmer TGA7/4 thermal analysis apparatus (TG-DTG) which worked with a heating rate of 10 K/min under an Ar atmosphere with a flow rate of 60 cm^3/min; 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.

Table 2. Solubility Data of the Saturated Solution of the Ternary System $CdCl_2-PrCl_3-H_2O$ at 298 ± 1 K

	composition of solution (%)[a]		composition of wet residue (%)		
no.	$CdCl_2$	$PrCl_3$	$CdCl_2$	$PrCl_3$	solid phase[b]
1	54.57	0.00	79.30	0.00	A1
2	51.15	3.54	72.82	1.05	A1
3	47.67	8.00	72.61	2.25	A1
4	47.06	10.54	72.48	2.36	A1
5	46.67	10.71	70.04	3.74	A1
6	44.07	15.45	70.97	3.42	A1
7	43.98	16.43	70.20	4.77	A1
8	45.37	15.76	68.17	6.69	A1 + A
9	44.84	16.10	68.92	6.63	A1 + A
10	44.34	15.80	65.94	8.51	A
11	44.35	16.90	65.35	9.46	A
12	45.22	16.60	62.80	10.23	A
13	45.26	17.58	62.21	11.59	A
14	45.28	17.24	61.41	12.05	A + B
15	44.20	17.14	63.07	13.02	A + B
16	44.65	17.25	56.30	14.94	B
17	43.57	20.75	52.77	17.52	B
18	29.51	32.04	50.16	21.10	B
19	28.19	34.47	51.22	22.83	B
20	39.93	20.05	49.00	20.15	C
21	40.38	20.71	48.48	20.30	C
22	33.26	25.75	45.85	24.15	C
23	33.72	27.80	44.19	24.72	C
24	28.50	32.75	52.75	23.33	C
25	24.42	37.03	21.58	42.98	C + D
26	25.33	36.09	42.53	30.05	C + D
27	25.95	36.25	39.92	31.38	C + D
28	21.90	37.5	11.50	52.03	D
29	17.12	39.00	7.53	55.11	D
30	13.81	41.25	6.57	54.76	D
31	11.63	41. 61	6.73	52.69	D
32	9.38	43.24	3.11	58.96	D
33	1.85	48.65	0.64	61.08	D
34	0	50.33	0	65.42	D

[a] Double saturation point (average): E_1, $CdCl_2$ 44.63 %, $PrCl_3$ 16.02 %; E_2, $CdCl_2$ 44.85 %, $PrCl_3$ 17.30 %; E_3, $CdCl_2$ 25.23 %, $PrCl_3$ 36.46 %. [b] Compounds: A1, $CdCl_2 \cdot 2.5H_2O$; A, $CdCl_2 \cdot H_2O$; B, $Cd_8PrCl_{19} \cdot 20H_2O$; C, $Cd_4PrCl_{11} \cdot 12H_2O$; D, $PrCl_3 \cdot 7H_2O$.

Results and Discussion

$CdCl_2-PrCl_3-HCl$ (8.3 mass %)$-H_2O$ and $CdCl_2-PrCl_3-H_2O$ Systems at 298 K. The solubility data of the $CdCl_2-PrCl_3-HCl$ (8.3 mass %)$-H_2O$ quaternary system and the central projection data on the trigonal basal face of the $CdCl_2-PrCl_3-H_2O$ at 298 K are listed in Table 1 and plotted in Figure 1a. It was established that, in addition to the initial components $CdCl_2 \cdot H_2O$ (A) and $PrCl_3 \cdot 7H_2O$ (D), two new compounds $Cd_8PrCl_{19} \cdot 20H_2O$ (B) and $Cd_4PrCl_{11} \cdot 12H_2O$ (C) also crystallized from the saturated solutions. The compounds of the 8:1 and 4:1 types are congruently soluble in the aqueous system. The chemical analyses in mass percent are 91.08 % for $CdCl_2$ in $CdCl_2 \cdot H_2O$ (theoretical, 91.06 %), 11.61 % $PrCl_3$ and 70.76 % $CdCl_2$ in the 8:1 type compound (theoretical, 11.90 % $PrCl_3$, 70.72 % $CdCl_2$), $PrCl_3$ 20.72 % and 61.21 % $CdCl_2$ in the 4:1 type compound (theoretical, 20.67 % $PrCl_3$, 61.28 % $CdCl_2$), and 66.90 % $PrCl_3$ in $PrCl_3 \cdot 7H_2O$ (theoretical, 66.24 % $PrCl_3$), respectively. This indicates that the formation of the solid compounds determined by the Schreinemakers method is reliable. It should be noted that similar compounds $Cd_8LaCl_{19} \cdot 16H_2O$ (8:1 type) and $Cd_4LaCl_{11} \cdot 12H_2O$ (4:1 type) were found in another $CdCl_2-LaCl_3-HCl$ (9.7 mass %)$-H_2O$ system,[17] indicating that the phase behavior in the quaternary system $CdCl_2-RECl_3-HCl-H_2O$ for the light rare earth elements La and Pr is similar.

The solubility data of the $CdCl_2-PrCl_3-H_2O$ ternary system at 298 K are listed in Table 2 and plotted in Figure 1b. It can be seen that the phase diagram of the $CdCl_2-PrCl_3-H_2O$ ternary system consists of five solubility curves which correspond to the equilibrium solid phases $CdCl_2 \cdot 2.5H_2O$ (A1), $CdCl_2 \cdot H_2O$ (A), $Cd_8PrCl_{19} \cdot 20H_2O$ (B), $Cd_4PrCl_{11} \cdot 12H_2O$ (C), and $PrCl_3 \cdot 7H_2O$ (D), respectively. Of the five equilibrium solid phases, phase B is metastable (dashed line), while the phases A1, A, C, and D are stable. The solid compounds $Cd_8PrCl_{19} \cdot 20H_2O$ and $Cd_4PrCl_{11} \cdot 12H_2O$ of the ternary system are both incongruently soluble in the aqueous system. The results of chemical analyses of these compounds are 11.46 % $PrCl_3$ and 71.23 % $CdCl_2$ and 20.49 % $PrCl_3$ and 61.25 % $CdCl_2$, respectively, which are in acceptable agreement with the analyses of these compounds found in the quaternary system.

When parts a and b of Figure 1 are compared, the quaternary system is quite different from the ternary system. It shows that the interaction of $CdCl_2$ and $PrCl_3$ in a medium of ∼8.3 mass % HCl is different from that in the pure aqueous medium. The equilibrium solid-phase $CdCl_2 \cdot 2.5H_2O$ (A1) exists only in the ternary system but does not exist in the quaternary system. It indicates that the compound $CdCl_2 \cdot 2.5H_2O$ is dehydrated in the presence of HCl in the aqueous medium. The compounds of the 8:1 and 4:1 types are not only congruently soluble in the quaternary system but also obtained easily, while the 8:1 and 4:1 type compounds are incongruently soluble in the ternary system and the 8:1 type compound was difficult to obtain. The solubility data of all the compounds decreased when HCl was

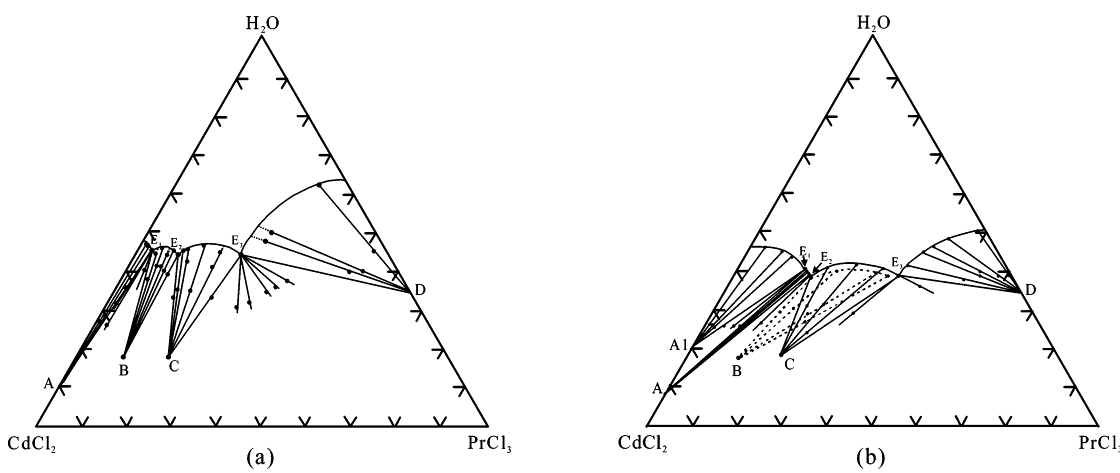

Figure 1. Solubility diagrams of the quaternary system $CdCl_2-PrCl_3-HCl$ (8.3 mass %)$-H_2O$ projected on $CdCl_2-PrCl_3-H_2O$ (a) and the ternary system $CdCl_2-PrCl_3-H_2O$ (b) at 298 ± 1 K.

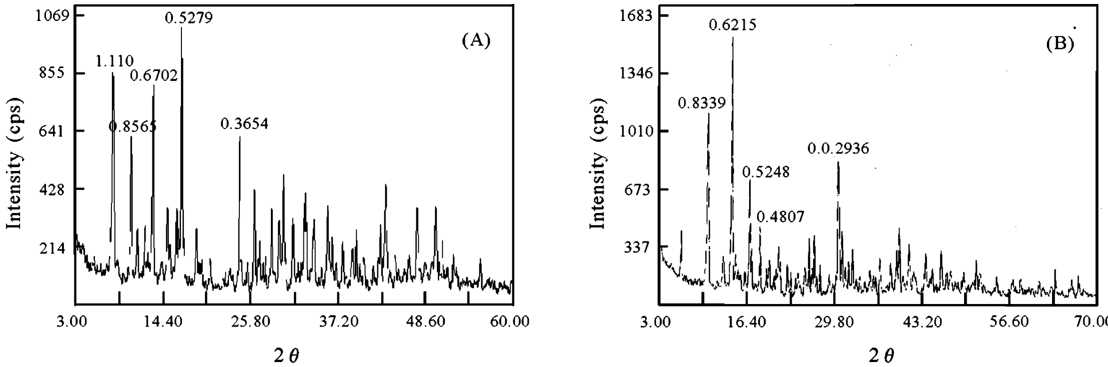

Figure 2. X-ray powder diffraction spectrum of $Cd_8PrCl_{19}\cdot 20H_2O$ (A) and $Cd_4PrCl_{11}\cdot 12H_2O$ (B).

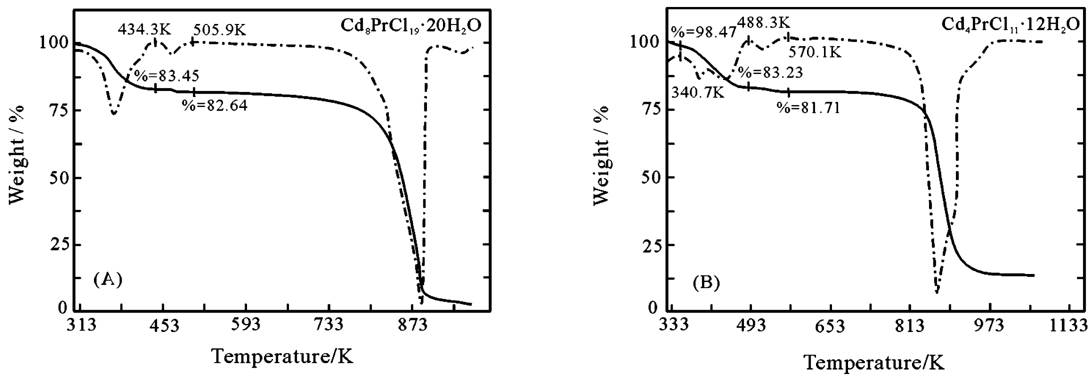

Figure 3. Thermogravimetric curves of the $Cd_8PrCl_{19}\cdot 20H_2O$ (A) and $Cd_4PrCl_{11}\cdot 12H_2O$ (B) compounds: solid line, TG; dashed line, DTG.

present in the aqueous medium. The larger the HCl mass percentage (acidity) included in the equilibrium liquid phase, the smaller the solubility of the compounds.

Characterization of $Cd_8PrCl_{19}\cdot 20H_2O$ and $Cd_4PrCl_{11}\cdot 12H_2O$. X-ray powder diffraction data and patterns of the $Cd_8PrCl_{19}\cdot 20H_2O$ and $Cd_4PrCl_{11}\cdot 12H_2O$ compounds obtained are shown in Figure 2. They are obviously different from the literature XRD data of the two starting salts: $CdCl_2$, d (nm) = 0.5850 (100), 0.2648 (90), 0.3270 (70), 0.1826 (55) and $PrCl_3$, d (nm) = 0.2570 (100), 0.2110 (80), 0.3560 (65), 0.6460 (55). This demonstrates that the two compounds are new.

TG-DTG data for the two compounds is presented in Figure 3. Curve A shows that there are two obvious mass-loss steps for $Cd_8PrCl_{19}\cdot 20H_2O$ in the temperature range of 303−505 K and the total mass-loss value is basically in accordance with the dehydration of this compound. The same investigation was performed for $Cd_4PrCl_{11}\cdot 12H_2O$. One observes that on curve B for the 4:1 type compound, the three obvious mass-loss steps in the temperature range 323−570 K, the total mass-loss value is also in agreement with theoretical dehydration data. On the basis of these results, we suggest that the dehydration equations for the two compounds are as follows

$$Cd_8PrCl_{19}\cdot 20H_2O \xrightarrow[303-434K]{-19H_2O} Cd_8PrCl_{19}\cdot H_2O \xrightarrow[434-505K]{-H_2O} Cd_8PrCl_{19} \quad (1)$$

$$Cd_4PrCl_{11}\cdot 12H_2O \xrightarrow[323-341K]{-H_2O} Cd_4PrCl_{11}\cdot 11H_2O \xrightarrow[341-488K]{-10H_2O} Cd_4PrCl_{11}\cdot H_2O \xrightarrow[488-570K]{-H_2O} Cd_4PrCl_{11} \quad (2)$$

Conclusion

The equilibrium solubilities of the quaternary system $CdCl_2-PrCl_3-HCl$ (8.3 mass %)$-H_2O$ and the ternary system $CdCl_2-PrCl_3-H_2O$ at 298 K were measured. The corresponding phase diagrams were prepared to search for new compounds and obtain the equilibrium data for transition metal chloride/rare earth metal chloride in aqueous solution. The compositions of the solid phases were determined by the Schreinemakers method and confirmed by chemical analysis. The results showed that phase equilibrium in the quaternary system is quite different from the ternary system. Both $CdCl_2\cdot 2.5H_2O$ and $CdCl_2\cdot H_2O$ exist in the ternary system, while in the quaternary system only $CdCl_2\cdot H_2O$ was established. Moreover, both compounds $Cd_8PrCl_{19}\cdot 20H_2O$ (8:1 type) and $Cd_4PrCl_{11}\cdot 12H_2O$ (4:1 type) were found to exist in the ternary and the quaternary systems. The compounds of the 8:1 and 4:1 types are congruently soluble in the quaternary system, but they are incongruently soluble in the ternary system.

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