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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

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The equilibrium solubility of the quaternary system $CsCl-LuCl_3-HCl-H_2O$ was determined at 298.15 K, and the corresponding equilibrium diagram was constructed. The quaternary system is complicated with five equilibrium solid phases, CsCl, $Cs_4LuCl_7{\cdot}5H_2O$ (4:1 type), $Cs_9Lu_5Cl_{24}{\cdot}29H_2O$ (9:5 type), $Cs_2LuCl_5{\cdot}2H_2O$ (2:1 type), and $LuCl_3{\cdot}6H_2O$, of which the new compounds $Cs_4LuCl_7{\cdot}5H_2O$ and $Cs_9Lu_5Cl_{24}{\cdot}29H_2O$ were found to be congruently soluble and the new compound $Cs_2LuCl_5{\cdot}2H_2O$ was found to be incongruently soluble in the system. The three new compounds obtained were identified and characterized by the methods of X-ray diffraction, thermogravimetry, and differential thermogravimetry. The standard molar enthalpy of solution of $Cs_4LuCl_7{\cdot}5H_2O$, $Cs_9Lu_5Cl_{24}{\cdot}29H_2O$, and $Cs_2LuCl_5{\cdot}2H_2O$ in deionized water was measured to be (15.6 ± 0.3) $kJ{\cdot}mol^{-1}$, (−78.8 ± 0.6) $kJ{\cdot}mol^{-1}$, and (−62.5 ± 0.5) $kJ{\cdot}mol^{-1}$, respectively, by heat conduction microcalorimetry. Their standard molar enthalpies of formation were calculated to be (−4313.0 ± 2.1) $kJ{\cdot}mol^{-1}$, (−17871.6 ± 5.3) $kJ{\cdot}mol^{-1}$, and (−2526.5 ± 1.2) $kJ{\cdot}mol^{-1}$, respectively.

Introduction

In recent years, extensive studies on quaternary systems of $CsCl-RECl_3-HCl$ (13 %)−H_2O (RE = La, Pr, Nd, Sm, Y, Ce, Eu, Gd, Tm), $MCl-GdCl_3-HCl-H_2O$ (M = K, Rb), $CsCl-RECl_3-CH_3COOH$ (42 %)−H_2O (RE = La, Pr, Sm), and $MBr-REBr_3-HBr$ (13 %)−H_2O (M = K, Cs; RE = La, Pr, Nd, Sm, Dy) at 298.15 K have been reported.[1−16] Twenty-one new compounds were obtained from the systems: $RbGdCl_4{\cdot}4H_2O$ and $CsRECl_4{\cdot}nH_2O$ (RE = La, Ce, Pr, Nd) of the 1:1 type, $Cs_2RECl_5{\cdot}nH_2O$ (RE = Sm, Nd, Eu, Gd) of the 2:1 type, $Cs_3RECl_6{\cdot}nH_2O$ (RE = La, Ce, Pr) of the 3:1 type, $Cs_3RE_2Cl_9{\cdot}nH_2O$ (RE = Tm, Y) of the 3:2 type, $Cs_4RECl_7{\cdot}nH_2O$ (RE = Gd, Y) of the 4:1 type, $Cs_5EuCl_8{\cdot}14H_2O$ of the 5:1 type, $Cs_5RE_2Br_{11}{\cdot}nH_2O$ (RE = La, Pr, Nd, Sm) of the 5:2 type and $Cs_5Dy_3Br_{14}{\cdot}24H_2O$ of the 5:3 type. Optical investigation shows that some of them have upconversion fluorescence properties in the near-infrared region. Comparison of the quaternary systems finds that the quaternary systems $KX-REX_3-HX-H_2O$ (X = Cl, Br) is simple. However, the quaternary system $RbCl-GdCl_3-HCl-H_2O$ is simple when the concentration of HCl is below 22 % and complicated when HCl is over 22 %. For the three quaternary systems $CsCl-RECl_3-HCl-H_2O$ (La, Ce, Pr), their phase chemical reactions are very similar because they all have 3:1 and 1:1 type compounds. For the four quaternary systems $CsCl-RECl_3-HCl-H_2O$ (Nd, Sm, Eu, Gd), their phase chemical reactions have both similarities (all having 2:1 type compounds) and dissimilarities (all having various types of other compounds). Similarly, the quaternary systems $CsCl-RECl_3-HCl-H_2O$ (Y, Tm) also have both similarities and dissimilarities. For the rare alkali metal and rare earth chloride systems $CsCl-RECl_3-HCl-H_2O$ and $CsCl-RECl_3-CH_3COOH$ (42 %)−H_2O (RE = La, Pr, Nd, Sm), the effect of hydrochloric acid and acetic acid in both systems is the same. In the quaternary systems $CsBr-REBr_3-HBr-H_2O$, the phase chemical behavior of the systems is similar when RE is a light rare earth bromide. To compare the difference of the phase chemical relationship between rare alkali metals and rare earth halides in quaternary systems, the phase equilibrium relationship of the $CsCl-LuCl_3-HCl$ (10.06 %)−H_2O system at 298.15 K and properties of three new compounds established in the system have been investigated and their standard molar enthalpy of formation determined.

Experimental Section

Preparing Samples. All chemicals (CsCl) and solvents [H_2O and HCl (37 mass %)] were analytically pure and purchased from the market. $LuCl_3{\cdot}6H_2O$ was prepared by the reaction of Lu_2O_3 (99.99 mass %) with hydrochloric acid (37 mass % HCl). The composition of $LuCl_3{\cdot}6H_2O$ was confirmed by analyzing the Cl^- content by titration with a normal solution of silver nitrate and the Lu^{3+} content by titration with EDTA. The purity reached in this way was found to be 99.9 %. The analysis errors for those ions were relative ones and better than ± 0.23 %.

Investigations on the System at 298.15 K and Analysis Methods. For the investigation of the solubility of the $CsCl-LuCl_3-HCl$ (10.06 %)−H_2O quaternary system, different samples were first assigned on the phase diagram cross section on which the HCl mass percentage of the liquid phase was initially 10 mass %. Different weight ratios of CsCl, $LuCl_3{\cdot}6H_2O$, 37 mass % hydrochloric acid, and H_2O were mixed for each sample according to the mass percentage of the different points of the quaternary system $CsCl-LuCl_3-HCl-H_2O$ projected on the trigonal basal face $CsCl-LuCl_3-H_2O$. 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. All the sealed samples were put in a big water tank with a thermostat fixed at 298.15 K and agitated by an electrical stirrer. The precision of the temperature was ± 0.1 K. The acidity (HCl mass %) of the liquid-phase could deviate from 10 mass % in the first 2−3 days due to the gradual establishment of equilib-

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Table 1. Solubility Data of the Saturated Solution of the Quaternary System CsCl−LuCl$_3$−HCl (10.06 mass %)−H$_2$O at 298 ± 0.1 K, and Central Projection Data on the Trigonal Basal Face

	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 tetrahedral trigonal basal face		
no.	HCl	CsCl	LuCl$_3$	CsCl	LuCl$_3$	HCl	CsCl	LuCl$_3$	CsCl	LuCl$_3$	solid phase[b]
1	10.45	48.35	0.00	51.83	0.00						A
2	10.61	46.56	3.66	52.09	4.09	1.57	92.69	0.61	94.17	0.62	A
3	10.29	45.32	6.61	50.52	7.37	1.55	92.21	0.99	93.66	1.00	A
4	10.60	44.43	7.36	49.70	8.23	2.31	73.49	12.92	75.23	13.22	A + B
5	10.51	44.84	7.45	50.11	8.32	2.19	66.30	18.46	67.78	18.87	A + B
6	10.44	43.90	8.26	49.02	9.22	2.63	59.23	22.26	60.83	22.86	B
7	10.13	40.37	11.19	44.92	12.45	2.85	57.56	22.51	59.25	23.17	B
8	9.56	35.71	15.31	39.48	16.93	1.46	60.39	25.44	61.28	25.82	B
9	9.53	33.71	16.97	37.26	18.76	1.92	58.48	24.90	59.62	25.39	B
10	9.65	30.49	19.48	33.75	21.56	2.29	56.68	25.19	58.01	25.78	B
11	9.62	29.52	20.22	32.66	22.37	3.85	42.77	28.65	44.48	29.80	B + C
12	9.71	28.35	21.12	31.40	23.39	4.60	36.09	30.70	37.83	32.18	C
13	9.32	25.60	23.61	28.23	26.04	4.14	35.01	32.65	36.52	34.06	C
14	9.91	24.77	23.25	27.49	25.81	4.55	34.82	32.11	36.48	33.64	C
15	9.82	23.73	24.54	26.31	27.21	4.21	33.55	32.67	35.02	34.11	C
16	10.04	21.18	25.25	23.54	28.07	2.41	45.83	39.69	46.96	40.67	D
17	10.17	18.04	26.60	20.08	29.61	2.35	45.61	39.76	46.71	40.72	D
18	9.93	17.83	27.51	19.79	30.54	2.59	43.88	39.76	45.05	40.82	D
19	9.73	16.63	28.42	18.42	31.48	2.13	45.56	40.50	46.55	41.38	D
20	10.04	13.97	29.86	15.53	33.19	2.24	44.42	40.85	45.44	41.79	D
21	10.04	14.11	29.96	15.68	33.30	2.02	36.87	45.81	37.63	46.75	D + F
22	10.07	14.22	29.94	15.81	33.29	2.08	36.04	46.03	36.80	47.01	D + F
23	10.21	14.00	29.80	15.59	33.19	1.71	20.54	55.42	20.90	56.38	D + F
24	10.25	14.27	29.59	15.90	32.97	1.96	5.48	62.67	5.59	63.92	D + F
25	10.38	11.35	30.79	12.66	34.36	2.12	2.50	63.69	2.55	65.07	F
26	10.28	5.75	33.47	6.41	37.30	2.27	1.47	63.55	1.50	65.03	F
27	10.24	0.00	36.29	0.00	40.43						F

[a] Double saturation point (average): E$_1$, CsCl 49.90 %, LuCl$_3$ 8.27 %; E$_2$, CsCl 32.66 %, LuCl$_3$ 22.37 %; E$_3$, CsCl 15.74 %, LuCl$_3$ 33.19 %. [b] Compounds: A, CsCl; B, Cs$_4$LuCl$_7$·5H$_2$O; C, Cs$_9$Lu$_5$Cl$_{24}$·29H$_2$O; D, Cs$_2$LuCl$_5$·2H$_2$O; F, LuCl·6H$_2$O.

rium in the system. As a consequence, the liquid phase of the samples may vary from 10 mass % HCl and was subsequently adjusted to this concentration. This process was done repetitively until the HCl mass percentage was maintained at 10 mass %. The samples were sealed again and agitated continuously for another 5−6 days until a new equilibrium was attained. The composition of the saturated solutions and the corresponding solid (wet residue point) was established after the composition no longer changed.

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 was analyzed by titration with a solution of sodium hydroxide, (2) the total amount of Cl$^-$ by titration with a normal solution of silver nitrate, and (3) Lu^{3+} by titration with a normal solution of EDTA. (4) The amount of Cs$^+$ equals the amount that remains after that of total Cl$^-$ is subtracted from that of Cl$^-$ combined with Lu^{3+} and H$^+$. The composition of the saturated solution and the corresponding wet solid-phase points were determined by calculating the individual contents of HCl, LuCl$_3$, and CsCl according to the analysis results of the H$^+$, Lu^{3+}, and Cl$^-$ ions. The solid-phase compositions were determined graphically by the Schreinemakers method.[17] According to this method, every sample in a system consists of two parts, namely saturated liquid phase and the wet residue (the wet residue is the mixture of the saturated liquid and the established solid under the condition of equilibrium). For every sample, the saturated liquid phase, the wet residue, and the solid form a straight line with the saturated liquid and the solid being the two extreme points, and the wet residue is inside the line. When the contents of the saturated liquid and the wet residue are known, a radial can be drawn through these two phases. In a system, it is possible that the samples of the different liquid phases possess the same solid phases. Therefore, the radials of the same solid samples are all through one point. The content of this point is what we need to know about the solid. The results of analyses of each sample for the quaternary system are shown in Table 1. As shown in Table 1, the HCl mass percentage in the liquid phase of the quaternary system is an average of the acidity (10.06 %).

Equipment and Conditions. Thermal characterization of the new compounds was undertaken with a SDT Q600 V8.0 thermal analysis apparatus (TG-DTG) that worked with a heating rate of 10 K/min under a N$_2$ atmosphere with a flow rate of 100 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.

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. This microcalorimeter is composed of a precision temperature-controlling system, an electric energy calibration system, a constant-temperature thermostat, and a data-processing system. The working temperature of the calorimeter lies in the range of T = (77.15 to 473.15) K. It has a 16 cm^3 sample cell and a 16 cm^3 reference cell. The thermal effect can be determined through a thermoelectric pile composed of 496 thermocouples, which are converted to an electric voltage. The electric voltage is amplified through a microvolt amplifier, converted by the modulus, collected, and processed by a computer. The functions of controlling the temperature of the system (running on chemical and electrical calibrations) and a sensitivity calibration (measuring the thermal effect) and acquiring and storing the results are achieved by a program. The microcalorimeter is described in the literature.[18−19]

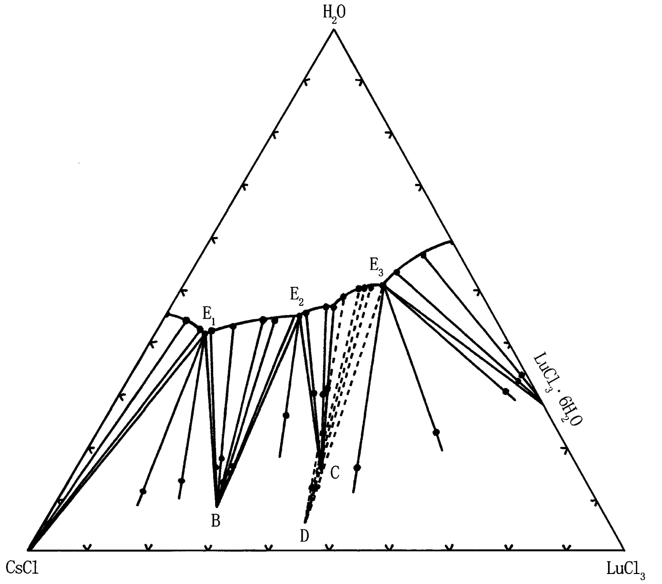

Figure 1. Solubility diagram of the quaternary system $CsCl-LuCl_3-HCl$ (10.06 mass %)$-H_2O$ projected on $CsCl-LuCl_3-HCl-H_2O$ at 298.15 K.

To check the performance of the RD496-III-2000 heat conduction microcalorimeter, the calorimetric constant at 298.15 K was determined 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 ± 0.043) $\mu V \cdot mW^{-1}$. The reliability of the calorimeter was verified by measuring the enthalpy of solution of KCl (s) in deionized water. The average experimental value of $\triangle_{sol}H_m$(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 lierature.[20] 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, and 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

$CsCl-LuCl_3-HCl$ (10.06 mass %)$-H_2O$ quaternary System at 298.15 K. The solubility data of the $CsCl-LuCl_3-HCl$ (10.06 mass %)$-H_2O$ quaternary system and the central projection data on the trigonal basal face of the $CsCl-LuCl_3-H_2O$ at 298.15 K are listed in Table 1 and are plotted in Figure 1. It can be seen that the phase diagram of the $CsCl-LuCl_3-HCl-H_2O$ quaternary system consists of five solubility curves that correspond to the equilibrium solid phases CsCl (A), $Cs_4LuCl_7 \cdot 5H_2O$ (B), $Cs_9Lu_5Cl_{24} \cdot 29H_2O$ (C), $Cs_2LuCl_5 \cdot 2H_2O$ (D) (dashed lines in Figure 1) and $LuCl_3 \cdot 6H_2O$ (F), respectively. The solid compounds $Cs_4LuCl_7 \cdot 5H_2O$ and $Cs_9Lu_5Cl_{24} \cdot 29H_2O$ are both congruently soluble and are obtained easily. $Cs_2LuCl_5 \cdot 2H_2O$ is incongruently soluble in the medium of ~10.06 mass % HCl, and the pure crystalloid is obtained only by the method of establishing phase equilibrium and is difficult to obtain by other methods. The composition of double saturation points that correspond to the equilibrium solid phases $Cs_9Lu_5Cl_{24} \cdot 29H_2O$ and $Cs_2LuCl_5 \cdot 2H_2O$ was not caught because of a close molar ratio between the two compounds. The three new compounds $Cs_4LuCl_7 \cdot 5H_2O$, $Cs_9Lu_5Cl_{24} \cdot 29H_2O$, and $Cs_2LuCl_5 \cdot 2H_2O$ obtained from this system were analyzed by a titration method. The compositions in mass percent are 64.39 % CsCl and 26.99 % $LuCl_3$ in $Cs_4LuCl_7 \cdot 5H_2O$ (theoretical, 64.46 % CsCl, 26.93 % $LuCl_3$), 44.21 % CsCl and 40.65 % $LuCl_3$ in $Cs_9Lu_5Cl_{24} \cdot 29H_2O$ (theoretical, 44.00 % CsCl, 40.84 % $LuCl_3$), and 51.32 % CsCl and 43.15 % $LuCl_3$ in $Cs_2LuCl_5 \cdot 2H_2O$ (theoretical, 51.48 % CsCl, 43.01 % $LuCl_3$), respectively. This indicates that the formation of the solid compounds determined by the Schreinemakers method is reliable. It should be noted that the 4:1 type compounds could only be obtained in the quaternary

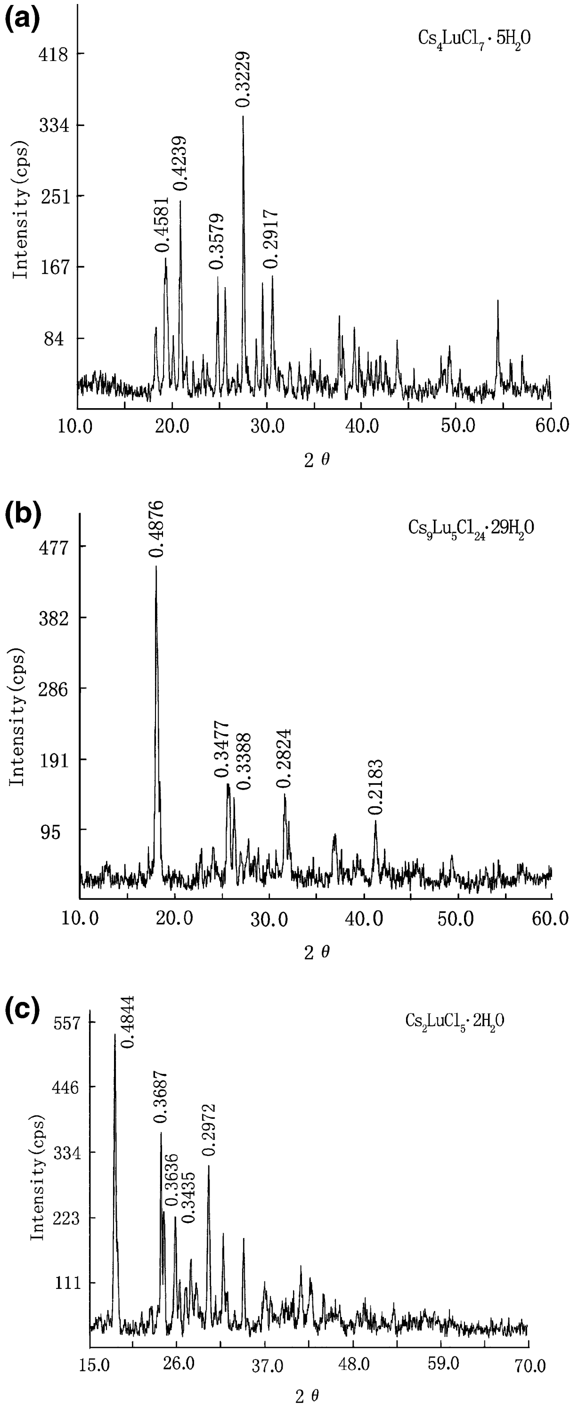

Figure 2. X-ray powder diffraction spectrum of (a) $Cs_4LuCl_7 \cdot 5H_2O$, (b) $Cs_9Lu_5Cl_{24} \cdot 29H_2O$, and (c) $Cs_2LuCl_5 \cdot 2H_2O$.

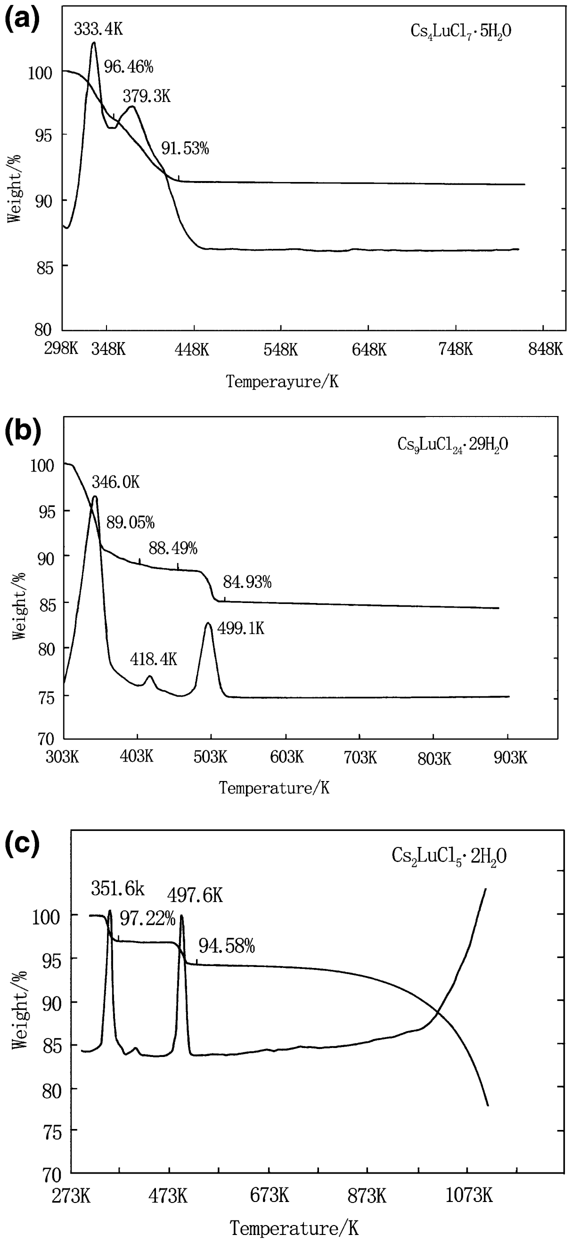

Figure 3. Thermogravimetric curves of (a) $Cs_4LuCl_7·5H_2O$, (b) $Cs_9Lu_5Cl_{24}·29H_2O$, and (c) $Cs_2LuCl_5·2H_2O$.

systems $CsCl-RECl_3-HCl-H_2O$ (RE = Gd, Y),[6,9] while the 2:1 type compounds could only be obtained in the quaternary systems $CsCl-RECl_3-HCl-H_2O$ (RE = Sm, Nd, Eu, Gd).[3,5,8,9] In the present system, both 4:1 type and 2:1 type compounds were obtained, and the 9:5 type compound that was not reported up to now was also obtained, indicating that the phase behavior of $LuCl_3$ and $RECl_3$ (Gd, Y, Sm, Nd, Eu) in the present system exhibits both similarity and dissimilarity.

Characterization of $Cs_4LuCl_7·5H_2O$, $Cs_9Lu_5Cl_{24}·29H_2O$, and $Cs_2LuCl_5·2H_2O$. X-ray powder diffraction data and patterns of the $Cs_4LuCl_7·5H_2O$, $Cs_9Lu_5Cl_{24}·29H_2O$, and $Cs_2LuCl_5·2H_2O$ compounds obtained are shown in Figure 2. They are obviously different from the literature XRD data of the two starting salts: CsCl, d (nm) = 0.2917 (100), 0.4120 (45), 0.1683 (25) and $LuCl_3$, d (nm) = 0.2690 (100), 0.1935 (100), 0.5840 (80), 0.3300 (80), 0.1495 (80), 0.1184 (80). This demonstrates that the three compounds are new.

TG-DTG data for the three compounds is presented in Figure 3. The curve for the compound $Cs_4LuCl_7·5H_2O$, shows that there are two obvious mass-loss steps in the temperature range (311 to 448) K and the total mass-loss value is in agreement with theoretical dehydration data. The curve for the compound $Cs_9Lu_5Cl_{24}·29H_2O$ shows that there are three obvious mass-loss steps in the temperature range (323 to 518) K and the total mass-loss value is basically in accordance with the dehydration of this compound. The same investigation was performed for $Cs_2LuCl_5·2H_2O$. One observes that on the curve, the two obvious mass-loss steps are in the temperature range (334 to 513) K, and 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 three compounds are as follows:

$$Cs_4LuCl_7·5H_2O \xrightarrow[(311\text{ to }353)\text{ K}]{-2H_2O} Cs_4LuCl_7·3H_2O \xrightarrow[(353\text{ to }448)\text{ K}]{-3H_2O} Cs_4LuCl_7 \quad (1)$$

$$Cs_9Lu_5Cl_{24}·29H_2O \xrightarrow[(323\text{ to }409)\text{ K}]{-21H_2O} Cs_9Lu_5Cl_{24}·8H_2O \xrightarrow[(409\text{ to }444)\text{ K}]{-H_2O} Cs_9Lu_5Cl_{24}·7H_2O \xrightarrow[(444\text{ to }518)\text{ K}]{-7H_2O} Cs_9Lu_5Cl_{24} \quad (2)$$

$$Cs_2LuCl_5·2H_2O \xrightarrow[(334\text{ to }373)\text{ K}]{-H_2O} Cs_2LuCl_5·H_2O \xrightarrow[(473\text{ to }513)\text{ K}]{-H_2O} Cs_2LuCl_5 \quad (3)$$

Enthalpies of Solution. The molar enthalpy of solution $\Delta_{sol}H_m(1)$, $\Delta_{sol}H_m(2)$, and $\Delta_{sol}H_m(3)$ of $Cs_4LuCl_7·5H_2O$, $Cs_9Lu_5Cl_{24}·29H_2O$, and $Cs_2LuCl_5·2H_2O$ are (15.6 ± 0.3) $kJ·mol^{-1}$, (−78.8 ± 0.6) $kJ·mol^{-1}$, and (−62.5 ± 0.5) $kJ·mol^{-1}$ in water at 298.15 K, respectively. 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 = 5); x_i is the experimental value of each repeated measurement; and $\bar{x}$ is the mean value.

Table 2. Molar Enthalpies of Solution of $\Delta_{sol}H_m(1)$, $\Delta_{sol}H_m(2)$, $\Delta_{sol}H_m(3)$ in deionized water at 298.15 K[a]

no.	m mg	$\Delta_{sol}H$ mJ	$\Delta_{sol}H_m(1)$ $kJ·mol^{-1}$	m mg	$\Delta_{sol}H$ mJ	$\Delta_{sol}H_m(2)$ $kJ·mol^{-1}$	m mg	$\Delta_{sol}H$ mJ	$\Delta_{sol}H_m(3)$ $kJ·mol^{-1}$
1	57.42	856.210	15.580	95.67	−2204.194	−79.355	18.22	−1733.900	−62.241
2	55.27	812.206	15.354	97.52	−2246.535	−79.345	18.12	−1736.011	−62.661
3	59.12	910.340	16.087	95.33	−2191.350	−79.174	18.11	−1743.923	−62.981
4	54.08	789.988	15.262	97.15	−2201.347	−78.034	18.31	−1724.354	−61.595
5	59.31	902.494	15.897	96.21	−2185.532	−78.231	18.17	−1744.563	−62.796
mean			15.6 ± 0.3			−78.8 ± 0.6			−62.5 ± 0.5[b]

[a] In each experiment, 5.0 cm^3 water was used. [b] Uncertainty is twice the standard deviation of the mean.

Standard Molar Enthalpies of Formation. The molar enthalpies of formation of $Cs_4LuCl_7{\cdot}5H_2O$, $Cs_9Lu_5Cl_{24}{\cdot}29H_2O$, and $Cs_2LuCl_5{\cdot}2H_2O$ can be calculated as shown in following equations:

$$\triangle_f H_m^{\Theta}(Cs_4LuCl_7{\cdot}5H_2O)\ (s) = 4\triangle_f H_m^{\Theta}(Cs^+)\ (aq) + \triangle_f H_m^{\Theta}(Lu^{3+})\ (aq) + 7\triangle_f H_m^{\Theta}(Cl^-)\ (aq) + 5\triangle_f H_m^{\Theta}(H_2O)\ (l) - \triangle_{sol} H_m^{\Theta}(Cs_4LuCl_7{\cdot}5H_2O)\ (s)$$

$$\triangle_f H_m^{\Theta}(Cs_9Lu_5Cl_{24}{\cdot}29H_2O)\ (s) = 9\triangle_f H_m^{\Theta}(Cs^+)\ (aq) + 5\triangle_f H_m^{\Theta}(Lu^{3+})\ (aq) + 24\triangle_f H_m^{\Theta}(Cl^-)\ (aq) + 29\triangle_f H_m^{\Theta}(H_2O)\ (l) - \triangle_{sol} H_m^{\Theta}(Cs_9Lu_5Cl_{24}{\cdot}29H_2O)\ (s)$$

$$\triangle_f H_m^{\Theta}(Cs_2LuCl_5{\cdot}2H_2O)\ (s) = 2\triangle_f H_m^{\Theta}(Cs^+)\ (aq) + \triangle_f H_m^{\Theta}(Lu^{3+})\ (aq) + 5\triangle_f H_m^{\Theta}(Cl^-)\ (aq) + 2\triangle_f H_m^{\Theta}(H_2O)\ (l) - \triangle_{sol} H_m^{\Theta}(Cs_2LuCl_5{\cdot}2H_2O)\ (s)$$

The standard molar enthalpies of formation of Cs^+, Cl^-, and H_2O were taken from the CODATA key values,[21] namely, (−258.28 ± 0.50) $kJ{\cdot}mol^{-1}$, (−167.16 ± 0.10) $kJ{\cdot}mol^{-1}$, and (−285.83 ± 0.042) $kJ{\cdot}mol^{-1}$ for Cs^+, Cl^-, and H_2O, respectively. Lu^{3+} was taken from the NBS table,[22] (−665.00 ± 0.10) $kJ{\cdot}mol^{-1}$. Through the use of these schemes and data, the standard molar enthalpies of formation of $Cs_4LuCl_7{\cdot}5H_2O$, $Cs_9Lu_5Cl_{24}{\cdot}29H_2O$, and $Cs_2LuCl_5{\cdot}2H_2O$ were calculated to be (−4313.0 ± 2.1) $kJ{\cdot}mol^{-1}$, (−17871.6 ± 5.3) $kJ{\cdot}mol^{-1}$ and (−2526.6 ± 1.2) $kJ{\cdot}mol^{-1}$.

Conclusion

The equilibrium solubility of the quaternary system $CsCl-LuCl_3-HCl$ (10.06 mass %)$-H_2O$ at 298.15 K was measured, and the corresponding phase diagram was prepared to search for new compounds and to obtain the equilibrium data for rare alkali metal chloride/rare earth metal chloride in aqueous solution. The compositions of the solid phases were determined by the Schrienemakers method and confirmed by chemical analysis. Both the compounds $Cs_4LuCl_7{\cdot}5H_2O$ and $Cs_9Lu_5Cl_{24}{\cdot}29H_2O$ are congruently soluble, and $Cs_2LuCl_5{\cdot}2H_2O$ is incongruently soluble in the quaternary system. Through measuring the standard molar enthalpy of solution, the standard molar enthalpies of formation of the three new compounds were calculated.

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