

## TRI-*n*-BUTYL PHOSPHATE AS AN EXTRACTING SOLVENT FOR INORGANIC NITRATES—II

### YTTRIUM AND THE LOWER LANTHANIDE NITRATES

D. SCARGILL, K. ALCOCK, J. M. FLETCHER, E. HESFORD, and H. A. C. MCKAY  
Atomic Energy Research Establishment, Harwell, Didcot, Berks

(Received 22 January 1957)

**Abstract**—Tri-*n*-butyl phosphate (TBP) can be used to extract and separate yttrium and the lower lanthanides (lanthanum-gadolinium). Extraction from nitric acid solutions generally increases with acidity, sometimes very steeply, though there is often a region of falling partition coefficients between say 4 and 7 M  $\text{HNO}_3$ . Extraction at low acidity but high nitrate ion concentration (added, for example, as sodium nitrate) is usually high.

Extractability increases with atomic number in the lanthanide series, with yttrium more extractable than any lanthanide at acidities  $>c. 5 \text{ M } \text{HNO}_3$ , though less extractable at low acidities. The separation factors for successive lanthanides increase with acidity and reach values as high as 2. They are also high in systems of low acidity but high nitrate concentration, and in presence of TTA (thenoyl-trifluoroacetone) in the organic phase.

Experiments at varying TBP concentrations indicate the formation of  $\text{Y}(\text{NO}_3)_3 \cdot 3\text{TBP}$  and  $\text{Ce}(\text{NO}_3)_3 \cdot 3\text{TBP}$ . (See also note added in proof.)

THE trivalent rare-earth nitrates are moderately well extracted by TBP, and very high partition coefficients indeed can be obtained under suitable conditions. Moreover, there is sufficient gradation in extractability along the lanthanide series to obtain good separations of the different elements. Solvent extraction using TBP must be considered a serious rival of ion exchange for this purpose.<sup>(1)</sup> On the other hand, with sufficiently dilute TBP, conditions are readily found such that the rare earths remain behind when uranium or plutonium is extracted. Yttrium, cerium, and other rare-earth fission products may thus be removed from fissile materials.

The present paper is concerned with yttrium and with the trivalent lanthanides from lanthanum to gadolinium, i.e. up to the point where the 4*f* shell is half-filled. The literature<sup>(2–12)</sup> already contains results for all these elements, though often of rather limited scope because the main aim has been a practical separation process. Our work extends the information available, covering all the elements in question except samarium and gadolinium. We have used effectively trace concentrations ( $<0.01 \text{ M}$ ) of the rare earths throughout.

(1) J. M. FLETCHER Paper No. 2, *Extraction and Refining of the Rarer Metals* Institute of Mining and Metallurgy, London (1957).

(2) D. F. PEPPARD, J. P. FARIS, P. R. GRAY, and G. W. MASON *J. Phys. Chem.* **57**, 294 (1953).

(3) D. F. PEPPARD, P. R. GRAY, and M. M. MARKUS *ANL-WMM-989* (1953?).

(4) A. C. TOPP *ORNL-1409* (1952).

(5) B. WEAVER, F. A. KAPPELMANN, and A. C. TOPP *J. Amer. chem. Soc.* **75**, 3943 (1953).

(6) A. C. TOPP and B. WEAVER *ORNL-1811* (1954).

(7) B. WEAVER *Electromagnetically Enriched Isotopes and Mass Spectrometry* p. 86. (Ed. M. L. SMITH) Butterworths, London (1956).

(8) J. F. SUTTLE and J. F. STAMPFER *Prog. Rep. No. 12, Contract SC-5* Univ. of New Mexico (1954).

(9) J. F. SUTTLE and A. POSKANZER *Prog. Rep. No. 13, Contract SC-5*, Univ. of New Mexico (1955).

(10) J. G. CUNINGHAME, P. SCARGILL, and H. H. WILLIS *A.E.R.E. C/M* 215 (1954).

(11) R. H. BLACKMORE, A. E. BEARSE, and G. D. CALKINS *BMI-261* (1952).

(12) J. BOCHINSKI, M. SMUTZ, and F. H. SPEDDING *ISC-348* (1953); see also R. A. FOOS and H. A. WILHELM *ISC-695* (1954).

The combined data show that under given conditions (acidity, TBP concentration, etc.) the partition or distribution coefficients

$$D_{\text{La}}, D_{\text{Ce}}, D_{\text{Pr}} \dots D_{\text{Gd}}$$

form an approximately geometrical series. That is to say,

$$D_{\text{Ce}} = S D_{\text{La}}$$

$$D_{\text{Pr}} = S^2 D_{\text{La}}$$

$$D_{\text{Gd}} = S^7 D_{\text{La}}$$

where  $S$  is the separation factor (ratio of distribution coefficients) for an adjacent pair of elements. In general,  $D = S^{Z-57} D_{\text{La}}$ , where  $Z$  is the atomic number, or

$$\log D = Z \log S + \text{constant} \quad (1)$$

A relation of this form was first proposed by PEPPARD, FARIS, GRAY, and MASON.<sup>(12)</sup>

It is found in practice that good separation factors can be obtained both at high acidities, when  $S$  may be as high as 2, and at a low acidity with a high nitrate-ion concentration. Systems of both types have therefore been studied.

## EXPERIMENTAL

The techniques employed were similar to those described in Part 1 of this series.<sup>(13)</sup>

To facilitate analysis, radioactive isotopes of the rare earths were used as tracers either carrier-free or with <1 g/l. of the corresponding natural isotopes as carriers.  $\text{Y}^{91}$ ,  $\text{Ce}^{144}$ ,  $\text{Pr}^{147}$  and  $\text{Eu}^{152}$  (with some  $\text{Eu}^{154}$ ) were supplied by the Radiochemical Centre, Amersham.  $\text{La}^{140}$  was obtained by irradiation of the oxide and  $\text{Nd}^{147}$  by irradiation of the nitrate.  $\text{Ce}^{141}$  and  $\text{Pr}^{143}$  were obtained from ceric oxide irradiated in BEPO for 7 days and cooled for about 20 days to allow complete decay of  $\text{Ce}^{143}$  to  $\text{Pr}^{143}$ . The two elements were separated by means of a ceric iodate precipitation, purified by further precipitation cycles, and tested for radiochemical purity by means of absorption curves.

$\text{Y}^{91}$ ,  $\text{La}^{140}$ ,  $\text{Ce}^{141}$ ,  $\text{Ce}^{144}$ ,  $\text{Pr}^{143}$ , and  $\text{Pr}^{147}$  were  $\beta$ -counted,  $\text{Ce}^{144}$  after allowing samples to stand for at least 2 hours to enable  $\text{Pr}^{144}$  to reach its equilibrium value. In order not to have too much material on the counting trays in the experiments with high concentrations of nitrates, aliquots from both the organic and aqueous phase were in such cases converted to their oxalates by coprecipitation with a standard quantity of calcium, and the oxalates, after being filtered, washed, and dried, were mounted for counting. The appropriate allowance (usually 2–3%) for self-absorption by the oxalate present was estimated from blank experiments with known quantities of the lanthanides.  $\text{Nd}^{147}$  and  $\text{Eu}^{152+154}$  in both organic and aqueous phases were analysed by evaporating aliquots to dryness and  $\gamma$ -counting.

The diluents, "odourless" kerosene and xylene, were not specially purified. The TBP concentrations chiefly employed, 19%, 48%, 50%, and 100% v/v, correspond to 0.69, 1.76, 1.83, and 3.66 M respectively; after equilibration with an aqueous phase, the concentrations are, of course, rather lower owing to passage of water, nitric acid, etc., into the organic phase. In all cases, the cerium was in the trivalent state. All the experiments in Tables 1 and 2, except those for europium at 48% TBP, were carried out in a thermostat at 25°C, but the remainder were at room temperature, 20–23°C.

## RESULTS AND DISCUSSION

### *Effect of varying the TBP concentration*

Our partition results for yttrium and cerium at low TBP concentrations are plotted logarithmically in Fig. 1. The best lines through the points are in all cases of slope 2.7, and in our view they almost certainly imply a limiting cube law, and hence the formation of tri-solvates,  $\text{Y}(\text{NO}_3)_3 \cdot 3\text{TBP}$  and  $\text{Ce}(\text{NO}_3)_3 \cdot 3\text{TBP}$ ; some confirmation of the

<sup>(13)</sup> K. ALCOCK, F. C. BEDFORD, W. H. HARDWICK, and H. A. C. MCKAY *J. inorg. nucl. Chem.* **4**, 100 (1957).

latter formula is given by the composition of a saturated solution of cerium(III) nitrate in TBP.<sup>(14)</sup> Moreover, there is good evidence that the analogous elements, thulium and americium, form corresponding compounds.

At higher TBP concentrations there is generally a tendency towards a law of lower power than the third. This tendency is more marked at the lower acidities. For

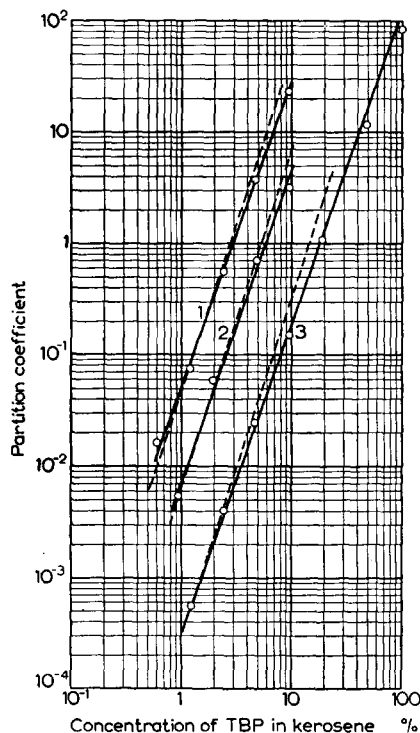


FIG. 1.—The partition coefficient as a function of TBP concentration.

Curve 1— $D_Y$  from 5.2 M  $\text{HNO}_3$ , 0.8 M  $\text{NaNO}_3$

2— $D_{\text{Ce}}$  from 0.005 M  $\text{HNO}_3$ , 4.18 M  $\text{Ca}(\text{NO}_3)_2$

3— $D_Y$  from 13.5 M  $\text{HNO}_3$ .

Curve 1 has been displaced upwards by a factor of 10.

— Lines of slope 2.7

- - - Lines of slope 3.0

example, our yttrium results in Fig. 2 for 19, 48, and 100% TBP in kerosene give a roughly 1.5-power law at 1 M  $\text{HNO}_3$ , a square law at 4 M  $\text{HNO}_3$  and a cube law at 10 M  $\text{HNO}_3$ . Similarly, PEPPARD, FARIS, GRAY, and MASON<sup>(2)</sup> found an approximately square law for scandium, yttrium, and promethium at 1 M  $\text{HNO}_3$ , but a cube law at 4 and 11.5 M  $\text{HNO}_3$  over the range 10–100% TBP in dibutyl ether. At 0.1 M  $\text{HNO}_3$  in presence of 5 and 7 M  $\text{NH}_4\text{NO}_3$ , CUNINGHAME, SCARGILL, and WILLIS<sup>(10)</sup> found an approximately square-law dependence for praseodymium and neodymium for 30–100% TBP in kerosene. It should not be inferred from such results that the tri-solvates give place to lower solvates at the higher TBP concentrations; this would be contrary to the law of mass action. Rather must the deviations from limiting cube law be ascribed to deviations from ideality.<sup>(15)</sup>

<sup>(14)</sup> T. V. HEALY and H. A. C. MCKAY *Trans. Faraday Soc.* **52**, 633 (1956); *Rec. trav. chim.* **75**, 730 (1956).

<sup>(15)</sup> H. A. C. MCKAY To be published.

TABLE 1

Rare earth	TBP conc. (kerosene diluent)	HNO <sub>3</sub> conc. (aq)	Partition coefficient (org/aq)	Rare earth	TBP conc. (kerosene diluent)	HNO <sub>3</sub> conc. (aq)	Partition coefficient (org/aq)
Yttrium	19% v/v	0.48 M	0.0024	Lanthanum	100%	13.8 M 15.0	0.142 0.22
		0.90	0.0044				
		2.26	0.0141	Cerium(III)	48%	0.40 1.12 1.50 2.70 3.98 5.28 7.06 9.30 11.2 13.0	0.0186 0.050 0.057 0.056 0.040 0.025 0.0155 0.0160 0.023 0.039
		3.68	0.0196				
		4.62	0.020				
		6.13	0.0162				
		7.72	0.0185				
		9.65	0.035				
		12.1	0.22				
		13.5	1.05				
Yttrium	48%	0.42	0.0088	Cerium(III)	100%	0.27 0.72 0.98 1.82 2.38 3.64 5.20 6.00 6.85 8.15 8.95 9.88 11.3 12.0 12.9 13.9 14.5 15.0	0.028 0.099 0.123 0.168 0.172 0.169 0.133 0.110 0.098 0.090 0.096 0.108 0.133 0.137 0.195 0.28 0.36 0.42
		0.50	0.013				
		1.29	0.033				
		1.95	0.048				
		3.23	0.082				
		3.70	0.101				
		5.78	0.120				
		7.07	0.148				
		9.32	0.40				
		11.2	1.40				
Yttrium	100%	4.7*	4.6*	Promethium	48%	0.47 0.83 1.62 2.57 3.53 5.85 6.94 7.46 9.51 11.2 12.8	0.027 0.051 0.094 0.116 0.108 0.068 0.062 0.056 0.077 0.146 0.29
		12.5	4.8*				
		0.71	0.044				
		1.52	0.100				
		3.23	0.27				
		4.84	0.64				
		6.55	1.10				
		7.14	1.38				
		7.83	2.2				
		9.10	3.6				
Lanthanum	48%	10.4	9.0	Europium	48%	0.05 1.00 2.00 3.00 4.00 5.00 7.00 8.00 9.00 10.0 12.0	0.0027 0.074 0.136 0.160 0.164 0.156 0.118 0.144 0.146 0.191 0.47
		10.9	13.8				
		11.9	25				
		12.2	32				
		13.1	62				
		13.8	113				
		14.6	198				
		15.0	220				
		5.22	0.0189				
		6.88	0.0109				
Lanthanum	100%	10.8	0.0085				
		12.7	0.0135				
		0.63	0.074				
		1.21	0.108				
		2.15	0.123				
		3.17	0.124				
		4.27	0.102				
		6.10	0.076				
		8.05	0.057				
		10.2	0.060				
		12.1	0.088				

\*Repeat experiments

TABLE 1—continued

Rare earth	TBP conc. (kerosene diluent)	HNO <sub>3</sub> conc. (aq)	Partition coefficient (org/aq)	Rare earth	TBP conc. (kerosene diluent)	HNO <sub>3</sub> conc. (aq)	Partition coefficient (org/aq)
Europium	100%	0.64 M	0.105	Europium	100%	8.54 M	0.72
		1.67	0.30			8.92	0.76
		2.38	0.39			9.35	0.89
		3.76	0.49			10.1	1.24
		5.38	0.53			10.4	1.26
		6.11	0.54			11.2	1.80
		6.30	0.54			11.6	2.2
		7.27	0.59			12.5	3.4
		7.22	0.58 (?)			14.6	9.7
		8.46	0.73			16.0	19.9
						18.7	64

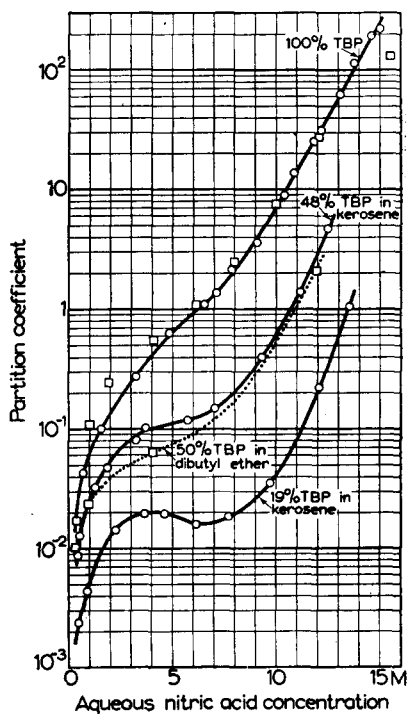


FIG. 2.—The partition coefficient of yttrium nitrate.

○ Our data  
 □ PEPPARD, FARIS, GRAY, and MASON<sup>(2)</sup>

#### Extraction from nitric acid solutions

Our results are given in Table 1, and plotted in Figs. 2–4 along with comparable results by other authors. The latter are subject to the following comments:

(1) PEPPARD, FARIS, GRAY, and MASON'S<sup>(2)</sup> and PEPPARD, GRAY, and MARKUS'S<sup>(3)</sup> results are directly comparable with ours, except for their use of dibutyl ether as diluent. This must affect the results (except, of course, with 100% TBP), because dibutyl ether dissolves quite large amounts of nitric acid.

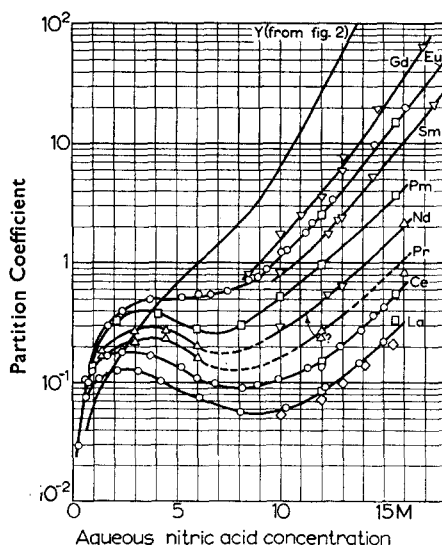


FIG. 3.—The partition coefficients of the lower lanthanide nitrates: 100% TBP.

- Our data
- △ CUNINGHAME, SCARGILL, and WILLIS<sup>(10)</sup>
- PEPPARD, FARIS, GRAY, and MASON<sup>(2)</sup>; PEPPARD, GRAY, and MARKUS<sup>(3)</sup>
- ▽ TOPP and WEAVER<sup>(4-7)</sup>
- ◇ SUTTLE and STAMPFER<sup>(8)</sup>

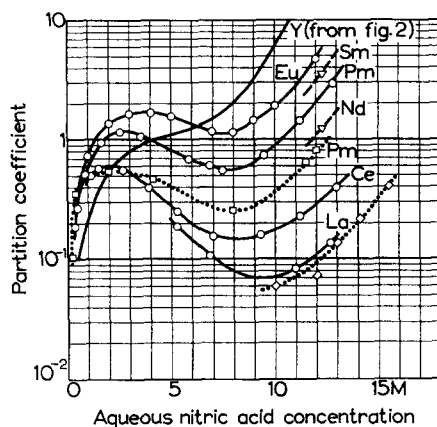


FIG. 4.—The partition coefficients of the lower lanthanide nitrates: 48% TBP in diluent (50% for PEPPARD *et al.*'s results).

- Our data (diluent: kerosene)
- PEPPARD, FARIS, GRAY, and MASON<sup>(2)</sup> (diluent: dibutyl ether)
- ▽ TOPP<sup>(4)</sup> (diluent: Varsol)
- ◇ SUTTLE and STAMPFER<sup>(8)</sup> (diluent: *n*-hexane)

(2) The Oak Ridge<sup>(4-7)</sup> results were generally obtained gravimetrically at a series of macro rare-earth concentrations. In extrapolating to trace concentration, it is necessary to ignore the anomalously high partition coefficients usually quoted for the lowest concentrations studied (where the analytical errors are presumably greatest). This procedure leads to figures consistent with those obtained with radioactive tracers. The two points in Fig. 4 necessitated a further extrapolation, since the TBP dilution data only covered the range 60–100% TBP in Varsol (a hydrocarbon diluent).

(3) The points ascribed to SUTTLE and STAMPFER<sup>(8)</sup> in Fig. 4 involved a similar extrapolation from the range 60–100% TBP in *n*-hexane.

(4) CUNINGHAME, SCARGILL, and WILLIS's<sup>(10)</sup> results were mainly obtained by gravimetric analysis at a low rare-earth concentration (0.4 g/l. initially), and are of limited accuracy.

BLACKMORE, BEARSE, and CALKINS' results<sup>(11)</sup> with 50% TBP in Sohio Solvent (another hydrocarbon diluent) have not been plotted, partly because they used macro rare-earth concentrations, but their data provide general confirmation of the curves in Fig. 4.

The shapes of the curves in Figs. 2-4 will be discussed in detail in another paper.<sup>(15)</sup> Briefly, the factors operating are:

- (1) Salting-out from the aqueous phase by the nitrate ion.
- (2) Formation of nitrate complexes.
- (3) Nitric acid competition for the available TBP.
- (4) Activity coefficient effects.

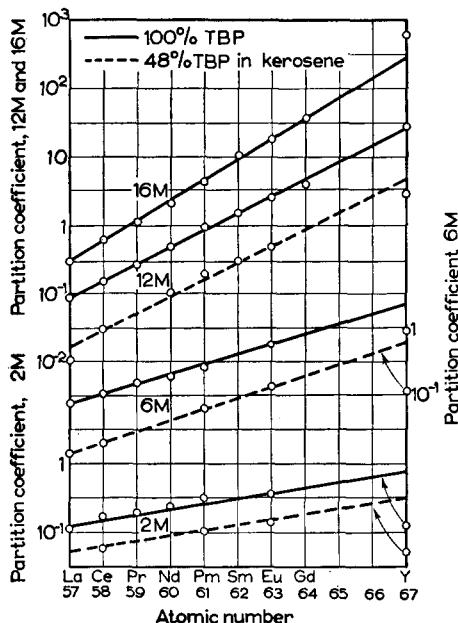


FIG. 5.

(1) accounts for the initial steep rise in the curves, at low acidities, while (2) and (3) provide a check on this rise at rather higher acidities, and often cause the partition coefficient to pass through a maximum. The further steep rise frequently observed at very high acidities (say  $>10$  M) has not been properly explained, but may be due to (4).

The partition coefficient curves for the series of elements from lanthanum to gadolinium form a regularly spaced family. The family is characterized by a relation of the form of equation (1), as discussed in the first part of this paper. This is illustrated in Fig. 5. The logarithmic relation probably does not hold perfectly, but some of the deviations in Fig. 5 may be due to uncertainties in the experimental results.

*Separation factors.* The important quantity  $S$ , the separation factor for an adjacent pair of elements, may be obtained from the partition data for any pair of elements by taking the  $(Z_1 - Z_2)$ th root of the ratio of partition coefficients ( $Z$  = atomic number). It may, of course, also be obtained from the slopes of the lines in Fig. 5, and if equation (1) held exactly, the two results would agree. The most reliable values of  $S$  can

probably be obtained from our cerium and europium data, as has been done in Fig. 6. Rather different curves are obtained with 48% and 100% TBP.

The principal feature of Fig. 6 is a steady rise in  $S$  from an extrapolated value of just over unity at zero acidity to nearly 2.0 at 16 M. The values of  $S$  at 12 and 15.6 M are rather larger than those given by PEPPARD, FARIS, GRAY, and MASON.<sup>(2)</sup> The high separation factors found at high acidities have been exploited at Oak Ridge for the separation of rare earths on a kilogram scale.

*The position of yttrium.* The behaviour of yttrium in relation to the lanthanides is of interest. This element is often regarded as a pseudo-lanthanide of atomic number *c.* 67, a position which accords with its Zachariasen ionic radius. PEPPARD,

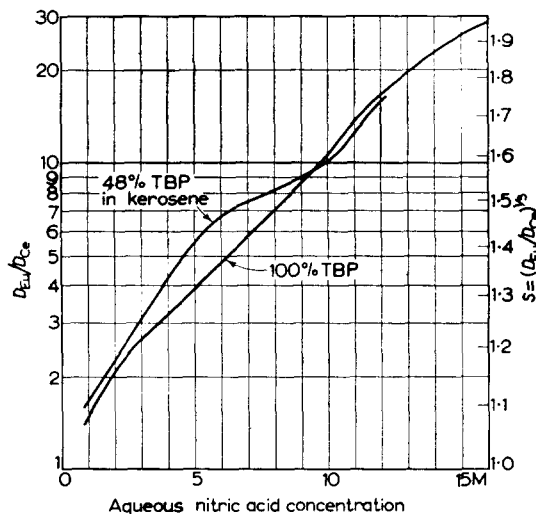


FIG. 6.—Separation factors.

FARIS, GRAY, and MASON<sup>(2)</sup> have pointed out that the TBP partition data at high acidities fit in fairly well with this idea, as can be seen from Fig. 5. At low acidities, however, yttrium behaves quite differently, becoming less extractable by nearly an order of magnitude than might have been expected. This will be discussed further in a later paper in this series, which deals with the higher lanthanides.

#### *Extraction in presence of other nitrates*

CUNINGHAME, SCARGILL, and WILLIS<sup>(10)</sup> have shown that praseodymium and neodymium extract much more readily from aqueous ammonium nitrate containing a little nitric acid, than from pure nitric acid of similar concentration. SUTTLE and POSKANZER<sup>(9)</sup> have made analogous observations with lanthanum, using calcium nitrate as the salting-out agent. In Table 2 we present some new results with cerium extracted from 6 M ( $\text{HNO}_3 + \text{NaNO}_3$ ), illustrating the same point. The effect is not confined to the rare earths: it also occurs with thorium<sup>(16)</sup> and plutonium(IV).<sup>(17)</sup>

The results show that the partition coefficient can increase by several orders of magnitude when nitric acid in the aqueous phase is replaced by another nitrate at

<sup>(16)</sup> D. SCARGILL, quoted by H. A. C. MCKAY *Int. Conf. on the Peaceful Uses of Atomic Energy, Geneva* P/441. Vol. 7, p. 314. (1955).

<sup>(17)</sup> G. F. BEST, H. A. C. MCKAY, and P. R. WOODGATE *J. inorg. nucl. chem.* **4**, 315 (1957).



constant (stoichiometric) nitrate concentration. The effect becomes more marked as the nitrate concentration increases, at least up to 6–7 M. Moreover, it is in the last stages of replacement, when the nitric acid concentration is quite small, that the greatest rate of increase of extraction is observed.

TABLE 2.—48% TBP IN KEROSENE

HNO <sub>3</sub> conc. (aq)	4.00	1.50	0.50	0.20	0.05	0.005 M
NaNO <sub>3</sub> conc. (aq)	2.00	4.50	5.50	5.80	5.95	6.00 M
<i>D</i> <sub>Ce</sub>	0.030	0.113	0.56	1.90	8.6	17.6

An explanation of the phenomenon can readily be given in terms of the factors listed earlier. Removal of nitric acid from the system means that less of the TBP is combined with the acid, i.e. more of the TBP is free; whilst the presence of an in-extractable nitrate maintains the salting-out effect of the nitrate ion. The nitric acid partition data in Table 4 enable us indeed to make a calculation showing that the rare-earth partition coefficients are roughly proportional to the cube of the concentration of free TBP; this is the power we should expect if tri-solvates  $M(\text{NO}_3)_3 \cdot 3\text{TBP}$  are formed. The calculation emphasises the importance of reducing the aqueous acidity to a low value in order to obtain efficient utilization of the TBP.

TABLE 3.—50% TBP IN XYLENE

HNO <sub>3</sub> conc. (aq)	1.00	0.50	0.10	0.01 M	0.50 M
Metal nitrate (aq)	—	6.00 M	NaNO <sub>3</sub>	—	1.00 M Al(NO <sub>3</sub> ) <sub>3</sub>
HNO <sub>3</sub> conc. (org)	1.15	0.96	0.46	0.09 M	—
Free TBP conc. (org)*	0.59	0.80	1.33	1.73 M	—
<i>D</i> <sub>Ce</sub>	0.16	0.45	3.4	8.5	—
<i>D</i> <sub>Pr</sub>	0.20	0.71	4.0	11.1	1.29
<i>D</i> <sub>Nd</sub>	0.35	1.0	5.7	12.6	1.75
<i>D</i> <sub>Pr</sub> / <i>D</i> <sub>Ce</sub>	1.2	1.6	1.2	1.3	—
<i>D</i> <sub>Nd</sub> / <i>D</i> <sub>Pr</sub>	1.8	1.4	1.4	1.2	1.4
<i>D</i> <sub>Nd</sub> / <i>D</i> <sub>Ce</sub>	2.2	2.2	1.7	1.5	—

\* Assuming that all the acid in the organic phase forms a 1:1-compound with TBP.

*Separation factors.* Earlier work, e.g. that of CUNINGHAME, SCARGILL, and WILLIS,<sup>(10)</sup> indicates that good separation factors as well as high extraction can be obtained by working at low acidity but high nitrate concentration. Moreover, BOCHINSKI, SMUTZ, and SPEDDING<sup>(12)</sup> have used such conditions for the practical separation of the rare earths, utilizing the rare-earth nitrates themselves to obtain a high nitrate concentration. (One of their graphs, indeed, seems to indicate separation factors of 10 or more, but we think that a decimal point has been omitted and that their true *S*-value was about 1.4).

The results of a further study of the separation factors are shown in Table 3. The figures are somewhat scattered, but they indicate an *S*-value of about 1.4 for 6 M NaNO<sub>3</sub> plus small amounts of nitric acid; there is also possibly a trend towards

increasing separation factors as the acidity is increased. It is interesting to note, too, that 1 M  $\text{Al}(\text{NO}_3)_3$  is apparently about as effective as 6 M  $\text{NaNO}_3$  as regards both extraction and separation of the lanthanides. An isolated result with europium ( $D_{\text{Eu}} = 67$  for 48% TBP in kerosene, and a 6 M  $\text{NaNO}_3$ , 0.05 M  $\text{HNO}_3$  aqueous phase) yields a  $D_{\text{Eu}}/D_{\text{Ce}}$  ratio of 7.8, corresponding to  $S = 1.5$ .

#### *Extraction in presence of complexing agents*

One or two experiments have been carried out in the presence of lactic acid (Table 4). It will be seen that this reagent holds the rare earths back in the aqueous phase, and yields very poor separation factors. Addition of TTA (thenoyltrifluor-

TABLE 4.—50% TBP IN XYLENE  
Aqueous phase: 6 M  $\text{NaNO}_3$ , 0.5 M lactic acid

pH (aq)* TTA conc. (org)	2.0 Nil	3.5 Nil	2.0 0.20	3.5 0.20 M
$D_{\text{Ce}}$	0.71	0.010	19	>300
$D_{\text{Pr}}$	—	0.010	—	>300
$D_{\text{Nd}}$	0.68	0.011	21	>300

\* Adjusted by adding ammonia.

acetone) to the system results in high extraction again, but the separation factors still seem poor. On the other hand, CUNINGHAME, SCARGILL, and WILLIS<sup>(10)</sup> have shown that good separation factors as well as high extraction are obtained with TTA-TBP mixtures in the absence of lactate.

#### *Survey of separation factors*

Typical values of  $S$  obtained under a variety of conditions are assembled in Table 5. These show that very high acidities probably yield the best separations,

TABLE 5

Aqueous phase	Organic phase*	Separation factor, $S$
Infinite dilution (extrapolated)	100% TBP	1.03
6 M $\text{HNO}_3$	48% TBP in kerosene	1.5
	100% TBP	1.4
12.3 M $\text{HNO}_3$	60–100% TBP in Varsol	1.7 <sup>(4)</sup>
15.6 M $\text{HNO}_3$	100% TBP	2.0
6 M $\text{NaNO}_3$ , 0.05 M $\text{HNO}_3$	48% TBP in kerosene	1.5
5–7 M $\text{NH}_4\text{NO}_3$ , 0.1 M $\text{HNO}_3$	100% TBP	1.5 <sup>(10)</sup>
1 M $\text{Al}(\text{NO}_3)_3$ , 0.5 M $\text{HNO}_3$	50% TBP in xylene	1.4
6 M $\text{NaNO}_3$ , 0.5 M lactic acid, pH 2	50% TBP in xylene	1.0
6 M $\text{NaNO}_3$ , 0.5 M lactic acid, pH 2	50% TBP in xylene, 0.2 M TTA	1.05
1 M $\text{NH}_4\text{NO}_3$ , pH 3.55	30% TBP in kerosene, 0.2 M TTA	2.4 <sup>(10)</sup>

\* The separation factors do not usually vary much with the dilution of the TBP.

though the device of using TTA-TBP mixtures deserves further study. Good separations can also be obtained at low acidities combined with high nitrate concentrations.

Our thanks are due to E. JACKSON for some of the europium results given in this paper.

Many of the results quoted here appeared originally in A.E.R.E. C/R 1514 (1954) by MCKAY, ALCOCK, and SCARGILL. The results quoted there for cerium(IV) nitrate are, however, erroneous.

*Note added in proof.* E. JACKSON has recently obtained the following results with europium at 15.6 M  $\text{HNO}_3$  and varying TBP concentration:

TBP conc.	1 %	2 %	3 %	4 %	5 % in kerosene
$D_{Eu}$	0.00029	0.0024	0.0076	0.0174	0.032
					0.032

The best line through these points is of slope 3.0, indicating the formation of  $\text{Eu}(\text{NO}_3)_3 \cdot 3\text{TBP}$ .