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

THE PLUTONIUM NITRATES

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Abstract—Plutonium(III) nitrate is relatively inextractable by tri-*n*-butyl phosphate (TBP), but plutonium(IV) and plutonyl nitrates are freely extractable. Plutonyl nitrate is, however, less extractable than uranyl nitrate by a factor of about 10.

Experiments in which the TBP concentration was varied indicated the formation of $Pu(NO_3)_4 \cdot 2TBP$ and $PuO_2(NO_3)_2 \cdot 2TBP$.

In the case of plutonium(IV) nitrate it was shown that the temperature coefficient of extraction is small, that salting-out by sodium nitrate causes a striking increase in extraction, and that uranyl nitrate depresses the extraction. Increase in the plutonium(IV) nitrate concentration may either raise or lower the partition coefficient according to the conditions.

TRI-*n*-BUTYL phosphate (TBP) is a good solvent for the extraction of plutonium from nitrate solutions. It was, for example, utilized in the isolation of plutonium from natural sources.[1] The tetra- and hexavalent states are very readily extracted, but trivalent plutonium, like the trivalent rare earths,[2] is relatively weakly extracted under most conditions. Plutonium can therefore be rendered extractable or inextractable by oxidation or reduction.

EXPERIMENTAL

The general techniques used were described in the first paper in this series.[3]

The plutonium was available initially in the tetravalent state in 6 M HNO_3. Plutonium(III) was prepared when required by dilution and addition of ferrous sulphamate and hydroxylamine as reductants; the latter reagent served to maintain a high Fe(II) : Fe(III) ratio, and hence to ensure complete reduction of the plutonium. Plutonium(VI) was prepared by anodic oxidation, but no steps were taken to remove residual plutonium(IV); this we now recognize as a blemish on our work, though we do not think it was of much effect numerically.

When the partition coefficients were fairly high, they were measured by a back-extraction technique. The plutonium was extracted into an organic phase, and this was then equilibrated with two successive portions of aqueous phase. This procedure should have eliminated traces of plutonium(III) in plutonium(IV) or (VI) partitions, and also traces of Am^{241} which might have grown from Pu^{241}; the agreement between the two successive measurements indicated whether the procedure had been successful. When the partition coefficients were low, forward partitions were used; two successive measurements again afforded a check on the presence of impurities, including especially higher valency states contaminating plutonium(III). Results for successive partitions seldom differed in fact by more than 2%; the results for plutonium(VI) showed the largest discrepancies, probably owing to the presence of plutonium(IV).

In most of the work the plutonium was used at a concentration of *c.* 0·1 g/1 (0·0004 M). This is effectively a trace concentration, i.e. it is negligible in comparison with the concentrations of the major

[1] D. F. PEPPARD, M. H. STUDIER, M. V. GERGEL, G. W. MASON, J. C. SULLIVAN, and J. F. MECH *J. Amer. chem. Soc.* **73**, 2529, 3278 (1951).
[2] D. SCARGILL, K. ALCOCK, J. M. FLETCHER, E. HESFORD, and H. A. C. McKAY *J. inorg. nucl. Chem.* **4**, 304 (1957).
[3] K. ALCOCK, F. C. BEDFORD, W. H. HARDWICK, and H. A. C. McKAY *J. inorg. nucl. Chem.* **4**, 100 (1957).

components (nitric acid, TBP, etc.). Moreover, it is low enough to ensure that plutonium(IV) will not disproportionate appreciably during the time of the experiment. According to Hall's data,[4] less than 1 % disproportionation will occur in 10 min at 25°C (a) with 2 g/l of plutonium at acidities above 0·25 M HNO₃, and (b) with 5 g/l at acidities above 0·40 M HNO₃. Hence even our experiments at higher plutonium concentrations should be unaffected by disproportionation.

Some of the partitions were carried out at room temperature (20–23°C), and some in a thermostat (25°C or 40°C). The TBP was diluted throughout with "odourless" kerosene.

Plutonium was determined by α-counting, and acidities by titration with alkali. In the series at higher plutonium concentrations, the plutonium was precipitated as ferrocyanide prior to alkali titration of the aqueous phase.[5] The general level of reproducibility of the final results was ±10%.

Such other data as are available for comparison are in general agreement with ours, but very little numerical information has appeared in the open literature.

RESULTS AND DISCUSSION
Plutonium(III) nitrate

Plutonium(III) nitrate only extracts weakly into 19 % v/v (0·69 M) TBP in kerosene: These results, which are plotted in Fig. 1, are in general accord with those for other

Table 1

HNO₃ conc (aq.)	0·20	0·65	1·20	2·0	3·0	4·0	5·0 M
Partition coeff. (org./aq.)	0·0027	0·0089	0·0157	0·0167	0·0161	0·0126	0·0116

trivalent lanthanides[2] and actinides. They imply, of course, that nearly all the plutonium(III) will be left behind in the aqueous phase in an extraction under the conditions in question.

Plutonium(IV) nitrate

Extraction from nitric acid solutions—Plutonium(IV) nitrate is highly extractable by 19 % TBP in kerosene, maximum extraction from nitric acid solutions being observed at c. 7 M HNO₃. Our results are given in Table 2. The two series at 20–23°C

Table 2

HNO₃ conc (aq.)	0·15	0·21	0·44	0·52	0·62	0·82	0·84	0·86	0·91	1·28	1·41	2·65 M
Partition coeff. 25°C (org./aq.) 40°C	0·114 —	0·204 0·166	0·39 0·33	0·41 —	0·72 —	1·01 —	1·14 1·01	1·20 1·19	1·30 —	2·20 —	2·37 2·54	5·7 5·9

HNO₃ conc (aq.)	2·2	3·0	4·0	5·0	6·0	7·0	8·0	10·0	11·5	13·5 M
Partition coeff. (org./aq) 20–23°C	3·9	6·8	11·5	16·6	19·6	20·2	18·2	13·0	6·1	3·0

and 25°C fit reasonably well together, as Fig. 1 shows; the 25°C data represent later and more careful work. The 40°C measurements were carried out on the same solutions as the 25°C measurements in order to obtain good comparisons: equilibrium was established at 25°C, samples were taken for analysis, the temperature was raised to 40°C, equilibrium was re-established, and further samples were taken for analysis.

[4] G. R. Hall, private communication.
[5] B. A. J. Lister, I. L. Jenkins, and N. J. Keen A.E.R.E. C/M 165 (1953).

The temperature coefficient is clearly low, and corresponds to a heat of transference of plutonium(IV) nitrate between phases of less than 2000 cal/mole.

Further measurements were made at 20–23°C at lower TBP concentrations:

TABLE 3

HNO$_3$ conc (aq.)	Partition coeff. (org./aq.)		
	1·9%	4·8%	9·5% TBP in kerosene
1·0 M	0·015	0·13	0·43
7·0	0·50	2·4	8·7
11·5	0·13	0·65	2·3

These, in combination with data from Table 2 (interpolated in one instance), indicate that, as a limiting law at low TBP concentrations, the partition coefficient depends on the square of the TBP concentration (see Fig. 2). This implies the formation of a di-solvate Pu(NO$_3$)$_4$·2TBP, analogous to the corresponding zirconium compound.[3]
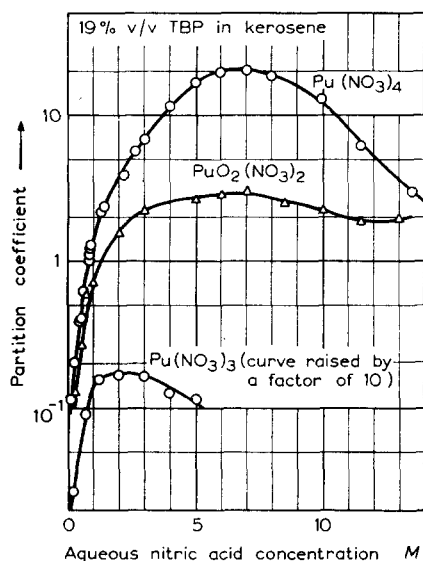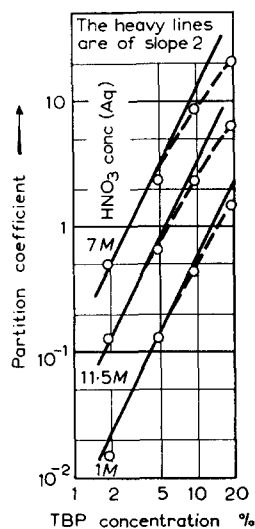

FIG. 1

FIG. 2

Spectroscopic evidence supports the postulate that there are four nitrate groups in the complex[6].

The deviations from the square law in Fig. 2 (due presumably to nonideality) are appreciable but hardly sufficient to make us doubt that it is the true limiting law. They are, moreover, similar at all acidities. This means that the curve in Fig. 1 retains its shape as the TBP concentration is varied; it merely suffers a vertical displacement.

Another series of measurements has been carried out at 25°C at rather higher plutonium concentrations, with the results given in Table 4. Fig. 3 gives smoothed curves based on these data. The check indicated by the footnote to the table shows that disproportionation did not vitiate the results, even at the lowest acidities.

Table 4.—19% v/v TBP in kerosene

HNO₃ conc (aq.)	Plutonium concentrations (g/l.)		Partition coefficient (org./aq.)
	Aqueous	Organic	
0·22 M	2·07	0·38	0·18
0·31	2·42	0·62	0·26
0·34	0·71	0·19	0·27
0·39	2·20*	0·76	0·37
0·43	6·22	2·96	0·48
0·50	5·39	3·86	0·71
0·55	1·18	0·72	0·61
0·63	2·18	1·50	0·69
0·65	4·28	3·05	0·71
0·70	4·26	4·00	0·94
0·85	1·50	1·80	1·20
0·89	2·68	3·39	1·27
0·90	7·16	8·35	1·47
1·15	3·64	6·07	1·67
1·32	4·97	8·40	1·69(?)
1·33	3·50	8·45	2·40
1·64	4·43	11·6	2·61

* Unchanged after 5 hr equilibration

The rise in the partition coefficient with plutonium concentration at low acidities may be ascribed to increased salting-out, due to additional nitrate ion present in the aqueous phase. If there were no complications, the partition coefficient would be proportional to the fourth power of the nitrate ion concentration. On increasing the plutonium concentration from trace level to 4·8 g/l. (0·02 M), the partition coefficient would therefore increase by a factor of $(0·58/0·50)^4 = 1·80$ at 0·5 M HNO₃ and $(1·08/1·00)^4 = 1·40$ at 1·0 M HNO₃. The actual increases are by factors of 1·38 and 1·10 respectively. These are smaller than those just calculated, mainly on account of nitrate-complexing of Pu^{4+} ions in the aqueous phase; if, for example, we assume that all the plutonium is complexed as $PuNO_3^{3+}$ at 0·5 M HNO₃, then we should expect a factor of $(0·56/0·50)^3 = 1·40$, which is very close to the experimental figure. At higher acidities, when most of the plutonium is in the organic phase, a further effect becomes important, namely (partial) plutonium saturation of the TBP, which reduces the partition coefficient. Our data suggest that the null region, where the partition coefficient is independent of plutonium concentration, is around 1·2 M HNO₃.

Beyond a certain plutonium concentration (c. 10 g/l.) the organic phase divides into two, a TBP-rich and a kerosene-rich fraction.[6]

Extraction in presence of sodium nitrate—There is a striking rise in the partition coefficient for plutonium(IV) when nitric acid in the aqueous phase is replaced, mole for mole, by sodium nitrate; similar results have been obtained for the rare earths[2] and thorium. Our results for plutonium are given in Fig. 4, and were obtained at 20–23°C. The true figures may be somewhat lower than our measurements indicate, as we may have underestimated the plutonium concentrations in the aqueous phase.

[6] T. V. Healy and H. A. C. McKay *Trans. Faraday Soc.* **52**, 633 (1956).

GOULDEN, DURHAM, and CORRIVEAN's results[7] on the extraction of plutonium in presence of 0·45 M $Al(NO_3)_3$ show that aluminium nitrate is a more powerful salting-out agent than sodium nitrate. 0·45 M $Al(NO_3)_3$ is about as effective as 2 M $NaNO_3$ at 1–2 M HNO_3, and about as effective as 3 M $NaNO_3$ at 4–5 M HNO_3. A similar difference between the two nitrates has been noted in relation to the lanthanides.[2]
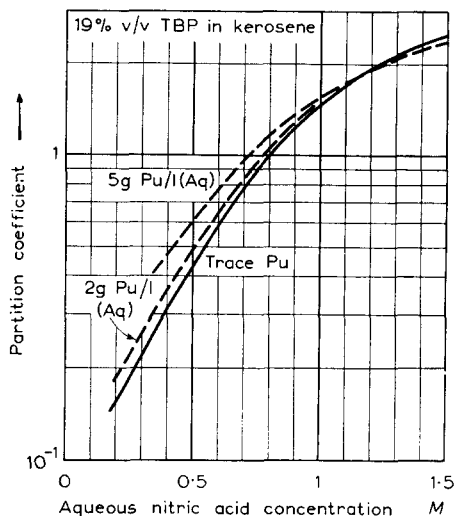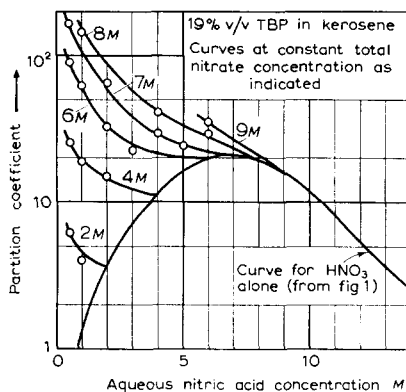

FIG. 3

FIG. 4

Extraction in presence of uranyl nitrate—Uranyl nitrate depresses the extraction of plutonium(IV), just as it does that of zirconium.[3] A typical series of results at 25°C is given in Table 5. The figures in brackets refer to partition at zero or trace uranyl

TABLE 5.—19% v/v TBP IN KEROSENE

Concentrations			Partition coefficients (org./aq.)	
HNO₃ (aq.)	UO₂(NO₃)₂ (aq.)	UO₂(NO₃)₂ (org.)	Pu(IV)	UO₂
0·20 M	0·024 M	0·011 M	0·13 (0·16)	0·48 (0·5)
0·50	0·024	0·039	0·43 (0·47)	1·6 (1·6)
0·70	0·024	0·063	0·62 (0·83)	2·7 (3·0)
1·00	0·027	0·087	0·90 (1·5)	3·2 (4·2)
1·50	0·028	0·131	1·18 (2·6)	4·8 (7·4)

nitrate concentration; for plutonium(IV) they have been taken from Fig. 1, and for uranyl nitrate from unpublished results by G. F. BEST.

The main reason for the lowering of the partition coefficients is loading of the organic phase with uranyl nitrate, so that there is less free TBP. This causes a parallel lowering of all partition coefficients, including that of uranyl nitrate itself, as the last two columns illustrate.

[7] P. D. GOULDEN, R. W. DURHAM, and V. CORRIVEAN   CRDC-640 (1955).

Plutonyl nitrate

Our results for the distribution of traces of plutonyl nitrate in presence of nitric acid at 20–23°C for 19% TBP in kerosene are shown in Fig. 1. As has already been mentioned, we have reason to suspect the presence of a small proportion of plutonium (IV) nitrate in our material. 5% of plutonium(IV) would mean an overestimation of the partition coefficient of 9% at the maximum in the curve, with the backextraction procedure used, and rather less elsewhere. The true curve may therefore be a few per cent lower than that shown in Fig. 1.

We have also obtained some results at lower TBP concentrations; though rather erratic, they suggest a square-law dependence of partition coefficient on TBP concentration in the limit, and hence the formation of $PuO_2(NO_3)_2 \cdot 2TBP$, analogous to $UO_2(NO_3)_2 \cdot 2TBP$.

It is noteworthy that plutonyl nitrate is less extractable than uranyl nitrate by a factor of about 10. This is a reversal of the usual trend of increasing extractability with increasing atomic number in the lanthanide and actinide series.