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Abstract

Full Text

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CHEMISTRY

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MUTUAL INFLUENCE OF THORIUM AND CERIUM (IV) NITRATES DURING JOINT EXTRACTION WITH TRIBUTYL PHOSPHATE

It was previously shown by one of us ([1]) that, during the joint extraction of trivalent rare-earth elements (r.e.e.) and cerium (IV) with tributyl phosphate (TBP), the r.e.e. are completely salted out from the organic phase into the aqueous phase. However, the r.e.e. themselves are extracted by TBP relatively poorly; therefore, it is of considerable interest to study the mutual influence of cerium (IV) and actinides that are well extracted by TBP. We studied the extraction by TBP of thorium and cerium (IV) nitrates in the presence of 1.5 N nitric acid in the equilibrium aqueous phase.

Thorium was determined by titration with Trilon B using xylenol orange ([2,3]). Cerium (IV) was reduced by a definite amount of a titrated solution of Mohr' s salt, the excess of which was back-titrated with potassium permanganate ([4]). Nitric acid was determined by potentiometric titration with sodium hydroxide solution in the presence of ammonium oxalate. TBP was twice distilled in vacuum (140–145° at a pressure of 15 mm Hg) and saturated with water. Extraction was carried out in graduated cylinders with ground-glass stoppers at room temperature.

The experimental results are given in Table 1.

The presence in the aqueous phase of small amounts of cerium causes a sharp decrease in the distribution coefficients of thorium (K_t). Increasing the cerium concentration above 100 g/l causes a further, but less abrupt, decrease in K_t.

The influence of thorium' s own concentration on its distribution in the presence of cerium is less significant than in its absence. This effect is smaller the lower the cerium concentration. At a constant thorium concentration, its coeff–

Table 1

No.	Equilibrium concentration in the aqueous phase, g/l	Equilibrium concentration in the aqueous phase, g/l	Distribution coefficients*	Distribution coefficients*	No.	Equilibrium concentration in the aqueous phase, g/l	Equilibrium concentration in the aqueous phase, g/l	Distribution coefficients*	Distribution coefficients*
	cerium	thorium	K_c	K_t		cerium	thorium	K_c	K_t
1	–	1.06	–	6.50	25	43.60	–	3.24	–
2	–	5.45	–	5.02	26	46.00	81.50	3.55	0.30
3	–	19.90	–	3.95	27	43.90	164.4	3.56	0.35
4	–	42.10	–	3.12	28	46.06	244.6	3.08	0.19
5	–	74.70	–	2.29	29	43.14	302.0	3.34	0.21
6	–	89.00	–	1.95	30	43.10	358.0	3.25	0.19
7	–	108.0	–	1.63	31	92.25	–	1.81	–
8	–	167.0	–	1.06	32	92.00	40.24	1.80	0.14
9	–	220.0	–	0.80	33	98.00	148.5	1.74	0.25
10	0.28	–	181	–	34	98.00	194.0	1.81	0.21
11	0.45	–	153	–	35	95.00	202.0	1.80	0.21
12	9.61	–	8.93	–	36	97.25	260.0	1.79	0.21
13	0.14	40.24	275	2.10	37	180.0	–	1.04	–
14	0.25	58.17	208	1.84	38	180.7	48.71	1.00	0.11
15	0.28	184.2	208	0.77	39	173.8	80.46	1.04	0.22
16	1.89	88.24	54.7	0.86	40	183.0	117.0	1.05	0.09
17	3.51	116.5	21.4	0.63	41	179.0	160.0	1.04	0.15
18	10.40	11.65	15.5	0.47	42	177.6	243.6	1.09	0.16
19	9.86	89.64	13.4	0.29	43	234.0	–	0.96	–
20	18.00	–	7.00	–	44	226.0	42.10	0.90	0.25
21	17.55	54.00	9.50	0.70	45	229.0	54.10	0.87	0.14
22	16.80	68.80	9.48	0.54	46	228.0	72.00	0.79	0.16
23	19.00	87.90	8.50	0.45	47	228.0	96.36	0.79	0.17
24	13.90	200.0	8.10	0.45					

* The concentration for both phases in the calculations was expressed in grams per liter.

distribution coefficients depend on the cerium concentration; this influence is the more significant, the lower the thorium concentration.

These regularities are explained by the fact that cerium displaces thorium from the organic phase. The salting-out effect of thorium (increase in K_c) in the

aqueous phase appears only at low cerium concentrations. At a cerium concentration of about 18 g/l, thorium is a weak salting-out agent, and at cerium concentrations above 40 g/l, thorium has practically no effect on the extraction of cerium. An increase in the equilibrium concentration of cerium in the aqueous phase reduces the influence of thorium practically to zero, which is explained by the proximity of the equilibrium organic phases to saturation with cerium. Cerium at no concentration displaces thorium from the organic phase.

Such behavior of thorium and cerium during their joint extraction is explained by the fact that the stability of the cerium solvate is considerably greater than the stability of the thorium solvate.

The data presented make it possible to draw a number of practical conclusions. The question of the possibility of separating the two elements by fractional extraction can be correctly resolved only on the basis of a study of the corresponding system. Thorium and cerium (IV) can be separated by fractional extraction with TBP. The introduction of hydrogen peroxide to reduce cerium (IV) during the extraction recovery of thorium nitrate from monazite-processing products not only increases the purity of the final product, but also increases the recovery of thorium.

The established regularities in the mutual influence of thorium and cerium (IV) nitrates are valid not only for 100% TBP, but also for its solutions in carbon tetrachloride, as is confirmed by the data given in Table 2.

Table 2

No.	Initial conc. TBP, vol. % CCl_4	Equilibrium thorium concentration, g/l (aqueous phase)	Equilibrium thorium concentration, g/l (organic phase)	K_T	Equilibrium cerium concentration, g/l (aqueous phase)	Equilibrium cerium concentration, g/l (organic phase)	K_c
1	20	19.05	4.01	0.21	–	–	–
2	20	20.05	1.75	0.09	0.59	11.28	22.5
3	20	25.10	0.50	0.02	2.78	22.13	7.94
4	20	25.10	–	–	15.0	32.84	2.19
5	60	36.10	55.16	1.53	–	–	–
6	60	87.25	84.24	0.96	–	–	–
7	60	45.12	48.14	1.07	0.18	23.56	132
8	60	52.14	43.12	0.83	0.78	49.25	62.7
9	60	69.20	12.03	0.17	10.00	107.0	10.7
10	60	93.25	4.01	0.04	146.3	135.0	0.92

No qualitative change in the mutual influence of thorium and cerium upon dilution of TBP is observed.

A very interesting fact is the possibility of obtaining cerium that contains practically no thorium during extraction with a 20% solution of TBP in CCl_4 while maintaining the cerium content in the aqueous phase at about 15 g/l. In extraction with 100% TBP, such selective extraction of cerium was not observed at any of its concentrations. On the other hand, at certain concentrations of thorium, cerium, and TBP, it is possible to obtain an aqueous solution (raffinate) containing practically thorium alone.

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Note: Figure translations are in progress. See original paper for figures.