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Phase equilibria of the systems of CsCl + $HoCl_3$ + H_2O and CsCl + $HoCl_3$ + HCl (~10%) + H_2O at T = 298.15 K and the thermodynamic and fluorescent properties of the new solid-phase compounds

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ABSTRACT

(Solid + liquid) equilibria in the ternary system CsCl + $HoCl_3$ + H_2O and in the quaternary system CsCl + $HoCl_3$ + HCl (~10%) + H_2O at T = 298.15 K and atmospheric pressure were investigated by using isothermal solution saturation and moist residue method. Based on the measured solubility data, the corresponding phase diagrams were plotted. In the ternary system, three crystallization regions corresponding to CsCl, $Cs_2HoCl_5 \cdot 6H_2O$ and $HoCl_3 \cdot 6H_2O$ were found. However, there were four crystallization regions corresponding to CsCl, $Cs_5HoCl_8 \cdot 4H_2O$, $Cs_2HoCl_5 \cdot 6H_2O$ and $HoCl_3 \cdot 6H_2O$ in the quaternary system. The phase diagrams of the ternary and quaternary systems were compared, and it showed that (1) new solid-phase compound $Cs_2HoCl_5 \cdot 6H_2O$ was obtained which was congruently soluble in the two systems; (2) a new double salt $Cs_5HoCl_8 \cdot 4H_2O$ was formed in the quaternary system which was congruently soluble in an average medium of ~10 mass% HCl, and (3) the area of the crystallization region of CsCl decreased with the increasing concentration of HCl in the equilibrium liquid phase. The new solid-phase compounds $Cs_5HoCl_8 \cdot 4H_2O$ and $Cs_2HoCl_5 \cdot 6H_2O$ were characterized by chemical analysis, XRD and TG-DTG techniques. The standard molar enthalpies of solution of $Cs_5HoCl_8 \cdot 4H_2O$ and $Cs_2HoCl_5 \cdot 6H_2O$ in water were confirmed to be (53.09 ± 0.53) kJ · mol^{-1} and (4.26 ± 0.24) kJ · mol^{-1} by microcalorimetry in the condition of infinite dilution and their standard molar enthalpies of formation were determined to be $-(4530.1 \pm 1.4)$ kJ · mol^{-1} and $-(3776.6 \pm 0.9)$ kJ · mol^{-1}. The fluorescence excitation and emission spectra of the new solid phase compounds were measured. The results indicate that upconversion spectra of the compounds $Cs_5HoCl_8 \cdot 4H_2O$ and $Cs_2HoCl_5 \cdot 6H_2O$ at the same wavelength 474 nm, when the former was excited at 701 nm and the latter was excited at 713 nm.

1. Introduction

Compounds, containing lanthanide ions, exhibiting extraordinary physical and biological function have been found. Some of them have been applicated in many field, such as photoelectrode of solar cells [1,2], optical communication [3], biomedical therapy [4,5] and magnetic molecular materials [6]. Therefore, many efforts have been absorbed in this work to search for more new compounds. Some new compounds synthesized in the corresponding equilibrium systems were reported [7–10]. As the search moves along, more and more thermodynamic properties, magnetic properties and optical properties of the compounds were measured [11–14] and the scientists hope to learn more about how to use them to facilitate our life.

As part of this work, several new kinds of these compounds have been synthesized in Wang *et al.* and our lab [15–27]. This paper is concerned with the phase equilibria of the systems of CsCl + $HoCl_3$ + H_2O and CsCl + $HoCl_3$ + HCl (~10%) + H_2O at T = 298.15 K and the thermodynamic and fluorometric properties of the new solid compounds of $Cs_5HoCl_8 \cdot 4H_2O$ and $Cs_2HoCl_5 \cdot 6H_2O$.

2. Experimental

2.1. Reagents

All reagents and solvents employed were commercially available and used without further purification. Quartz double

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TABLE 1
Reagents used in this study.

Reagent	Source	State	Mass fraction purity
CsCl	Sinopharm Chemical Reagent Co., Ltd.	Solid	0.995[a]
$HoCl_3 \cdot 6H_2O$	National Engineering Research Centre of Rare Earth Metallurgy and Function Materials	Solid	0.9999[a]
Hydrochloric acid	Luoyang Haohua Chemical Reagent Company	Aqueous	Guaranteed reagent[a]
$Cs_5HoCl_8 \cdot 4H_2O$	Synthesized	Solid	0.994[b]
$Cs_2HoCl_5 \cdot 6H_2O$	Synthesized	Solid	0.995[b]

[a] As stated by the supplier.
[b] Evaluated by averaging based on the measured contents of $HoCl_3$ and CsCl.

deionized water was used (resistivity = 5.7 MΩ · cm). Table 1 summarizes relevant information on sample material purity.

2.2. Investigations on the system at T = 298.15 K and analysis methods

The two systems of CsCl + $HoCl_3$ + H_2O and CsCl + $HoCl_3$ + HCl (~10%) + H_2O were studied in terms of references [23,27]. The sealed plastic tubes with sold and liquid were kept in a big water tank with an electrical stirrer at T = 298.15 K. The precision of the temperature was 0.1 K. The phase equilibrium of the systems of CsCl + $HoCl_3$ + H_2O and CsCl + $HoCl_3$ + HCl (~10%) + H_2O can be reached in about 3 days and 6 days, respectively. The analysis methods of saturated solutions and the corresponding solid phases of the samples see references [23,27]. The concentrations of Ho^{3+} and Cl^- were determined by complexometry titration with EDTA and a normal solution of silver nitrate, respectively, and the measurement method of Cs^+ was gravimetry with the precipitation of $CsB(C_6H_5)_4$. The compositions of solid phases are determined by the Schreinemakers wet residues technique [28].

2.3. Synthesis of $Cs_5HoCl_8 \cdot 4H_2O$ and $Cs_2HoCl_5 \cdot 6H_2O$

Based on the phase region where $Cs_5HoCl_8 \cdot 4H_2O$ and $Cs_2HoCl_5 \cdot 6H_2O$ are in CsCl + $HoCl_3$ + HCl (~10%) + H_2O system, different ratios of CsCl, $HoCl_3 \cdot 6H_2O$, hydrochloric acid and H_2O were mixed and agitated at T = 298.15 K under the condition of concentration of HCl about 10 mass%. Upon the (solid + liquid) equilibrium was attained, the solid $Cs_5HoCl_8 \cdot 4H_2O$ and $Cs_2HoCl_5 \cdot 6H_2O$ were collected by suction filtration method.

2.4. Equipments and conditions

Thermogravimetric/differential thermogravimetric (TG-DTG) analysis was undertaken with a NETZSCH STA449C thermal analysis apparatus with a heating rate of 10 K · min^{-1} under a N_2 atmosphere with a flow rate of 30 cm^3 · min^{-1}. X-ray diffraction (XRD) measurements were performed by a D/Max-3C diffractometer using Cu Ka radiation at room temperature. The excitation and emission spectra of the compounds were recorded on the Hitachi model F-7000 fluorescence spectrophotometer equipped with the Xe lamp. The emission spectra of the compounds were detected when the excitation illuminants is continuously scanning in the range of (250 to 900) nm, the scanning rate is 12,000 nm · min^{-1}, and the excitation and emission slits are both 5.0 nm. The excitation voltage was 700 V.

2.5. Calorimetric technique

The enthalpies of solution were measured with RD496-2000 heat conduction microcalorimeter (Mianyang CP Thermal Analysis Instrument Co., LTD, China) [29]. The reliability of the calorimeter was verified with the sample of KCl (mass fraction ⩾ 0.9999) and its enthalpy of solution in water was (17.59 ± 0.10) kJ · mol^{-1} (reference 17.524 ± 0.028 kJ · mol^{-1}) [30].

3. Results and discussion

3.1. The ternary system of CsCl + $HoCl_3$ + H_2O at T = 298.15 K

The solubility data of the saturated solution and the corresponding wet residue of the ternary system of CsCl + $HoCl_3$ + H_2O at T = 298.15 K are listed in table 2, and the phase diagram of the system is revealed in figure 1. The salts compositions are expressed in mass percent.

Figure 1 shows that the CsCl + $HoCl_3$ + H_2O system has two invariant points (E_1,E_2) and three crystallization fields corresponding to the three solid phases CsCl, $Cs_2HoCl_5 \cdot 6H_2O$ (2:1 type) and $HoCl_3 \cdot 6H_2O$, respectively. The new compound $Cs_2HoCl_5 \cdot 6H_2O$ is congruently soluble in the aqueous system. The chemical analyses indicate that there are 47.15% CsCl and 37.79% $HoCl_3$ for $Cs_2HoCl_5 \cdot 6H_2O$ (theoretical, 47.02% CsCl, 37.88% $HoCl_3$).

The experiment data of CsCl in pure water at T = 298.15 K in this work and literature [31–36] were listed in table 3. The value of CsCl in present work is slightly higher than that from the literatures, the deviations should be caused by different measuring methods. The concentrations of Cl^- were determined by Fajans method [37] in our study, and the gravimetry with the precipitation of CsB $(C_6H_5)_4$ was used to measured the concentrations of Cs^+, the deviation of the results between Fajans method and gravimetry was estimated to be within ±0.5%.

3.2. The quaternary system of CsCl + $HoCl_3$ + HCl (~10%) + H_2O at T = 298.15 K

The solubility data of the quaternary system of CsCl + $HoCl_3$ + HCl (~10%) + H_2O and the central projection data on the trigonal

TABLE 2
Solubility data, in mass percent, for the ternary system CsCl + $HoCl_3$ + H_2O at T = 298.15 K and p = 0.1 MPa.[a]

No.	Composition of saturated solution[b]		Composition of wet residue		
	CsCl	$HoCl_3$	CsCl	$HoCl_3$	Solid phase[c]
1	66.47 [23]	0.00			A
2	57.44	7.79	94.89	1.07	A
3	51.40	14.64	95.80	1.55	A
4	45.64	21.53	93.70	2.83	A
5	42.72	26.62	92.17	4.01	A
6	41.75	27.89	66.55	19.36	A + C
7	41.97	27.86	54.08	27.95	A + C
8	37.04	31.18	46.11	36.24	C
9	34.53	32.77	45.16	36.99	C
10	31.95	34.12	44.73	37.23	C
11	29.72	35.61	43.66	37.50	C
12	27.04	37.29	43.63	37.86	C
13	19.23	42.19	29.26	44.94	C + D
14	19.70	42.08	25.71	47.69	C + D
15	19.94	42.03	20.07	52.98	C + D
16	16.41	43.17	3.90	65.72	D
17	8.97	46.42	1.97	67.03	D
18	0.00	50.15			D

[a] Standard uncertainties u are $u(T)$ = 0.1 K and $u(p)$ = 5 kPa. Expanded uncertainties U (w) for $HoCl_3$ and CsCl are ±0.20 mass% and ±0.55 mass%, respectively (0.95 level of confidence).
[b] Double saturation point (average): E_1: CsCl, 41.86%; $HoCl_3$, 27.87%. E_2: CsCl, 19.62%; $HoCl_3$, 42.10%.
[c] Compounds: A, CsCl; C, $Cs_2HoCl_5 \cdot 6H_2O$; D, $HoCl_6 \cdot 6H_2O$.