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Abstract

Full Text

CHEMISTRY

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INVESTIGATION OF THE EXTRACTION SYSTEM

$Th(NO_3)_4$–HNO_3–H_2O–$(C_4H_9O)_3PO$ AT 25°C BY THE METHOD OF EXTRACTION RAYS

Studies of extraction systems containing an actinide or lanthanide nitrate, nitric acid, water, and tributyl phosphate (TBP) are of considerable theoretical and practical interest. To date, the following systems have been studied and published: $UO_2(NO_3)_2$–HNO_3–H_2O–$(C_4H_9O)_3PO$ ([1]), $La(NO_3)_3$–HNO_3–H_2O –$(C_4H_9O)_3PO$, $Ce(NO_3)_4$–HNO_3–H_2O–$(C_4H_9O)_3PO$ ([2]). We have studied the analogous system with thorium nitrate, namely $Th(NO_3)_4$–HNO_3–H_2O–$(C_4H_9O)_3PO$.

Fig. 1. Extraction rays and isolines of K_{distr} for $Th(NO_3)_4$ in the system $Th(NO_3)_4$—HNO_3—H_2O—$(C_4H_9O)_3PO$ at 25°. Bold curves are saturation lines of the aqueous phase; dashed lines with dots are isolines of K_{distr} for $Th(NO_3)_4$;
I-VII are extraction rays; a, b, c are Schreinemakers rays.

Extraction was carried out in graduated test tubes at 25 ± 0.05°C. Before use, TBP was distilled twice in vacuum. Thorium was determined by titration with Trilon B using xylenol orange ([3]); nitric acid, by potentiometric titration with a solution of caustic potash in the presence of ammonium oxalate.

Table 1

Composition (mol/l) and specific gravities (g/cm^3) of the equilibrium phases

Rays	Aqueous phase: $Th(NO_3)_4$	Aqueous phase: HNO_3	Aqueous phase: sp. gr.	Organic phase: $Th(NO_3)_4$	Organic phase: HNO_3	Organic phase: H_2O	Organic phase: TBP*	Organic phase: sp. gr.**	$K_{calc.}^{Th(NO_3)_4}$	$K_{calc.}^{HNO_3}$***
I	2.56	1.24	1.960	1.25	0.25	–	2.9	1.410	0.49	0.21
I	2.12	1.24	1.821	1.19	0.24	–	3.1	1.396	0.56	0.20
I	1.02	1.20	1.422	1.04	0.26	–	3.1	1.352	1.02	0.21
I	0.35	0.74	1.150	0.76	0.26	–	3.1	1.248	2.17	0.35
I	0.28	0.38	1.113	0.60	0.25	–	3.1	1.197	2.14	0.64
I	0.27	0.27	1.106	0.51	0.19	–	3.2	1.163	1.91	0.67
II	2.44	3.11	1.978	1.26	0.64	–	3.0	1.447	0.51	0.20
II	2.11	3.16	1.853	1.24	0.52	–	2.9	1.397	0.59	0.16
II	0.57	3.16	1.317	1.02	0.44	–	2.9	1.346	1.78	0.14
II	0.31	2.57	1.202	0.89	0.56	–	3.0	1.321	2.82	0.22
II	0.21	1.82	1.136	0.72	0.61	–	3.1	1.239	3.49	0.33
II	0.16	0.65	1.085	0.39	0.46	–	3.2	1.141	2.42	0.71
III	1.63	4.57	1.740	1.09	0.58	0.50	3.0	1.361	0.66	0.13
III	1.15	4.57	1.581	1.08	0.70	0.60	3.0	1.373	0.94	0.15
III	0.65	4.52	1.397	1.02	0.67	0.51	3.0	1.350	1.57	0.15
III	0.30	4.46	1.258	0.90	0.76	0.49	3.1	1.317	3.03	0.17
III	0.12	3.60	1.173	0.73	0.96	0.68	3.1	1.254	6.07	0.27
III	0.07	2.11	1.113	0.44	1.51	1.32	3.2	1.162	6.05	0.72
IV	1.77	6.60	1.806	1.08	1.58	–	2.9	1.389	0.61	0.24
IV	1.00	6.87	1.563	1.02	1.23	–	2.9	1.362	1.02	0.18
IV	0.43	6.87	1.362	0.95	1.15	–	3.0	1.330	2.21	0.17
IV	0.17	6.26	1.250	0.81	1.23	–	2.9	1.296	4.79	0.20
IV	0.05	4.24	1.150	0.58	1.31	–	3.1	1.218	10.70	0.31
V	1.48	9.07	1.763	1.01	2.29	–	2.8	1.374	0.68	0.25
V	0.66	9.11	1.493	0.88	1.95	–	2.8	1.336	1.33	0.21
V	0.36	9.17	1.393	0.83	1.92	–	2.9	1.307	2.30	0.21
V	0.26	8.88	1.357	0.80	1.86	–	2.9	1.298	3.10	0.21
V	0.048	7.56	1.248	0.61	1.96	–	2.8	1.234	12.6	0.26
VI	1.13	11.50	1.700	0.90	3.16	–	2.5	1.360	0.79	0.27
VI	0.83	11.76	1.611	0.81	3.21	1.33	2.7	1.335	0.97	0.27
VI	0.59	11.86	1.541	0.78	2.91	1.28	2.75	1.313	1.32	0.25
VI	0.22	11.30	1.394	0.69	2.74	–	2.8	1.276	3.18	0.24
VI	0.14	11.10	1.365	0.66	2.77	–	2.8	1.266	4.80	0.25
VI	0.047	10.50	1.334	0.54	2.78	1.10	2.9	1.229	11.50	0.26
VI	0.038	9.96	1.305	0.53	2.69	–	3.0	1.222	13.9	0.27
VII	0.85	14.4	1.662	0.85	4.57	–	2.4	1.363	1.0	0.32
VII	0.81	14.3	1.639	0.82	4.39	–	2.5	1.360	1.0	0.31
VII	0.59	14.4	1.576	0.78	4.21	–	2.5	1.340	1.32	0.29
VII	0.23	14.4	1.458	0.66	3.89	–	2.7	1.288	2.84	0.27

Rays	Aqueous phase: $Th(NO_3)_4$	Aqueous phase: HNO_3	Aqueous phase: sp. gr.	Organic phase: $Th(NO_3)_4$	Organic phase: HNO_3	Organic phase: H_2O	Organic phase: TBP*	Organic phase: sp. gr.**	$K_{calc.}^{Th(NO_3)_4}$	$K_{calc.}^{HNO_3}$***
VII	0.052	13.5	1.381	0.51	3.72	–	2.8	1.238	9.85	0.27

* The concentration of TBP was found by calculation.
** On rays I–IV phase inversion is observed.
*** In the calculation, the concentration for both phases was expressed in moles per 1 liter.

The experimental data are presented in Fig. 1 and in Table 1. The extraction rays in this system, as in the preceding one ([2]), were constructed by carrying out a series of extractions from the same initial solution at different phase ratios. The curve ABC in Fig. 1 is the solubility curve in the system $Th(NO_3)_4$–HNO_3 –H_2O according to the data of ([4]): solutions corresponding to branch AB are saturated with thorium nitrate pentahydrate, and solutions of branch BC with tetrahydrate $Th(NO_3)_4 \cdot 4H_2O$. We obtained

the solubility curve corresponding to line CBD was plotted. Independently of the acidity, the solid phase was thorium nitrate tetrahydrate, as was established by the Schreinemakers residue method. Figure 1 shows three Schreinemakers rays (a, b, c), connecting the liquid phases at different portions of the solubility curve with the equilibrium solid phase (point E), containing 87% $Th(NO_3)_4$ or $Th(NO_3)_4 \cdot 4H_2O$. According to our data, the tetrahydrate proved to be stable also at low acidities.

The extraction rays I–VII (Fig. 1) are curvilinear over a considerable part of the field of unsaturated aqueous solutions of the system, which distinguishes this system from systems with uranyl nitrate and cerium(IV) nitrate ([1,2]). This is apparently explained by the fact that, at a 15–20% concentration of thorium nitrate, nitric acid becomes a serious competitor in the struggle for the extractant. The extraction rays do not converge at any definite point, and none of them passes through the point corresponding to $Th(NO_3)_4$. This also indicates the simultaneous extraction of thorium nitrate and nitric acid even when the content of the latter in the aqueous phase is low. At higher concentrations of thorium nitrate, good linearity of the rays is observed, and their curvature begins at the lower $Th(NO_3)_4$ concentration the higher the acidity.

As can be seen from Fig. 1 and Table 1, the distribution coefficients of thorium nitrate increase along the rays, with the exception of rays I and II, where, at a $Th(NO_3)_4$ concentration in the aqueous phase of 7-12%, K_{distr} for $Th(NO_3)_4$ passes through a maximum. The rays themselves sharply change direction—falling toward the abscissa axis—which is associated with the predominant transfer of acid into the extract. At a $Th(NO_3)_4$ concentration $\geq 20\%$, with increasing acidity, a small change in K_{distr} for $Th(NO_3)_4$ is observed, almost the same

for all its concentrations up to saturation. $K_{\text{distr}}^{\text{HNO}_3}$ for rays IV–VII are practically constant (0.2-0.3), which indicates the small influence of thorium nitrate on the distribution of nitric acid. However, in this concentration region K_{distr} in the presence of $Th(NO_3)_4$ is smaller than that of HNO_3 alone, i.e., salting-out of the latter from the organic phase takes place. At low concentrations of thorium nitrate and HNO_3, K_{distr} of the acid increases to a value of 0.67-0.71 (rays I and II); consequently, under these conditions the presence of thorium does not affect the extraction of nitric acid.

Analysis of the composition of the organic phases shows (Table 1) that nitric acid, apparently, either can dissolve in the solvate of thorium nitrate with TBP, without forming its own solvate, or extraction occurs here with the formation of two solvates (with $Th(NO_3)_4$ and HNO_3); but in both cases the rays obtained are the geometric sum of two rays with two composition poles ([5]). For rays III and VI, water in the organic phase was determined by Fischer' s method. As can be seen from the data obtained, the water content on the rectilinear portion of the ray is practically constant, while on the curved portion it changes (increases). Thorium nitrate is extracted in an anhydrous form.

Thus, three regions can be distinguished on the extraction ray: 1) predominant extraction of thorium (the content of water and nitric acid is constant, the course of the ray is rectilinear), 2) comparable extraction of $Th(NO_3)_4$ and HNO_3—the ray begins to curve, 3) predominant extraction of HNO_3—a steep downward deviation of the ray.

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