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Solubility of YF_3, CeF_3, PrF_3, NdF_3, and DyF_3 in Solutions Containing Sulfuric and Phosphoric Acids

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Abstract—The solubility of YF_3, CeF_3, PrF_3, NdF_3, and DyF_3 in solutions containing 0–4.496% mol/L (0–35 wt %) of H_2SO_4 and 0–27.6 g/L of H_3PO_4 (0–20 g/L of P_2O_5) at 20°C was determined. Higher solubility in sulfuric acid solutions compared to that in hydrochloric and phosphoric acid solutions was attributed to the formation of fluorosulfate complexes $M_2(SO_4)F_4$ (M = Y, Ce, Pr, Nd, Dy). The effect of minor concentrations of the phosphate ions on the solubility of YF_3, CeF_3, PrF_3, NdF_3, and DyF_3 in sulfuric acid solutions and the effect of fluoride ions on the recovery of lanthanides during sulfuric acid leaching from the phosphohemihydrate were discussed.

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The product called phosphohemihydrate, which is formed upon processing of Khibiny apatite concentrate into mineral fertilizers, is a promising industry-produced raw material for lanthanides [1]. Although the main bulk of lanthanides is contained in phosphohemihydrate as also hydrated orthophosphates [2], phosphohemihydrate also includes substantial amounts of sodium and potassium fluorosilicates, which are hydrolyzed to give fluoride ions; this may result in the formation of poorly soluble lanthanide fluorides. In view of the development of a sulfuric acid process for the recovery of lanthanides from phosphohemihydrate [3], knowledge of the solubility of lanthanide fluorides in solutions containing sulfuric and phosphoric acids is of considerable practical interest.

Data on the solubility of lanthanide fluorides in mineral acids, in particular, in sulfuric and phosphoric acids, are scarce. It was found that the solubility of LaF_3 and YbF_3 in solutions containing 0–2.355 mol/L (0–20 wt %) of H_2SO_4 and 0–27.6 g/L of H_3PO_4 (0–20 g/L of P_2O_5) is much higher than their solubility in monobasic acids, which was attributed to the formation of complex fluorosulfate anions SO_4F^{3-} [4].

In phosphoric acid solutions, LaF_3 is almost insoluble, whereas YbF_3 has a substantial solubility, which increases with increasing H_3PO_4 concentration. This was attributed to the fact that lanthanum precipitates from dilute solutions of phosphoric acid as $LaPO_4$, whereas ytterbium apparently forms more soluble hydrated compounds ($YbPO_4 \cdot 4H_2O$ or $YbPO_4 \cdot 2H_2O$) in dilute solutions of H_3PO_4 [4].

This work continues studies on the solubility of lanthanide fluorides with the concentration range of sulfuric acid being extended to 4.496 mol/L (35 wt %).

RESULTS AND DISCUSSION

Dysprosium fluoride (TU 6-09-4677-83), sulfuric acid (GOST 4204-77), and phosphoric acid (GOST 6552-80) were reagent grade chemicals. Yttrium, cerium, praseodymium, and neodymium fluorides were prepared by reacting lanthanide nitrates with hydrofluoric acid taken in a 20% excess with respect to the stoichiometry [5]. Gel-like precipitates were separated from the mother liquor by centrifugation, washed with distilled water to remove nitrate ions and excess HF, dried, and triturated in a mortar. Reagent grade chemicals were used for the synthesis. The procedure for investigation was similar to that reported previously [4]. The results are presented in Tables 1–5.

The solubilities of lanthanide fluorides in water were found to be much lower than those reported previously (calculated for the oxides Ln_2O_3, g/L) which were as follows: YF_3, 0.0024 [6]; CeF_3, 0.0051–0.0075; PrF_3, 0.0034–0.005; NdF_3, 0.0027–0.0168; and DyF_3, 0.0165 [7].

NdF_3 is almost insoluble in phosphoric acid solutions, while the other fluorides start to dissolve with an increase in the H_3PO_4 concentration. Apparently, this is due to the fact that neodymium precipitates from dilute solutions of phosphoric acid as poorly soluble anhydrous $NdPO_4$ [8], whereas yttrium, cerium, praseodymium, and dysprosium form more soluble hydrated compounds: $YPO_4 \cdot 2H_2O$ [9], $CePO_4 \cdot H_3PO_4 \cdot yH_2O$ [10], $PrPO_4 \cdot 2.5H_2O$ [11], and $PrPO_4 \cdot 3H_2O$ [12]; as the degree of hydration increases, the solubility increases.

Upon increase in the H_2SO_4 concentration in the concentration range studied, the YF_3 and CeF_3 solubil-

Table 1. Solubility of YF_3 in H_2SO_4–H_3PO_4 solutions at (20 ± 1)°C

$c_{H_2SO_4}$, mol/L	Content of Y_2O_3 at P_2O_5 concentration, g/L			
	0	5	12	20
0	0.0002	0.0008	0.0033	0.0061
0.312	0.33	0.34	0.38	0.41
0.635	0.59	0.61	0.63	0.66
0.971	0.79	0.81	0.81	0.82
1.32	0.96	1.0	1.0	1.1
1.81	1.2	1.2	1.2	1.27
2.325	1.35	1.40	1.40	1.43
3.004	1.46	n.d.*	n.d.	n.d.
3.727	1.47	n.d.	n.d.	n.d.
4.496	1.46	n.d.	n.d.	n.d.

* Here and in Tables 2–5, n.d. stands for not determined.

ities reach a maximum at $c_{H_2SO_4}$ = 3.004 mol/L and then remain almost invariable for $c_{H_2SO_4}$ = 3.004–4.496 mol/L. The solubilities of NdF_3 and DyF_3 increase with an increase in $c_{H_2SO_4}$ over the whole range studied. In terms of the solubility (mol/L) in solutions of sulfuric and phosphoric acids of the same composition, lanthanide fluorides can be arranged in the following sequence: $CeF_3 < LaF_3 < NdF_3 < YF_3 < PrF_3 < DyF_3 \ll YbF_3$.

As for LaF_3 and YbF_3, the solubilities of YF_3 in HNO_3 and $HClO_4$ [13] and YF_3 and NdF_3 in HCl [14] are lower than those in the sulfuric acid solution with the same normality.

The dissolution of lanthanide fluorides in sulfuric acid can be described by the reactions [4]

$$2MF_3 + 3H_2SO_4 \longleftrightarrow M_2(SO_4)_3 + 6\,HF, \quad (1)$$

$$2MF_3 + 2H_2SO_4 \longleftrightarrow 2MSO_4F + 4HF \quad (2)$$

or

$$2MF_3 + H_2SO_4 \longleftrightarrow M_2(SO_4)F_4 + 2HF, \quad (3)$$

with the following equilibrium constants, respectively [4]:

$$K_{c_1} = K_1\frac{6^6[M_2O_3]^7}{[H_2SO_4]^3}, \quad K_{c_2} = K_2\frac{4^4[M_2O_3]^5}{\gamma^2[H_2SO_4]^2} \quad \text{and } K_{c_3} = K_3\frac{2^2[M_2O_3]^3}{\gamma[H_2SO_4]}. \quad (4)$$

In Eqs. (4), $[M_2O_3]$ and $[H_2SO_4]$ are, respectively, the lanthanide oxide and sulfuric acid concentrations in solution, mol/L; and γ is the activity coefficient of sulfuric acid.

The K_{c_1}, K_{c_2}, and K_{c_3} values calculated from experimental data are presented in Table 6. In calculations, the activity coefficients of hydrofluoric acid and lanthanide cations were assumed to be fixed (they are taken into account by K_1, K_2, and K_3); the γ values for sulfuric acid at different concentrations were taken from [15].

The K_{c_1}/K_1, K_{c_2}/K_2, and K_{c_3}/K_3 values for YF_3, CeF_3, PrF_3, NdF_3, and DyF_3 calculated from experi-

Table 2. Solubility of CeF_3 in H_2SO_4–H_3PO_4 solutions at (20 ± 1)°C

$c_{H_2SO_4}$, mol/L	Content of Ce_2O_3 at P_2O_5 concentration, g/L						
	0	2	5	8	12	16	20
0	0.001	0.002	0.001	0.0016	0.001	0.001	0.003
0.312	0.0582	0.048	0.046	0.032	0.041	0.040	0.040
0.635	0.305	0.29	0.31	0.30	0.29	0.26	0.27
0.971	0.381	0.36	0.35	0.32	0.33	0.35	0.33
1.32	0.553	0.52	0.51	0.49	0.49	0.49	0.48
1.81	0.734	0.66	0.70	0.68	0.61	0.61	0.60
2.325	0.820	0.77	0.73	0.71	0.73	0.71	0.68
3.004	0.830	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3.727	0.830	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4.496	0.820	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 3. Solubility of PrF_3 in H_2SO_4–H_3PO_4 solutions at (20 ± 1)°C

$c_{H_2SO_4}$, mol/L	Content of Pr_2O_3 at P_2O_5 concentration, g/L			
	0	5	12	20
0	0.00023	0.00035	0.0008	0.0071
0.312	0.35	0.20	0.15	0.14
0.635	0.84	0.60	0.54	0.44
0.971	1.14	0.94	0.77	0.73
1.32	1.56	1.30	1.21	1.13
1.81	2.29	2.19	2.00	1.80
2.325	3.02	2.71	2.57	2.46
3.004	3.00	n.d.	n.d.	n.d.
3.727	3.08	n.d.	n.d.	n.d.
4.496	3.14	n.d.	n.d.	n.d.

mental data are summarized in Table 6. It can be seen that, upon variation of $c_{H_2SO_4}$ from 1.32 to 3.727 mol/L, K_{c_3}/K_3 changes little, which can imply the existence of complexes $M_2(SO_4)F_4$ (M = Y, Ce, Pr, Nd, Dy) in sulfuric acid solutions.

The formation of fluorosulfate ions in concentrated solutions of sulfuric and hydrofluoric acids was established experimentally. In a study of the Ln_2O_3–TiO_2–H_2SO_4–HF–H_2O systems (Ln = Y, Ce, Nd), the fluorosulfates $YSO_4F \cdot 2H_2O$ [16], $CeSO_4F \cdot 2H_2O$ [17], and $NdSO_4F \cdot nH_2O$ [18] crystallized at 50–75°C ($CeSO_4F \cdot 2H_2O$ was not formed at 50°C) from solutions containing 6–8 wt % HF, 0.15–3.52 wt % Ln_2O_3, and 44–60 wt % H_2SO_4. High concentrations of titanium did not hamper the formation of lanthanide fluorosulfates if the HF : TiO_2 molar ratio in the initial solution was not lower than 4 (mol/mol). For molar ratios HF : $TiO_2 > 4$, the solid phase consisted of a $CeSO_4F \cdot 2H_2O$ and CeF_3 mixture [17]. This attests indirectly to a high stability of fluorosulfate complexes of lanthanides.

A decrease in temperature may result in the formation of fluorosulfate complexes of more intricate composition.

Although a study of LaF_3 and YbF_3 solubility in solutions containing 0–2.325 mol/L H_2SO_4 demonstrated the formation of MSO_4F [4], the composition of complexes formed at room temperature might be determined more precisely by studying the solubilities of LaF_3 and YbF_3 over a broader range of $c_{H_2SO_4}$.

Table 4. Solubility of NdF_3 in H_2SO_4–H_3PO_4 solutions at (20 ± 1)°C

$c_{H_2SO_4}$, mol/L	Content of Nd_2O_3 at P_2O_5 concentration, g/L						
	0	2	5	8	12	16	20
0	0.001	0.001	0.001	0.001	0.001	0.001	0.001
0.312	0.19	0.13	0.11	0.093	0.085	0.079	0.078
0.635	0.39	0.37	0.35	0.36	0.37	0.37	0. 32
0.971	0.52	0.53	0.52	0.50	0.58	0.57	0.54
1.320	0.65	0.70	0.75	0.76	0.71	0.78	0.70
1.810	0.82	0.84	0.88	0.95	0.90	0.98	0.96
2.325	0.95	1.00	1.05	1.05	1.03	1.09	1.1
3.004	1.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3.727	1.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4.496	1.11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 5. Solubility of DyF_3 in H_2SO_4–H_3PO_4 solutions at (20 ± 1)°C

$c_{H_2SO_4}$, mol/L	Content of Dy_2O_3 at P_2O_5 concentration, g/L			
	0	5	12	20
0	0.0003	0.025	0.043	0.067
0.312	0.87	0.76	0.80	0.77
0.635	2.01	1.91	1.81	1.80
0.971	2.71	2.73	2.81	2.82
1.32	3.89	3.62	3.60	3.50
1.81	4.45	4.40	4.38	4.35
2.325	4.49	4.41	4.51	4.40
3.004	4.53	n.d.	n.d.	n.d.
3.727	4.59	n.d.	n.d.	n.d.
4.496	4.78	n.d.	n.d.	n.d.

The effects of the phosphoric acid concentrations on the solubility in sulfuric acid solutions are different. The solubility of YF_3 increases and those of CeF_3 and PrF_3 decrease with an increase in the H_3PO_4 concentration over the whole range of the H_2SO_4 concentrations studied. An especially pronounced decrease in the solubility was found for PrF_3. The solubilities of NdF_3 and DyF_3 decrease at low H_2SO_4 concentrations but remain almost invariable or slightly increase at higher $c_{H_2SO_4}$ concentrations. Generally, the change in the solubility of lanthanide fluorides in sulfuric and phosphoric acid solutions attests to an intricate nature of the lanthanide complexation in these solutions.

In view of the solubilities of lanthanide fluorides found experimentally in a previous study [4] and in the present study, sulfuric acid leaching of praseodymium, dysprosium, and ytterbium fluorides should proceed efficiently, while leaching of yttrium, lanthanum, cerium, and neodymium fluorides from phosphohemi-

Table 6. Dependence of K_{c_1}/K_1, K_{c_2}/K_2 and K_{c_3}/K_3 on H_2SO_4 concentration

Fluoride	$c_{H_2SO_4}$, mol/L								
	0.312	0.635	0.971	1.32	1.81	2.325	3.004	3.727	4.496
	K_{c_1}/K_1, $mol^4\,L^{-4}$								
YF_3	3.57×10^{-12}	4.67×10^{-11}	1.43×10^{-10}	2.45×10^{-10}	4.63×10^{-10}	4.45×10^{-10}	2.81×10^{-10}	1.06×10^{-10}	0.37×10^{-10}
CeF_3	3.37×10^{-18}	3.38×10^{-14}	6.36×10^{-14}	3.78×10^{-13}	10.9×10^{-13}	9.95×10^{-13}	3.96×10^{-13}	1.43×10^{-13}	0.47×10^{-13}
PrF_3	3.81×10^{-13}	3.92×10^{-11}	1.31×10^{-10}	5.18×10^{-10}	3.02×10^{-9}	8.82×10^{-9}	3.07×10^{-9}	1.33×10^{-9}	5.5×10^{-10}
NdF_3	4.64×10^{-15}	1.59×10^{-13}	4.70×10^{-13}	9.86×10^{-13}	19.8×10^{-13}	23.4×10^{-13}	15.1×10^{-13}	7.10×10^{-13}	3.31×10^{-13}
DyF_3	9.48×10^{-11}	7.46×10^{-9}	2.39×10^{-8}	13.2×10^{-8}	13.4×10^{-8}	6.01×10^{-8}	2.33×10^{-8}	0.92×10^{-8}	0.44×10^{-8}
	K_{c_2}/K_2, $mol^3\,L^{-3}$								
YF_3	5.23×10^{-10}	3.53×10^{-9}	8.18×10^{-9}	12.5×10^{-9}	20.6×10^{-9}	20.9×10^{-9}	15.8×10^{-9}	8.28×10^{-9}	4.05×10^{-9}
CeF_3	1.38×10^{-14}	2.02×10^{-11}	3.31×10^{-11}	12.3×10^{-11}	27.3×10^{-11}	26.7×10^{-11}	14.5×10^{-11}	7.36×10^{-11}	3.50×10^{-11}
PrF_3	1.06×10^{-10}	3.11×10^{-9}	7.71×10^{-9}	2.14×10^{-8}	0.79×10^{-7}	1.76×10^{-7}	0.87×10^{-7}	0.50×10^{-7}	0.28×10^{-7}
NdF_3	4.54×10^{-12}	6.09×10^{-11}	1.38×10^{-10}	2.44×10^{-10}	4.19×10^{-10}	4.93×10^{-10}	3.77×10^{-10}	2.31×10^{-10}	1.40×10^{-10}
DyF_3	5.44×10^{-9}	1.32×10^{-7}	3.17×10^{-7}	11.2×10^{-7}	11.8×10^{-7}	6.94×10^{-7}	3.71×10^{-7}	2.01×10^{-7}	1.24×10^{-7}
	K_{c_3}/K_3, $mol^2\,L^{-2}$								
YF_3	2.19×10^{-7}	7.59×10^{-7}	1.34×10^{-6}	1.82×10^{-6}	2.62×10^{-6}	2.79×10^{-6}	2.52×10^{-6}	1.83×10^{-6}	1.27×10^{-6}
CeF_3	3.89×10^{-10}	3.41×10^{-8}	4.9×10^{-8}	1.13×10^{-7}	1.95×10^{-7}	2.04×10^{-7}	1.51×10^{-7}	1.07×10^{-7}	0.74×10^{-7}
PrF_3	8.38×10^{-8}	7.03×10^{-7}	1.29×10^{-6}	2.51×10^{-6}	5.84×10^{-6}	10.0×10^{-6}	7.04×10^{-6}	5.42×10^{-6}	4.09×10^{-6}
NdF_3	1.27×10^{-8}	6.64×10^{-8}	1.15×10^{-7}	1.72×10^{-7}	2.52×10^{-7}	2.95×10^{-7}	2.69×10^{-7}	2.14×10^{-7}	1.7×10^{-7}
DyF_3	8.91×10^{-7}	6.68×10^{-6}	1.2×10^{-5}	2.69×10^{-5}	2.97×10^{-5}	2.28×10^{-5}	1.68×10^{-5}	1.24×10^{-5}	1.00×10^{-5}

hydrate may be difficult if the total lanthanide concentration in leaching solutions exceeds 1–1.5 g/L.

CONCLUSIONS

The solubility of YF_3, CeF_3, PrF_3, NdF_3, and DyF_3 in solutions containing 0–4.496% mol/L (0–35 wt %) of H_2SO_4 and 0–27.6 g/L of H_3PO_4 at 20°C was determined. NdF_3 is almost insoluble in phosphoric acid solutions, whereas the other fluorides studied start to dissolve with an increase in the H_3PO_4 concentration. In terms of the solubility in solutions of sulfuric and phosphoric acids of the same composition, lanthanide fluorides can be arranged in the following sequence $CeF_3 < LaF_3 < NdF_3 < YF_3 < PrF_3 < DyF_3 \ll YbF_3$.

The higher solubility of lanthanide fluorides in solutions of sulfuric acid with respect to their solubility in monobasic acids is due to the formation of fluorosulfate complexes. At room temperature, the formation of $M_2(SO_4)F_4$ is most probable.

Sulfuric acid leaching of praseodymium, dysprosium, and ytterbium fluorides from phosphohemihydrate should be efficient, while that of yttrium, lanthanum, cerium, and neodymium fluorides may be difficult if the total lanthanide concentration in leaching solutions exceeds 1–1.5 g/L.

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