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Abstract

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THERMOCHEMISTRY OF THE EXTRACTION OF CERIUM(IV) NITRATE WITH TRIBUTYL PHOSPHATE

As was shown earlier ([1]), the only sufficiently reliable method for determining the heat of extraction is direct calorimetric measurement. This applies all the more to cerium(IV) nitrate, since in the aqueous phase it is strongly hydrolyzed and can pass into the organic phase in the form of a basic salt ([2]), which makes it difficult to study its extraction at temperatures above room temperature and to carry out subsequent thermodynamic analysis of the results obtained.

The measurements were carried out by us in an ordinary variable-temperature calorimeter ([3]), the calorimetric beaker and stirrer being made of glass. The procedure for carrying out and calculating the calorimetric experiment was the same as before ([1,4,5]). The analytical and preparative methods that we used are described in ([6,7]). All calorimetric measurements were carried out at 25°. The signs of the heat effects are given according to the thermodynamic system.

Table 1

Heats of solution of cerium(IV) nitrates at 25°

	$Ce(NO_3)_4 \cdot 5H_2O$			$CeOH(NO_3)_3 \cdot 3H_2O$		
Solvent	ΔH, kcal/mole		$Ce(NO_3)_4 \cdot 5H_2O$ dilution	ΔH, kcal/mole		$CeOH(NO_3)_3 \cdot 3H_2O$ dilution
Water	12.34	0.30	2251—2650	7.130	0.045	1241—1542
TBP	−13.42	0.50	216—237	−13.39	0.25	133—134

We measured the heats of solution of the hydrates of the normal and basic cerium(IV) nitrates in water and tributyl phosphate (TBP). The results of these measurements are given in Table 1, from which it is seen that both salts dissolve in water with considerable absorption of heat, and in TBP with evolution of heat. At the same time, their heats of solution in TBP are practically identical.

The data obtained make it possible to calculate the heats of extraction of normal and basic cerium(IV) nitrates by TBP ([5]). The heats of solution of

$Ce(NO_3)_4 \cdot 5H_2O$ in water and TBP are the heat effects of the processes:

$$Ce(NO_3)_4 \cdot 5H_2O_s \rightarrow Ce(NO_3)^*_{4\,aq} + 5H_2O_l, \quad \Delta H_1 = 12.34;$$

$$Ce(NO_3)_4 \cdot 5H_2O_s + 2TBP_l \rightarrow Ce(NO_3)_4 \cdot 2TBP_l + 5H_2O_l, \quad \Delta H_2 = -13.42.$$

Consequently, the heat effect of extraction

$$Ce(NO_3)_{4\,aq} + 2TBP_l \rightarrow Ce(NO_3)_4 \cdot 2TBP_l, \quad \Delta H_3$$

is determined as $\Delta H_3 = \Delta H_2 - \Delta H_1 = -25.76$ kcal/mole. The heat effect of extraction calculated analogously for basic cerium(IV) nitrate is equal to 20.42 kcal/mole. These heats of extraction refer to conditions where the aqueous and organic phases are infinitely dilute. The results of direct calorimetric measurements of the heat of extraction of cerium(IV) nitrate by TBP under these conditions are given in Table 2 (except experiment 5).

* *aq* –infinite dilution.

The experimental results agree satisfactorily with the calculation. The difference observed between them and the scatter of the experimentally obtained values are explained by the fact that at low acidities (the initial solution of cerium(IV) salt was 1 N in HNO_3) simultaneous extraction occurs of both the basic and the neutral cerium(IV) nitrate, and their ratio is in a complex dependence on the concentration of cerium itself[(2)].

The considerable heat evolution during the extraction of cerium(IV) nitrate convincingly indicates the pronounced chemical nature of their interaction and the high stability of the solvate formed by them.

Table 2

Heat of extraction of cerium(IV) nitrate by TBP at 25°

Experiment no.	Dilution: initial aqueous phase	Dilution: equilibrium organic phase	ΔH, kcal/mol
1	231*	353	−29.45
2	244*	304	−27.69
3	184*	285	−24.45
4	153*	274	−23.29
5	8.8 (equilibrium–17.6)	55	−20.63

* The equilibrium aqueous phase contained no Ce(IV).

Table 3

Heats of mixing of $CeOH(NO_3)_3 \cdot 2TBP$ **with TBP at 25°**

Experiment no.	Mole fraction of TBP, N	Heat of mixing, ΔH, kcal/mol of solution	$A = \frac{\Delta H}{N(1-N)}$
1	0.160	−299	−2230
2	0.334	−393	−1770
3	0.455	−405	−1633
4	0.534	−365	−1466
5	0.581	−360	−1480
6	0.691	−292	−1374
7	0.769	−226	−1270
8	0.818	−174	−1168

Dissolution of the solvate in excess TBP is accompanied by heat evolution, as is seen from the data of Table 3. The solvate was prepared by dissolving $CeOH(NO_3)_3 \cdot 3H_2O$ in TBP to saturation and, according to analysis, had the composition $CeOH(NO_3)_3 \cdot 2.01TBP$. The heat of mixing of the cerium(IV) nitrate solvate with TBP depends on the mole fractions of the components in the final solution and is maximal at a TBP mole fraction of ~ 0.4. As in the case of uranyl nitrate[(1)], this solution is not regular. However, for an approximate calculation of the activity of the organic phase, the assumption of regularity of this solution may be justified and useful.

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