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Phase Equilibrium System of $RbCl-SmCl_3-HCl$(12.84, 22.66 % by Mass)$-H_2O$ at 298.15 K and Standard Molar Enthalpy of Formation of $RbSmCl_4\cdot 4H_2O$

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Solubility of the quaternary system $RbCl-SmCl_3-HCl$(12.84, 22.66 % by mass)$-H_2O$ was determined at 298.15 K, and corresponding equilibrium diagrams were constructed. The quaternary system is complicated with three equilibrium solid phases RbCl, $RbSmCl_4\cdot 4H_2O$ (1:1 type), and $SmCl_3\cdot 6H_2O$. The solubilities of RbCl, $RbSmCl_4\cdot 4H_2O$, and $SmCl_3\cdot 6H_2O$ decreased with an increase of the concentration of HCl. The crystallization field decreased for RbCl and $SmCl_3\cdot 6H_2O$ and increased for $RbSmCl_4\cdot 4H_2O$ with an increase in the HCl concentration. The new solid-phase compound $RbSmCl_4\cdot 4H_2O$ was found to be uncongruently soluble in the system. The compound $RbSmCl_4\cdot 4H_2O$ was characterized by the methods of X-ray diffraction, thermogravimetry, and differential thermogravimetry. The compound loses its crystal water by one step at (359 to 457) K. The standard molar enthalpy of solution of $RbSmCl_4\cdot 4H_2O$ in deionized water was measured to be $-(29.40 \pm 0.26)$ $kJ\cdot mol^{-1}$ by heat conduction microcalorimetry. Its standard molar enthalpy of formation was calculated to be $-(2725.3 \pm 1.0)$ $kJ\cdot mol^{-1}$.

Introduction

Equilibrium phase diagrams of quaternary systems of $CsCl-RECl_3-HCl$(13 %)$-H_2O$ (RE = La, Pr, Nd, Sm, Y, Ce, Eu, Gd, Tm, Lu) at 298.15 K have been investigated. The corresponding solubilities were determined and reported in the literature.[1−9] In these systems, in addition to the initial components CsCl and $RECl_3\cdot nH_2O$ ($n = 6, 7$), 19 new solid compounds were obtained from the systems: they are $CsRECl_4\cdot nH_2O$ (RE = La Ce, Pr, Nd), $Cs_2RECl_5\cdot nH_2O$ (RE = Sm, Nd, Eu, Gd, Lu), $Cs_3RECl_6\cdot nH_2O$ (RE = La, Ce, Pr), $Cs_3RE_2Cl_9\cdot nH_2O$ (RE = Tm, Y), $Cs_4RECl_7\cdot nH_2O$ (RE = Gd, Y, Lu), $Cs_5EuCl_8\cdot 14H_2O$, and $Cs_9Lu_5Cl_{24}\cdot 29H_2O$. Moreover, the research results on these systems showed that the phase chemical behavior of rare earth trichlorides with CsCl has both similarities and dissimilarities. These discoveries sparked us to study further phase equilibria systematically and find new compounds formed in the aqueous systems that had not been reported earlier in the related literature.

As a part of the systematic investigation on the quaternary systems of rare earth chlorides, phase equilibria of the $MCl-GdCl_3-HCl$(13.26 %, 21.65 %)$-H_2O$ (M = K, Rb) at 293.15 K and $RbCl-RECl_3-HCl$(∼13 %)$-H_2O$ (RE = La, Ce) at 298.15 K have been reported.[10−12] Wang et al.[10] reported the presence of two equilibrium solid-phase regions (KCl and $GdCl_3\cdot 6H_2O$) in the $KCl-GdCl_3-HCl-H_2O$ quaternary system. However, for the quaternary system $RbCl-GdCl_3-HCl-H_2O$, two equilibrium solid phases (RbCl and $GdCl_3\cdot 6H_2O$) were observed when the concentration of HCl was 13.26 %, but the presence of three equilibrium solid phases (RbCl, $RbGdCl_4\cdot 4H_2O$, and $GdCl_3\cdot 6H_2O$) was confirmed when HCl was 21.65 %. The compound $RbGdCl_4\cdot 4H_2O$ is uncongruently soluble, and its crystallization field is very small in the medium of ∼21.65 % HCl by mass. We re-examined the $RbCl-CeCl_3-HCl-H_2O$[11] and $RbCl-LaCl_3-HCl-H_2O$[12] systems and confirmed that the $RbCl-CeCl_3-HCl-H_2O$ system is composed of three equilibrium solid phases: RbCl, $RbCeCl_4\cdot 4H_2O$, and $CeCl_3\cdot 7H_2O$, respectively. For the $RbCl-LaCl_3-HCl-H_2O$ system, three similar equilibrium solid phases (RbCl, $RbLaCl_4\cdot 4H_2O$, and $LaCl_3\cdot 7H_2O$) were observed. The compounds $RbCeCl_4\cdot 4H_2O$ and $RbLaCl_4\cdot 4H_2O$ are congruently soluble, and both of their crystallization fields are big in the medium of ∼13 % HCl by mass. This indicates differences and similarity in behavior of La, Ce, and Gd trichlorides in aqueous salt systems with RbCl. To further contrast the difference of the phase chemical relationship of rare alkali metal and rare-earth chloride in aqueous salt systems and find more phase equilibrium information on the $RbCl-RECl_3-HCl-H_2O$ quaternary systems, it is necessary for us to further study the phase equilibria in systems containing $RbCl-SmCl_3-HCl-H_2O$ systematically. The present paper is concerned with the solubility and phase equilibrium relations of the $RbCl-SmCl_3-HCl$(12.84, 22.66 %)$-H_2O$ system at 298.15 K and related measurement of properties of a new solid-phase compound established in the system.

Experimental Section

Preparing Samples. All chemicals (RbCl) and solvents [H_2O and HCl (37 % by mass)] were analytically pure and commercially available. $SmCl_3\cdot 6H_2O$ was prepared by the reaction of Sm_2O_3 (99.99 % by mass) with hydrochloric acid (37 % HCl by mass). For detailed information on the preparation of $SmCl_3\cdot 6H_2O$, see ref 13. The composition of $SmCl_3\cdot 6H_2O$ was confirmed by analyzing the Cl^- content by titration with a normal solution of silver nitrate and the Sm^{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 ± 0.21 %.

Investigations on the System at 298.15 K and Analysis Methods. The method of investigation of the solubility of the $RbCl-SmCl_3-HCl$(12.84, 22.66 %)$-H_2O$ quaternary system

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Table 1. Solubility Data of the Saturated Solution of the Quaternary System $RbCl-SmCl_3-HCl$(12.84, 22.66 %)$-H_2O$ at (298.15 ± 0.1) K and Central Projection Data on the Trigonal Basal Face $RbCl-SmCl_3-H_2O$

	composition of solution (% weight)					composition of residue (% weight)					
	composition in the tetrahedral			composition in the trigonal basal face[a]		composition in the tetrahedral			composition in the trigonal basal face		
no.	HCl	Sm_3Cl	RbCl	$SmCl_3$	RbCl	HCl	$SmCl_3$	RbCl	$SmCl_3$	RbCl	solid phase[b]
					w(HCl) = 12.84 %						
1	12.10	0.00	24.29	0.00	27.63	---	---	---	---	---	A
2	12.85	3.20	22.52	3.67	25.84	2.69	0.73	83.78	0.75	86.09	A
3	12.40	6.76	21.17	7.72	24.17	2.02	1.56	87.43	1.59	89.23	A
4	12.35	10.56	19.26	12.05	21.97	2.79	2.31	81.67	2.38	84.01	A
5	13.07	13.19	17.55	15.17	20.09	2.70	2.70	83.50	2.77	85.82	A
6	12.90	16.33	17.00	18.75	19.52	2.30	3.00	85.17	3.07	87.17	A
7	12.62	18.24	17.31	20.87	19.81	2.59	3.69	82.74	3.79	84.94	A
8	12.68	19.12	17.30	21.89	19.81	3.34	14.67	65.34	15.17	67.59	A+B
9	12.82	19.04	16.79	21.84	19.26	3.10	46.34	26.39	47.82	27.23	A+B
10	12.85	19.25	16.27	22.09	18.67	3.35	48.09	24.21	49.76	25.05	B
11	12.84	19.98	15.01	22.92	17.22	2.94	48.56	24.23	50.03	24.96	B
12	12.71	20.72	14.00	23.74	16.04	2.42	50.98	22.34	52.24	22.89	B+C
13	12.54	21.26	14.05	24.31	16.06	2.02	54.43	18.29	55.56	18.67	B+C
14	13.21	22.87	9.81	26.08	11.19	1.75	62.00	1.98	63.11	2.01	C
15	13.11	23.30	5.30	26.81	6.10	2.55	60.99	1.50	62.58	1.54	C
16	13.32	23.41	3.77	27.01	3.35	2.81	60.23	0.85	61.97	0.87	C
17	13.42	24.24	1.15	27.99	1.33	1.88	63.13	0.60	64.34	0.61	C
18	13.29	24.47	0.00	28.22	0.00	---	---	---	---	---	C
					w(HCl) = 22.66 %						
1	23.09	0.00	15.41	0.00	20.04	---	---	---	---	---	A
2	22.31	3.58	15.37	4.61	19.78	5.13	0.84	81.02	0.88	85.40	A
3	22.20	5.37	15.60	6.90	20.05	3.63	9.40	76.29	9.75	79.16	A+B
4	22.11	5.50	15.47	7.06	19.86	3.32	32.10	47.03	33.20	48.64	A+B
5	22.33	5.36	15.33	6.90	19.76	6.24	36.61	31.20	39.05	33.28	A+B
6	22.35	5.25	15.14	6.76	19.50	6.00	42.88	23.90	45.62	25.42	B
7	22.82	5.96	12.71	7.72	16.47	5.38	45.15	23.49	47.72	24.82	B
8	22.67	7.49	9.80	9.68	12.67	5.07	52.43	25.22	55.23	26.57	B
9	23.40	6.77	9.66	8.84	12.61	5.44	48.71	16.17	51.51	17.10	B+C
10	23.14	7.04	9.36	9.16	12.18	3.37	57.70	8.27	59.71	8.56	B+C
11	23.06	7.20	7.14	9.36	9.28	3.73	60.02	1.54	62.34	1.60	C
12	22.37	9.41	3.72	12.12	4.79	3.88	59.56	0.41	61.96	0.43	C
13	22.77	10.10	0.00	13.08	0.00	---	---	---	---	---	C

[a] Double saturation point (average): HCl = 12.84 %: E_1: RbCl 19.53 %, $SmCl_3$ 21.86 %; E_2: RbCl 16.05 %, $SmCl_3$ 24.02 %. HCl = 22.66 %: E_1: RbCl 19.89 %, $SmCl_3$ 6.95 %; E_2: RbCl 12.39 %, $SmCl_3$ 9.00 %. [b] Compounds: A, RbCl; B, $RbSmCl_4 \cdot 4H_2O$; C, $SmCl_3 \cdot 6H_2O$.

has been previously reported.[9] 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 (5 to 6) days.

The saturated solutions and the corresponding wet solid phases 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 concentration of Sm^{3+} was determined by titration with a normal solution of EDTA, (3) the concentrations of Rb^+ were determined by gravimetry with the precipitation of $RbB(C_6H_5)_4$, (4) the concentration of Cl^- by titration with a normal solution of silver nitrate. The composition of the saturated solution and the corresponding wet solid-phase points were determined by calculating the individual contents of HCl, $SmCl_3$, and RbCl according to the analysis results of the H^+, Sm^{3+}, and Rb^+ ions. The solid-phase compositions in the system were determined graphically by the well-known wet residue method of Schreinemaker[14] and checked by chemical analysis. The new solid-phase compound was further demonstrated by XRD, 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 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.[9,15]

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 lierature.[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 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.

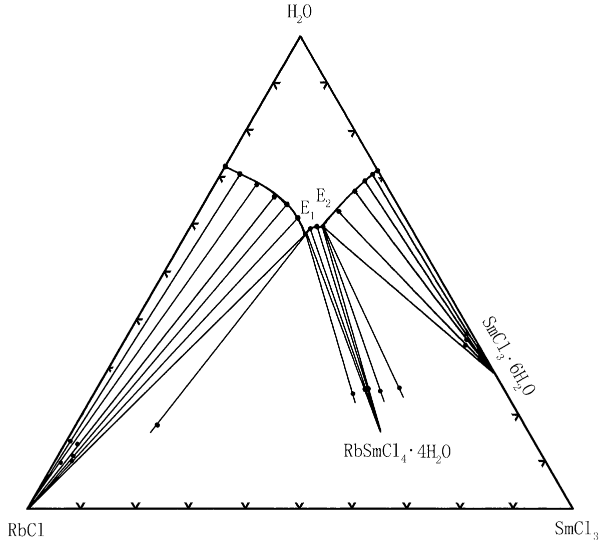

Figure 1. Solubility diagram of the quaternary system $RbCl-SmCl_3-HCl(12.84\ \%)-H_2O$ projected on $RbCl-SmCl_3-H_2O$ at (298.15 ± 0.1) K.

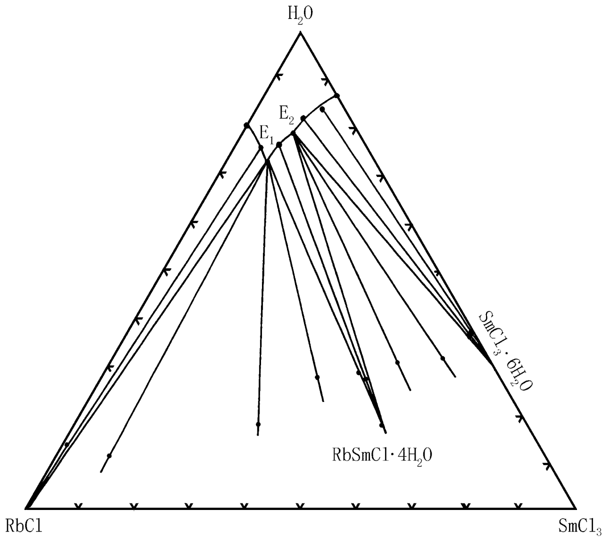

Figure 2. Solubility diagram of the quaternary system $RbCl-SmCl_3-HCl(22.66\ \%)-H_2O$ projected on $RbCl-SmCl_3-H_2O$ at (298.15 ± 0.1) K.

The thermal effect was then recorded automatically on a computer. The total time required for complete dissolution was about 0.3 h.

Results and Discussion

RbCl−SmCl₃−HCl(12.84, 22.66 %)−H₂O Quaternary System at 298.15 K. The solubility data of the $RbCl-SmCl_3-HCl(12.84, 22.66\ \%)-H_2O$ quaternary system and the central projection data on the trigonal basal face of $RbCl-SmCl_3-H_2O$ at 298.15 K are listed in Table 1 and plotted in Figure 1 and Figure 2. It can be seen that the phase diagrams of the $RbCl-SmCl_3-HCl(12.84\ \%)-H_2O$ and $RbCl-SmCl_3-HCl(22.66\ \%)-H_2O$ quaternary systems all consist of three solubility curves. In addition to the initial components RbCl (A) and $SmCl_3 \cdot 6H_2O$ (C), one new compound $RbSmCl_4 \cdot 4H_2O$ (B) (1:1 type) crystallized from the saturated solutions. The solid compound $RbSmCl_4 \cdot 4H_2O$ is uncongruently soluble in the medium of (∼12.84 and ∼22.66) % HCl by mass. The solubility data of all compounds decreased when the concentration of HCl increased. The larger the HCl mass percentage included in the equilibrium liquid phase, the smaller the solubility of the compounds. Comparing Figure 1 and Figure 2, the crystallization fields of RbCl and $SmCl_3 \cdot 6H_2O$ decreased, but the crystallization field of $RbSmCl_4 \cdot 4H_2O$ increased with an increase of the concentration of HCl in the equilibrium liquid phase. The new compound $RbSmCl_4 \cdot 4H_2O$ obtained from the system was analyzed by a titration method. Its composition by mass is Rb (19.07 %), Sm (33.49 %), and Cl (31.61 %) in $RbSmCl_4 \cdot 4H_2O$. The value is in agreement with theoretical data (19.00 % Rb, 33.44 % Sm, and 31.53 % Cl).

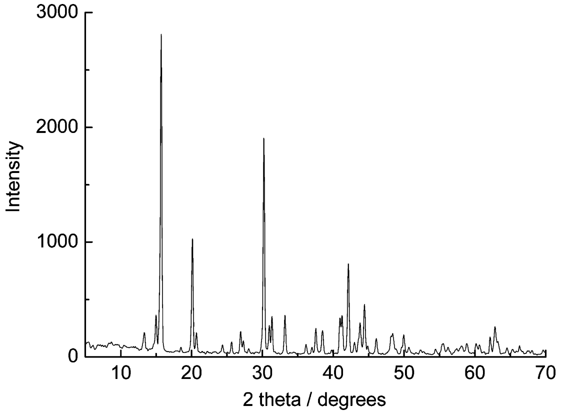

Figure 3. X-ray powder diffraction spectrum of $RbSmCl_4 \cdot 4H_2O$.

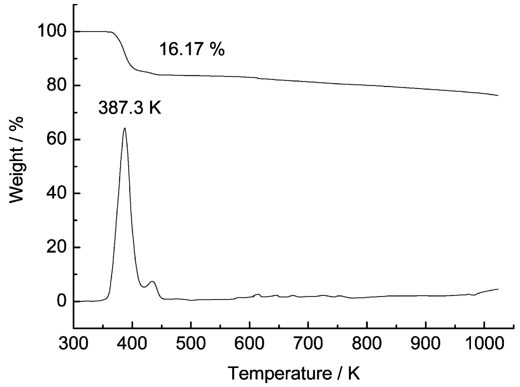

Figure 4. Thermogravimetric curve of $RbSmCl_4 \cdot 4H_2O$.

Comparing the reported quaternary systems[10−12] with the present quaternary system, for the three quaternary systems $RbCl-RECl_3-HCl(\sim 13\ \%)-H_2O$ (RE = La, Ce, Sm), their phase chemical reactions have comparability because they all have a 1:1 type compound. The new solid compounds $RbLaCl_4 \cdot 4H_2O$ and $RbCeCl_4 \cdot 4H_2O$ are congruently soluble, and their phase regions are large; however, the new solid compound $RbSmCl_4 \cdot 4H_2O$ is uncongruently soluble, and its phase region is small. This shows that $SmCl_3$ exhibits some differences from $LaCl_3$ and $CeCl_3$ with RbCl in its phase chemical behavior. For the quaternary systems $RbCl-GdCl_3-HCl(\sim 23\ \%)-H_2O$ and $RbCl-SmCl_3-HCl(\sim 23\ \%)-H_2O$, their phase chemical reactions are similar.

Characterization of RbSmCl₄·4H₂O. The X-ray powder diffraction pattern of the $RbSmCl_4 \cdot 4H_2O$ compound obtained is shown in Figure 3. The important X-ray data of the compounds are d (nm) = 0.5640 (100), 0.4410 (37), 0.2959 (78), 0.2144 (35), and 0.2039 (18). They are neither the same as RbCl and $SmCl_3 \cdot 6H_2O$ nor the simple superposition of RbCl and $SmCl_3 \cdot 6H_2O$. This demonstrates that $RbSmCl_4 \cdot 4H_2O$ is formed from a reaction between RbCl and $SmCl_3 \cdot 6H_2O$.

TG-DTG data for the compound are presented in Figure 4. The curve for the compound $RbSmCl_4 \cdot 4H_2O$ shows that there

Table 2. Molar Enthalpies of Solution of $RbSmCl_4 \cdot 4H_2O$ in Deionized Water at 298.15 K[a]

no.	m/g	Q_s mJ	$\Delta_{sol}H_m^{\ominus}$ ($kJ \cdot mol^{-1}$)
1	0.04978	−3226.2	−29.144
2	0.05080	−3353.6	−29.710
3	0.05049	−3260.5	−29.040
4	0.05030	−3330.7	−29.777
5	0.04950	−3211.0	−29.171
6	0.04965	−3264.9	−29.571
mean[b]	$\Delta_{sol}H_m^{\ominus} = -(29.40 \pm 0.26)\ kJ \cdot mol^{-1}$		

[a] In each experiment, 8.0 cm^3 water was used. [b] Uncertainty is twice the standard deviation of the mean.

is one obvious mass-loss step in the temperature range (359 to 457) K, and the mass-loss value (16.17 %) is in agreement with theoretical dehydration data (16.02 %). This indicates that the compound loses its crystal water by one step at (359 to 457) K. 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 $RbLSmCl_4 \cdot 4H_2O$ in water is $-(29.40 \pm 0.26)\ kJ \cdot mol^{-1}$ at 298.15 K. The values are listed in Table 2, in which m is the mass of sample and $\Delta_{sol}H_m$ 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 $RbSmCl_4 \cdot 4H_2O$ can be calculated as shown in the following equation

$$\Delta_f H_m^{\ominus}(s) = \Delta_f H_m^{\ominus}(Rb^+)(aq) + \Delta_f H_m^{\ominus}(Sm^{3+})(aq) + 4\Delta_f H_m^{\ominus}(C1^-)(aq) + 4\Delta_f H_m^{\ominus}(H_2O)(l) - \Delta_{sol}H_m^{\ominus}(RbSmC1_4{\cdot}4H_2O)(s)$$

The standard molar enthalpies of formation of Rb^+, Sm^{3+}, Cl^-, and H_2O were taken from the NBS tables,[17] namely, $-(251.17 \pm 0.56)\ kJ \cdot mol^{-1}$, $-(691.6 \pm 0.7)\ kJ \cdot mol^{-1}$, $-(167.159 \pm 0.1)\ kJ \cdot mol^{-1}$, and $-(285.83 \pm 0.042)\ kJ \cdot mol^{-1}$ for Rb^+, Sm^{3+}, Cl^-, and H_2O, respectively. Using these schemes and data, the standard molar enthalpy of formation of $RbSmCl_4 \cdot 4H_2O$ was calculated to be $-(2725.3 \pm 1.0)\ kJ \cdot mol^{-1}$.

Conclusion

The solubility of the quaternary system $RbCl-SmCl_3-HCl(12.84, 22.66\ \%)-H_2O$ at 298.15 K was measured, and the corresponding phase diagrams were prepared to search for new compounds and obtain equilibrium data for rubidium chloride/samarium chloride in aqueous solution. The composition of a new solid phase was determined by the Schrienemaker method and confirmed by chemical analysis. The compound $RbSmCl_4 \cdot 4H_2O$ is uncongruently soluble in a medium of (~12.84 and 22.66) % HCl. Through measuring the standard molar enthalpy of solution, the standard molar enthalpy of formation of the new compound $RbSmCl_4 \cdot 4H_2O$ was calculated.

Comparing the reported quaternary systems $RbCl-RECl_3-HCl(\sim 13\ \%)-H_2O$ (RE = La, Ce, Gd) with the present quaternary system, the phase behavior of La and Ce with Sm has both similarities and differences. The phase behavior for Gd and Sm is similar in the medium of ~23 % HCl.

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