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Abstract

Full Text

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ON THE JOINT EXTRACTION OF URANYL NITRATE AND CERIUM(IV) NITRATE BY TRIBUTYL PHOSPHATE (TBP)

As was shown earlier ([1]), the study of the joint extraction of two or more extractable compounds is of great theoretical and practical importance.

We have studied an isoconcentrate of the system

$$UO_2(NO_3)_2—Ce(NO_3)_4—1.5N\ HNO_3—H_2O—TBP.$$

The extraction was carried out in separatory funnels at a temperature of 25°. Before use, the TBP was twice distilled in vacuum and saturated with water. Uranium was determined by Sakharov's method ([2]), cerium by oxidimetric titration ([3]), and nitric acid by potentiometric titration with potassium hydroxide solution in the presence of ammonium oxalate.

The results obtained are collected in Table 1.

Table 1

No.	Conc. in equilibrium aqueous phase, g/l: uranyl nitrate	Conc. in equilibrium aqueous phase, g/l: cerium(IV) nitrate	Distribution coefficient: K_U	Distribution coefficient: K_{Ce}	No.	Conc. in equilibrium aqueous phase, g/l: uranyl nitrate	Conc. in equilibrium aqueous phase, g/l: cerium(IV) nitrate	Distribution coefficient: K_U	Distribution coefficient: K_{Ce}
1	20.4	–	15.2	–	24	104	254	1.28	1.72
2	60.1	–	7.73	–	25	94.7	562	0.89	0.86
3	109.8	–	4.07	–	26	106	954	0.55	0.55

No.	Conc. in equilibrium aqueous phase, g/l: uranyl nitrate	Conc. in equilibrium aqueous phase, g/l: cerium(IV) nitrate	Distribution coefficient: K_U	Distribution coefficient: K_{Ce}	No.	Conc. in equilibrium aqueous phase, g/l: uranyl nitrate	Conc. in equilibrium aqueous phase, g/l: cerium(IV) nitrate	Distribution coefficient: K_U	Distribution coefficient: K_{Ce}
4	223	–	2.60	–	27	201	9.7	2.47	8.1
5	433	–	1.42	–	28	206	136	1.33	2.23
6	645	–	0.97	–	29	196	198	1.23	1.80
7	745	–	0.87	–	30	311	392	0.96	1.00
8	–	40.3	–	11.2	31	235	661	0.56	0.68
9	–	71.6	–	6.8	32	218	897	0.47	0.53
10	–	224	–	2.46	33	408	7.9	1.38	4.76
11	–	424	–	1.33	34	410	38.1	1.20	2.78
12	–	610	–	0.93	35	449	50.5	1.12	2.07
13	–	839	–	0.70	36	417	77.6	1.09	1.95
14	–	1020	–	0.57	37	449	204	0.91	1.05
15	19.9	20.4	3.98	18.6	38	447	299	0.79	0.83
16	27.3	55.3	2.91	7.66	39	397	375	0.79	0.81
17	21.1	834.0	0.62	0.67	40	656	31.5	0.85	1.76
18	69.6	105	1.83	3.84	41	670	44.6	0.83	1.39
19	62.1	306	1.25	1.61	42	640	95.0	0.81	1.33
20	56.0	373	1.25	1.33	43	631	154	0.76	1.02
21	59.6	586	0.88	0.89	44	31.0	983	0.49	0.57
22	112	75.6	2.02	3.94	45	184	970	0.43	0.51
23	100	100	1.71	3.34	46	233	953	0.45	0.50

Uranyl nitrate and cerium(IV) nitrate, as individual substances, are extracted by TBP approximately equally (since their molecular weights are 394 and 388, respectively, comparison may also be made when the concentration is expressed in grams per liter). In joint extraction, K_U and K_{Ce} decrease. However, the effect of cerium(IV) nitrate on K_U is somewhat greater than that of uranyl nitrate on K_{Ce}, which is especially noticeable at concentrations of each component up to 200 g/l.

In this connection, for solutions with equal contents of both salts, $K_{Ce} > K_U$. At concentrations above 200 g/liter, the indicated difference in mutual influence approaches zero; the distribution coefficients of uranyl nitrate and cerium(IV) nitrate become very close. Consequently, separation of U(VI) and Ce(IV) by

fractional extraction is impossible.

As additional studies have shown, analogous regularities are also observed in extraction with TBP solutions in carbon tetrachloride. Such behavior of the compounds studied during joint extraction is explained by the fact that the stability of the solvate of cerium(IV) nitrate with TBP is only slightly greater than the stability of the uranyl nitrate solvate.

Thus, on the basis of an analysis of extraction systems, it is possible to make an approximate estimate of solvate stability. Comparing the data of the present work with the data of the preceding work [4], it is evident that the stability of solvates formed by TBP with nitrates decreases in the series: Ce(IV), U(VI), Th(IV). Therefore it should be assumed that the influence of uranyl nitrate on the extraction of thorium nitrate is similar in character to that described in [4]. Nevertheless, the displacement of thorium from the organic phase into the aqueous phase by cerium(IV) should proceed better than the analogous displacement by uranyl nitrate.

These conclusions are in good agreement with the possibility of separating uranium and thorium nitrates by fractional extraction with a 5% TBP solution [5].

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