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$Ce(NO_3)_4$—HNO_3—H_2O—$(C_4H_9O)_3PO$ at 25°

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Abstract

Full Text

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On the Mechanism of Extraction of Cerium(IV) Nitrate from Nitric-Acid Solutions by Tributyl Phosphate (TBP)

The extraction of cerium(IV) nitrate by TBP has been studied by a number of authors from different points of view (1–7), including technological and radiochemical aspects (2,4,6). However, the available data are insufficient for a complete description of the system $Ce(NO_3)_4$—HNO_3—H_2O—TBP, which would make it possible to judge reliably the mechanism of extraction of $Ce(NO_3)_4$ by tributyl phosphate.

Fig. 1. Quaternary extraction system $Ce(NO_3)_4$—HNO_3—H_2O—$(C_4H_9O)_3PO$ at 25°

At present there are two points of view: some authors (8) believe that $Ce(NO_3)_4$ passes into TBP, while others (6) believe it is $H_2[Ce(NO_3)_6]$. Earlier, one of us (9,10) showed that studying the course of extraction rays makes it possible to judge the composition of the extracted compound. We have used this method to investigate the system named above. Cerium(IV) was determined by potentiometric titration with hydrogen peroxide (11); nitric acid was titrated with a sodium hydroxide solution. The extraction was carried out at a temperature of $25 \pm 0.05°$.

Figure 1 presents the course of the extraction rays (I-VII) in the system $Ce(NO_3)_4$—HNO_3—H_2O—TBP, and the isolines of the distribution coefficients—

$Ce(NO_3)_4$ line (K_p from 0.95 to 4.9), as well as the saturation line of $Ce(NO_3)_4$ in the aqueous phase (BC). Most of the extraction rays are rectilinear over a wide range of concentrations of cerium(IV) nitrate and nitric acid. If cerium passed into the organic phase in the form of the complex acid $H_2[Ce(NO_3)_6]$, then the extraction rays would converge at point A, which corresponds to the composition of this acid.

Thus, for the system $(C_2H_5)_2O$–H_2O–$FeCl_3$–HCl, all extraction rays converge at the point of composition $H_2[FeCl_6] \cdot 6H_2O$ [10]. As is seen from Fig. 1, not a single ray arrives at this point. The course of rays I-IV indicates that nitric acid passes into the organic phase in different (nonstoichiometric) amounts, which depend on its concentration in the aqueous phase (see also Table 1). Rays V and VI converge at point D (100% $Ce(NO_3)_4$), and this unambiguously shows that cerium(IV) is extracted in the form $Ce(NO_3)_4$. On rays VI and VII, at a cerium(IV) nitrate concentration of ~30%, a bend is observed and, as is seen from the data of Table 1, a deficiency of nitric acid appears in the organic phase. This apparently indicates that, at the indicated cerium concentration and an HNO_3 concentration not higher than 15%, basic salts of cerium(IV) pass into the organic phase along with $Ce(NO_3)_4$. The bending of rays V, VI, and VII toward the H_2O corner indicates that, at small amounts of cerium(IV) in the aqueous phase, the salting-out of HNO_3 from the organic phase by it ceases. At these same points, with a low concentration of cerium(IV), its extraction is maximal (K_p reaches 400 and 500).

Table 1

Composition and specific gravities of equilibrium phases

Ray	Aqueous phase: $Ce(NO_3)_4$, mol/l	Aqueous phase: HNO_3, mol/l	Aqueous phase: sp. wt., g/cm^3	Organic phase: $Ce(NO_3)_4$, mol/l	Organic phase: HNO_3, mol/l	Organic phase: TBP, mol/l	Organic phase: sp. wt., g/cm^3	K_p $Ce(NO_3)_4$	K_p HNO_3
I	2.346	9.975	1.887	1.340	2.963	2.530	1.382	0.570	0.297
I	2.219	10.282	1.874	1.288	2.169	2.795	1.382	0.580	0.211
I	1.994	10.657	1.807	1.346	2.551	2.637	1.369	0.670	0.239
I	0.813	11.844	1.565	1.183	1.822	2.768	1.311	1.455	0.154
II	2.212	9.271	1.862	1.339	2.193	2.636	1.359	0.605	0.236
II	1.382	10.030	1.694	1.274	1.730	2.770	1.340	0.922	0.172
II	0.592	10.670	1.540	1.188	1.585	2.778	1.320	2.006	0.148
II	0.246	10.620	1.455	1.045	1.637	2.930	1.289	4.248	0.154
II	0.107	10.160	1.408	0.993	1.685	2.898	1.264	9.280	0.166
III	1.848	8.493	1.744	1.358	0.977	2.821	1.341	0.730	0.115
III	1.737	8.530	1.690	1.296	1.578	2.722	1.344	0.746	0.185
III	1.466	8.853	1.648	1.257	0.635	3.196	1.380	0.870	0.072
III	0.363	9.694	1.398	1.219	1.038	2.863	1.302	3.358	0.107
IV	1.866	5.980	1.669	1.407	0.366	2.912	1.343	0.754	0.061
IV	1.721	6.080	1.637	1.407	0.366	2.922	1.345	0.818	0.060
IV	1.366	6.380	1.566	1.387	0.293	2.909	1.332	1.015	0.046
IV	0.837	6.746	1.445	1.372	0.335	2.924	1.322	1.639	0.050
IV	0.258	7.195	1.317	1.307	0.529	2.941	1.326	5.066	0.074

Ray	Aqueous phase: $Ce(NO_3)_4$, mol/l	Aqueous phase: HNO_3, mol/l	Aqueous phase: sp. wt., g/cm^3	Organic phase: $Ce(NO_3)_4$, mol/l	Organic phase: HNO_3, mol/l	Organic phase: TBP, mol/l	Organic phase: sp. wt., g/cm^3	K_p $Ce(NO_3)_4$	K_p HNO_3
V	2.366	3.367	1.756	1.443	0.272	2.871	1.341	0.610	0.081
V	2.012	3.582	1.673	1.393	0.282	2.952	1.344	0.692	0.079
V	1.552	3.778	1.566	1.370	0.208	2.985	1.339	0.883	0.055
V	1.165	4.020	1.483	1.365	0.244	2.970	1.337	1.172	0.060
V	0.317	4.575	1.310	1.328	0.360	2.992	1.334	4.189	0.079
V	0.042	4.418	1.194	1.158	0.512	3.102	1.307	27.57	0.116
VI	2.535	1.376	1.769	1.491	0.243	2.819	1.344	0.588	0.177
VI	1.736	1.666	1.590	1.370	0.127	2.950	1.338	0.789	0.076
VI	1.400	1.743	1.511	1.363	0.102	3.020	1.339	0.974	0.058
VI	0.796	2.151	1.373	1.338	–	3.070	1.336	1.681	–
VI	0.584	2.290	1.327	1.321	−0.105	–	1.325	2.262	–
VI	0.437	2.410	1.276	1.331	−0.128	–	1.327	3.046	–
VI	0.156	2.688	1.210	1.363	−0.224	–	1.321	8.737	–
VI	0.01	2.470	1.173	1.048	–	–	1.277	500	–
VII	1.382	0.915	1.442	1.406	−0.215	–	1.331	1.017	–
VII	1.025	1.090	1.360	1.395	−0.398	–	1.334	1.361	–
VII	0.731	1.328	1.287	1.380	−0.537	–	1.326	1.888	–
VII	0.044	1.961	1.113	1.307	−0.699	–	1.299	29.7	–
VII	0.005	1.417	1.077	0.845	−0.057	–	1.199	400	–

The isolines of the distribution coefficients of cerium(IV) over the entire field of the system are practically rectilinear, and the angle of their inclination to the cerium axis is close to 90°. This indicates that HNO_3 has little effect on the extraction of cerium(IV) nitrate.

Analysis of the data presented in Table 1 also confirms that in the organic phase there is no constant ratio between the amounts of $Ce(NO_3)_4$ and HNO_3. Consequently, only their joint extraction takes place, and not the extraction of any compound between them.

From consideration of the composition of the equilibrium organic phases at a cerium(IV) concentration in the aqueous phase of more than 1 mol/l, it is seen that $Ce(NO_3)_4 : TBP = 1 : 2$, i.e., a solvate of composition $Ce(NO_3)_4 \cdot 2TBP$ is formed. The distribution coefficients of nitric acid in most cases do not exceed 0.2. Such low extraction of nitric acid is explained by its salting out by ce—

of cerium(IV) from the organic phase into the aqueous phase, which is analogous to the effect of cerium(IV) on the extraction of thorium (^{7}) and rare earths (^{2,4}).

The data presented indicate the possibility of successfully extracting cerium(IV) from solutions 1-2 *M* in nitric acid.

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