LA--9155-MS

DE82 008898

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SOLVENT EXTRACTION OF THORIUM FROM NITRATE SOLUTIONS
BY DIBUTYL BUTYLPHOSPHONATE IN ISOPAR H

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ABSTRACT

Solvent extraction of thorium by 30 vol% di-butyl butylphosphonate-70 vol% Isopar H from salted and nonsalted nitric acid solutions was studied.

Thorium distribution coefficients D_{Th} 's were obtained for nitric acid solutions of ~ 0.3 to ~ 12 N and for solutions of 1 and 2 M NH_4NO_3 over the HNO_3 concentration range of ~ 0.5 to ~ 9 N.

The nitric acid solution D_{Th} 's varied from ~ 4.3 at the lowest acidity, increased to a maximum of ~ 40 at $\sim 3-4$ N H^+ , and then gradually decreased to ~ 18 at ~ 11.5 N H^+ .

The solutions containing 1 and 2 M NH_4NO_3 gave definite "salting-out effects" with D_{Th} 's of 79 to 90, respectively, at the lowest acidities; these values then decreased with acidity increases to those of the nonsalted acid solutions at ~ 5 N HNO_3 and paralleled the acid solution values up to ~ 12 N.

I. SOLVENT SYSTEM

The extracting solvent system used was dibutyl butylphosphonate (DBBP) in the diluent Isopar H (I). Fresh 30 vol% DBBP-70 vol% I solvent was used for the bulk of the extractions reported; however, three tests are reported for fresh solvent systems of 15, 10, and 5 vol% DBBP. These were done at a nominal feed acidity of $\sim 4 \text{ N HNO}_3$ that represented the acid range for the maximum extraction found for the 30 vol% DBBP system.

II. FEED SOLUTIONS

A stock solution of 1-liter volume containing $0.353 \text{ M Th(NO}_3)_4$ and 0.5 N HNO_3 was prepared. Aliquots assayed for ThO_2 gave a value within $\sim 1.1\%$ of that calculated from the weight of $\text{Th(NO}_3)_4 \cdot 4\text{H}_2\text{O}$ added.

Extraction test feed solutions were made by pipetting an aliquot (generally 25 ml) of the stock solution into a 100-ml volumetric flask, then adding the appropriate amounts of concentrated HNO_3 and NH_4NO_3 so that final H_2O dilution to 100 ml gave the feed of the desired concentrations.

Feed solutions covered the following ranges.

- (1) 0.088 M Th^{+4} solutions with no NH_4NO_3 and HNO_3 from ~ 0.3 to 12 N .
- (2) 0.088 M Th^{+4} solutions 1 M in NH_4NO_3 with HNO_3 from ~ 0.5 to 5.75 N .
- (3) 0.088 M Th^{+4} solutions 2 M in NH_4NO_3 with HNO_3 from ~ 2.0 to 10 N .
- (4) Some additional solutions with Th^{+4} varying from $\sim 0.35 \text{ M}$ to $\sim 0.04 \text{ M}$ as listed in the tabulated data.

III. EXTRACTION AND STRIPPING PROCEDURES

Solvent (25 ml) was measured out and placed into a 125-ml separatory funnel with an equal amount of the desired feed solution. This solvent-to-feed ratio of 1:1 was used throughout the tests.

The stoppered funnel was shaken for 3 to 5 minutes, allowed to settle, and then the aqueous raffinate phase was drawn off into a stoppered bottle. The organic phase was decanted from any residual aqueous phase.

Previous exploratory stripping tests showed that the thorium could be stripped from the organic phase with two 50-ml portions of H₂O followed by a 25-ml H₂O strip. For the higher acidity feeds, another strip pass with 25 ml of H₂O was necessary. All strip-passes were kept separated and then were assayed for ThO₂ as was the raffinate.

IV. THORIUM DETERMINATIONS AND H⁺ TITRATIONS

Aliquots of each strip and raffinate were pipetted into tared crucibles. These were taken to dryness slowly on a hot plate set at low heat to prevent splattering. Next, they were placed in a muffle furnace and slowly taken to 600°C or higher and held for 30 minutes or more. This decomposes the solids leaving a ThO₂ residue. After cooling, the weight of ThO₂ was obtained.

A mass balance was then struck with the sums of the ThO₂ values for the strips and raffinate as compared with that previously found in the feed. The balances for all reported tests agreed to 3.5% or better.

These results are tabulated in Tables I and II.

The equilibrium aqueous phase H⁺ concentration was determined by taking an appropriate aliquot of the raffinate and titrating with a standard NaOH solution (either 0.1 or 1.0 N) to a methyl-orange end point. Additions of H₂O and ~15-30 ml of 2 M KF were made before titration to prevent the hydrolysis of the Th⁺⁴ during titration. Experimental results are listed in Tables I and II.

V. DISTRIBUTION COEFFICIENTS (D_{Th})

The distribution coefficient D_{Th} is defined as the concentration of thorium in the organic phase divided by its concentration in the aqueous phase when the two phases are in equilibrium. Therefore, these were calculated by dividing the total ThO₂ obtained in the strips by that obtained for the raffinate because these experiments used organic-to-feed volumes of 1:1.

The obtained D_{Th}'s are given in Tables I and II.

TABLE I
Th EXTRACTIONS WITH 30 Vol% DBBP--70 Vol% ISOPAR H

Extraction Test XT	Feed, Nominal [HNO ₃], M	Equilibrium Aqueous [H ⁺], M	Feed, [Th(NO ₃) ₄], M	Feed, [NH ₄ NO ₃], M	Raffinate ThO ₂ , g	Total Strip ThO ₂ , g	Raffinate Plus Strip ThO ₂ , g	Feed, ThO ₂ , g	% Deviation from Mass Balance	D _{Th}
28	0.3	0.25	0.088		0.1103	0.4765	0.587	0.583	0.7	4.3
14	0.5	0.41	0.088		0.0788	0.5100	0.589	0.583	1.0	6.5
16	0.9	0.72	0.088		0.0410	0.5445	0.586	0.583	0.5	13.3
17	1.0	0.78	0.088		0.0375	0.5398	0.577	0.583	1.0	14.4
13	1.25	1.0	0.088		0.0273	0.5660	0.593	0.583	1.8	20.8
4	2.0	1.5	0.088		0.0198	0.5698	0.590	0.583	1.1	29.0
9	4.0	2.97	0.088		0.0143	0.5753	0.590	0.583	1.1	40.0
5	6.0	5.1	0.088		0.0135	0.5643	0.578	0.583	0.9	42.0
19	6.5	5.8	0.088		0.0200	0.5603	0.580	0.583	0.5	28.0
18	7.5	6.7	0.088		0.0235	0.5558	0.579	0.583	0.6	24.0
12	8.0	6.8	0.088		0.0195	0.5517	0.571	0.583	2.0	28.0
24	11.2	10.5	0.088		0.0233	0.5615	0.585	0.583	0.3	24.0
27	12.0	11.6	0.088		0.0298	0.5568	0.587	0.583	0.6	19.0
11 ^a	2.0	1.5	0.044		0.0065	0.2825	0.289	0.292	1.0	44.0
6 ^a	3.0	2.3	0.044		0.0058	0.2858	0.292	0.292	0.0	49.0
3 ^a	0.5	0.45	0.349		0.7703	1.5463	2.3166	2.303	0.6	2.0
22	0.5	0.36	0.088	1.0	0.0073	0.5708	0.578	0.583	0.5	79.0
15	0.5	0.39	0.088	1.0	0.0105	0.5783	0.589	0.583	1.0	55.0
21	2.0	1.5	0.088	1.0	0.0108	0.5665	0.577	0.583	1.0	53.0
20	3.0	2.35	0.088	1.0	0.012	0.5695	0.582	0.583	0.2	47.0
29	5.75	4.9	0.088	1.0	0.0145	0.5733	0.588	0.583	0.8	40.0
7 ^a	1.0	0.82	0.044	1.0	0.0036	0.2643	0.268	0.290	7.5	73.0
1	2.0	1.7	0.08	2.0	0.0058	0.5173	0.523	0.528	0.9	89.0
2	2.0	1.72	0.08	2.0	0.0068	0.5206	0.527	0.528	0.2	77.0
10	4.0	3.1	0.088	2.0	0.0080	0.5635	0.572	0.583	1.9	70.0
26	4.5	3.7	0.088	2.0	0.0113	0.5518	0.563	0.583	3.4	49.0
23	6.0	5.2	0.088	2.0	0.0163	0.5580	0.574	0.583	1.5	34.0
25	9.9	9.4	0.088	2.0	0.0328	0.5475	0.580	0.583	0.5	17.0
8 ^a	1.0	0.71	0.04	2.0	0.0033	0.3118	0.315	0.317	0.6	94.0

^aThese data points are not plotted on Fig. 1.

TABLE II
Th EXTRACTIONS WITH 30 vol% DBBP--70 vol% ISOPAR H

Extraction Test XT	Feed, vol% DBBP	Feed, Nominal [HNO ₃], M	Equilibrium Aqueous [H ⁺], M	Feed, [Th(NO ₃) ₄], M	Raffinate, [ThO ₂], g	Total Strip ThO ₂ , g	Raffinate Plus Strip ThO ₂ , g	Feed, ThO ₂ , g	% Deviation from Mass Balance	D _{Th}
9	30	4.0	3.0	0.088	0.0143	0.5753	0.590	0.583	1.1	40.0
30	15	4.0	3.4	0.088	0.0800	0.5096	0.590	0.583	1.1	6.4
31	10	4.0	3.3	0.088	0.2028	0.3948	0.598	0.583	2.5	2.0
32	5	4.0	3.5	0.088	0.4130	0.1857	0.599	0.583	2.7	0.45

The Table I data for all feed solutions containing $\sim 0.088 \text{ M Th}^{+4}$ are plotted in Fig. 1 as D_{Th} versus the equilibrium aqueous phase acidity. Note that these data are for 30 vol% DBBP-70 vol% I. The data points of Table I that apply to Th^{+4} concentrations other than the above values are not shown in Fig. 1 because they clutter the figure. Examination of these points, however, shows that as the Th^{+4} concentration decreases to $\sim 0.04 \text{ M}$ for solutions similar to the 0.088 M cases the D_{Th} is higher; whereas, for the one case of 0.349 M Th^{+4} , the D_{Th} is depressed.

Fig. 1. D_{Th} Eq. Aqueous $[\text{H}^+]$, N

The Table II data are given in Fig. 2. Here a log-log plot is given of D_{Th} versus vol% DBBP in Isopar H. The line struck through these points has a slope of 2.5, indicating a dependency of D_{Th} upon the DBBP concentration of between two and three; therefore, these data do not establish whether the extractable complex contains two or three molecules of DBBP.

Fig. 2. D_{Th} vs Vol% DBBP

VI. CONCLUSIONS

Figure 1 shows that for unsalted HNO_3 solutions, the D_{Th} values for 30 vol% DBBP-70 vol% I go through a maximum of ~ 43 between ~ 3 to 5 N in HNO_3 and has a value of ~ 4 at the lowest acidity studied; that is, $\sim 0.25 \text{ N } H^+$.

At low acidities, adding 1 or 2 M of NH_4NO_3 gives a "salting-out effect," increasing the D_{Th} to values between ~ 50 to 100. This enhancement of D_{Th} decreases as the acidity increases until the salting-out effect is essentially gone from $\sim 5 \text{ N } H^+$ upward.

From the data obtained for variable DBBP concentrations in Isopar H, as shown in Fig. 2, we see that for solutions $\sim 3.3 \text{ N}$ in HNO_3 and containing $\sim 0.088 \text{ M } Th^{+4}$, the D_{Th} values vary as the 2.5 power of the DBBP concentration.