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Abstract

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Interaction of Certain Rare-Earth Elements with Dibutyl Phosphate and Their Extractive Separation

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Dialkyl esters of orthophosphoric acid (R_2HPO_4) have recently acquired great importance in connection with the extractive separation of metals ([1–11]). The published data make it possible to conclude that the use of dialkyl phosphates provides higher distribution and separation coefficients for rare-earth elements (r.e.e.) than extraction with tributyl phosphate (TBP); the difference is especially large at low solution acidity. The distribution coefficients in extraction with dialkyl phosphates increase with the atomic number of the lanthanides, as has also been established for tributyl phosphate. Increasing the concentration of r.e.e. nitrates in the aqueous solution causes, in extraction with dibutyl phosphate, a decrease in the distribution coefficients. The latter is apparently associated with the limited solubility of the extracted compounds in solutions of dibutyl phosphate in nonpolar solvents.

The separation coefficient for neighboring lanthanides in extraction with di-(2-ethylhexyl) phosphate, according to Peppard et al. ([1]), is 2.5; in extraction with dibutyl phosphate, according to Dikkerts et al. ([11]), it is 1.95 for the light lanthanides and 2.6 for the heavy ones. When TBP is used, the separation coefficients of nitrates of neighboring lanthanides, depending on the extraction conditions, lie within the range from 1 to 2 ([12,13]).

The processes of extraction and separation of r.e.e. by dibutyl phosphate have been little studied, although reactions involving this compound are of undoubted interest. In this connection, we studied the composition of the complexes formed in the interaction of r.e.e. ions with dibutyl phosphate, determined their instability constants, and also carried out the separation of several pairs of r.e.e.

Metal ions react with dialkyl phosphates according to the reaction

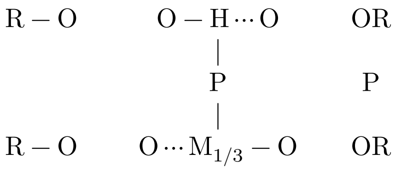
$$M^{n+} + nHA \rightleftharpoons MA_n + nH^+, \tag{1}$$

where HA is a monobasic acid, a dialkyl phosphate, in our case dibutyl phosphate $(C_4H_9O)_2HPO_2$, designated HDBP.

The value of n, i.e., the number of dibutyl phosphate molecules entering into interaction with the metal ions, was determined from data on the distribution of indicator amounts of r.e.e. at a constant nitric acid concentration as a function of the concentration of HDBP in CCl_4. n is determined as the tangent of the slope of the curve $\log q_m - \log[\mathrm{HDBP}]$ (q_m is the distribution coefficient of the r.e.e., equal to $[\mathrm{M}]_{\mathrm{org}}/[\mathrm{M}]_{\mathrm{aq}}$). It was found that for neodymium and praseodymium $n = 3$; this agrees with data obtained by other investigators for r.e.e. ([2,5,11]).

Dibutyl phosphate is dimerized in nonpolar solvents ([5,14]); therefore its compounds with metals formed during extraction are assigned the composition $\mathrm{M[H(DBP)_2]_3}$. These compounds, according to Peppard ([4]), are intra-

are complex and have the structure



$$\begin{array}{cccc} \mathrm{R-O} & \mathrm{O-H\cdots O} & & \mathrm{OR} \\ & \mid & & \\ & \mathrm{P} & & \mathrm{P} \\ & \mid & & \\ \mathrm{R-O} & \mathrm{O\cdots M_{1/3}-O} & & \mathrm{OR} \end{array}$$

To clarify the conditions for the formation of simple and complex compounds of rare-earth elements with dibutyl phosphate, we used the following methods of investigation: fractional extraction of the metal from aqueous solutions by solutions of HDBP in carbon tetrachloride, isolation of the compounds and their chemical analysis, determination of the solubility of individual compounds in solutions of dibutyl phosphate in a nonaqueous solvent, and distribution of rare-earth elements between the aqueous and nonaqueous phases.

In fractional extraction of yttrium from an aqueous solution by solutions of dibutyl phosphate in CCl_4, it was found that all the yttrium is extracted by the nonaqueous phase when the ratio

$$\frac{\mathrm{HDBP\ (g\text{-}mol)}}{\mathrm{Y\ (g\text{-}atom)}}$$

reaches 3. This indicates that, if there is no excess dibutyl phosphate, the compound formed is not solvated by it and has the composition $M(\mathrm{DBP})_3$.

Table 1

Solubility of $\mathrm{Yb(DBP)_3}$ in solutions of dibutyl phosphate in carbon tetrachloride

Conc. $\mathrm{(HDBP)_2}$ in CCl_4, mol/l	Solubility S, mol/l $\cdot 10^6$	$\log[\mathrm{(HDBP)_2}]$	$\log S$	$\log K$
0.0005	1.25	–3.3	–5.90	–0.95

Conc. $(HDBP)_2$ in CCl_4, mol/l	Solubility S, mol/l $\cdot 10^6$	$\log[(HDBP)_2]$	$\log S$	$\log K$
0.0010	3.68	−3.0	−5.44	−0.96
0.0025	18.5	−2.6	−4.73	−0.83
0.0050	32.0	−2.3	−4.50	−1.05

Individual solid compounds of neodymium and ytterbium were obtained by mixing, in different ratios, solutions of the corresponding nitrates with dibutyl phosphate or with its alcoholic solution. The precipitates that separated were washed free of the free component with water when rare-earth metal nitrate was in excess, or with alcohol and ether when dibutyl phosphate was in excess. The compounds dried over phosphorus anhydride corresponded to the composition $M(DBP)_3$.

The experiments described did not confirm the formation of complex compounds of rare-earth elements with a ratio of the number of dibutyl phosphate molecules to rare-earth element greater than 1 : 3. In this connection we also studied the solubility of $M(DBP)_3$ in solutions in CCl_4, for which the radioactive isotope Yb^{175} was used.

From the data in Table 1 it is evident that, with increasing concentration of HDBP in the solution, the solubility of $Yb(DBP)_3$ increases, which indicates an interaction

$$Yb(DBP)_3 + n(HDBP)_2 \rightleftharpoons Yb[H(DBP)_2]_3. \tag{2}$$

Assuming that the concentration of the complex formed is equal to the solubility S, one can calculate the equilibrium constant of the complex-formation reaction and determine the number of dibutyl phosphate molecules entering into reaction (2):

$$K = \frac{[Yb\{H(DBP)_2\}_3]}{[Yb(DBP)_3][(HDBP)_2]^n}, \tag{3}$$

or, since in the presence of a solid phase $[Yb(DBP)_3]$ may be regarded as constant,

$$K' = \frac{S}{[(HDBP)_2]^n}. \tag{4}$$

From the slope of the curve $\log S - n\log[(HDBP)_2]$, it was found that $n = 1.5$. This gives grounds to conclude that, in an excess of complexing agent, the compound $Yb(DBP)_3 \cdot 3HDBP$, or $Yb[H(DBP)_2]_3$, is formed.

The equilibrium constant K', characterizing the energy of attachment of solvating molecules, calculated from equation (4) and equal to ~ 0.1, confirms the weak bond between $Yb(DBP)_3$ and dibutyl phosphate.

The formation, during extraction, of the complex $M[H(DBP)_2]_3$ or $MA_3(HA)_3$ is described by Dyrssen and Hay (15) by the equation:

$$M^{3+} + 3A^- + 3HA \rightleftarrows MA_3(HA)_3. \tag{5}$$

Hence the equilibrium constant K is determined by the ratio:

$$K = \frac{[MA_3(HA)_3]_{org}}{[M^{3+}]_{aq}[A^-]^3_{aq}[HA]^3_{aq}}. \tag{6}$$

To determine the degree of electrolytic dissociation of the complexes under study in the aqueous phase, we measured the molecular electrical conductivity of a saturated solution of $Nd(DBP)_3$ ($6.2 \cdot 10^{-4}$ mol/l) at 20° and found it to be equal to 235.5, i.e., in aqueous solution the rare-earth complexes with dibutyl phosphate are dissociated to a considerable extent.

Taking this into account, in equation (6) the ratio

$$\frac{[MA_3(HA)_3]_{org}}{[M^{3+}]_{aq}}$$

may be replaced by the distribution coefficient q_m, and the equilibrium constant K may be represented by the equation

$$\log K = \log q_m - 3\log[A^-] - 3\log[HA] \tag{7}$$

Using the literature values of the distribution constants of dibutyl phosphate between nitric acid solutions and the nonaqueous phase, as well as the dimerization and dissociation constants of dibutyl phosphate in such systems (16,17), we determined the value of $\log K$ for complexes of praseodymium, neodymium, and ytterbium with dibutyl phosphate of the type $M[H(DBP)_2]_3$. These values, respectively equal to 15.0, 15.3, and 18.5, agree with the value $\log K = 16.8$ found by Dyrssen for the analogous europium complex (15).

The large difference in the stability of the complexes of yttrium and cerium elements during extraction with dibutyl phosphate can be used for their separation.

Table 2

Separation coefficients of rare-earth elements during extraction with TBP and HDBP

Separation pair (M'—M'')	Conc. HNO_3, mol/l	Conc. HDBP and TBP in CCl_4, mol/l	Ratio of components $M' : M''$	Separation coeff. —extraction with TBP	Separation coeff. —extraction with HDBP	Separation pair (M'—M'')	Conc. HNO_3, mol/l	Conc. HDBP and TBP in CCl_4, mol/l	Ratio of components $M' : M''$	Separation coeff. —extraction with TBP	Separation coeff. —extraction with HDBP
Nd—La	0.52	1.0	1:1	1.14	3.1	Ho—Nd	0.53	0.05	1:99	–	93
Nd—La	17.0	1.0	1:1	10.6	7.0	Ho—Nd	0.53	1.0	1:99	–	139
Y—Nd	0.6	1.0	1:1	0.84	202	Ho—Nd	0.53	1.0	1:1	–	466
Y—Nd	17.1	1.0	1:1	18.3	29.1						

As the data in Table 2 show, the separation coefficients during extraction with dibutyl phosphate depend on the position of the elements in the lanthanide group, on the content of nitric acid in the aqueous phase, on the concentration of dibutyl phosphate in the nonaqueous phase, and on the ratio of the separated elements in their mixture. Thus, for example, the average separation coefficient for neighboring lanthanides, calculated from the separation coefficient for the Nd—Ho pair depending on the extraction conditions, changes in our experiments from 1.9 to 2.4.

During re-extraction of elements from the nonaqueous phase, additional separation can be carried out, using the different stability of the complexes

rare-earth elements with dibutyl phosphate. Thus, the cerium-group elements are precipitated from the nonaqueous phase with oxalic acid; the yttrium elements, including yttrium, are not precipitated under these conditions, as a result of which additional separation occurs. The yttrium elements can be isolated from solutions in dibutyl phosphate by means of sodium hydroxide. As an example, one may cite the results of one of the experiments on the separation of neodymium and holmium from a mixture containing 10 mol.% $Ho(NO_3)_3$ in the sum of nitrates, in which, after one purification cycle (extraction and re-extraction), 99.4% of neodymium oxide with a purity of 99.2% and 98.7% of holmium oxide with a purity of 99.8% were obtained.

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