Studies on the Extraction of Metal Complexes

XXVIII. The Distribution of some Actinides and Fission Products between Tributyl Phosphate (TBP) and Aqueous Solutions of HNO₃ and Ca(NO₃)₂

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The distribution ratios of U(VI), Pu(VI), Pu(IV), Th(IV), Ru, Zr(IV), Nb(V), La(III), Sr(II) and Ca(II) between tributyl phosphate (TBP) and aqueous solutions of varying concentrations of HNO₃ have been determined at room temperature for different (constant) concentrations of Ca(NO₃)₂ in the aqueous phase. The extraction curves are discussed with respect to the different complexes formed and to the possibility of using the investigated systems for separating plutonium and uranium from the fission products.

In the previous paper of this series of investigations (Part XXVII[1]) the extraction of plutonium, uranium and some fission products from aqueous solutions into the organic solvent methyl *iso*butyl ketone (hexone) was studied as a function of the HNO₃ and Ca(NO₃)₂ concentrations in the aqueous phase. These investigations have here been extended to the organic solvent tributyl phosphate (TBP); in this paper, only the case of pure TBP is reported (*i.e.* no organic diluent added). No extensive investigations of metal extractions with 100 % TBP seem to have been reported previously [2,3].

The following metals (valency states in aqueous solutions — if known — are given within parenthesis) have been studied: U(VI), Pu(VI), Pu(IV), Th(IV), Ru, Zr(IV), Nb(V), La(III), Sr(II) and Ca(II). The concentration of the metal nitrates never exceeded 0.1 M (except for Ca), while the HNO₃ concentration was varied from $\sim$ 0.1 to 10 M, and the Ca(NO₃)₂ concentration from 0 to $\sim$ 4 M. The results are given in the form of curves (Figs. 1—7) showing the distribution ratio of a metal as a function of the equilibrium HNO₃ concentration in the aqueous phase at constant Ca(NO₃)₂ concentration.

EXPERIMENTAL

Chemicals. Tributyl phosphate, (C₄H₉)₃PO₄, of technical grade was obtained from AB Kebo. The solvent was treated with 5 % sodium carbonate and then washed with several portions of water.

UO$_3$ obtained from AB Atomenergi was dissolved in concentrated HNO$_3$, filtered and diluted. The uranium content was determined by weighing the oxide U$_3$O$_8$ after evaporation and ignition.

^{234}Th (UX$_1$) was used as tracer for thorium. The solutions were made $\sim 10^{-5}$ M by the addition of ^{232}Th.

A tracer solution of Pu(IV) in 10 M HNO$_3$ was available. Pu(VI) was obtained by oxidizing the Pu(IV) solution with 0.1 M K$_2$S$_2$O$_8$ in 1 M HNO$_3$ using Ag$^+$ as catalyst immediately before use. In one case the oxidizing agent was 0.2 M KBrO$_3$.

A carrier free solution of ^{95}Zr + ^{95}Nb in 0.3 M HCl and with 2 % oxalic acid was obtained from AERE, Harwell. In the distribution experiments this solution was diluted 1:50.

^{106}Ru in 0.4 M HCl was purchased from AERE, Harwell. The solution was carrier free and diluted 1:1000 before use.

^{140}La was obtained as the neutron irradiated oxide. The oxide was dissolved in 1 M HNO$_3$ to make the metal concentration $\sim 10^{-5}$ M.

^{89}Sr-carbonate was dissolved in concentrated HNO$_3$ and diluted.

The Ca(CO$_3$)$_2$ used was of reagent grade as were all other reagents.

Distribution experiments. All distribution experiments were carried out at room temperature (20$\pm$2°C) and were run with each metal separately. The metal nitrate was mixed with varying amounts of HNO$_3$ and Ca(NO$_3$)$_2$ and shaken vigorously for 5 min with an equal volume of TBP; equilibrium is usually attained within a few minutes. The two phases were separated by centrifuging. Samples of each phase were withdrawn to determine the HNO$_3$ concentration of the aqueous phase as well as the metal concentration in each phase. The distribution ratio q, *i.e.* the ratio of the metal concentration in the organic phase to that in the aqueous phase, could then be calculated.

Analyses. Ca was determined by a substitution titration with EDTA (ethylenediamine tetraacetic acid) at pH 10 using Eriochrome Black T as indicator [4]. Before the titration, Ca in the TBP phase was transferred to an aqueous phase by mixing 20 ml of water with 0.5 ml of the TBP phase diluted with 20 ml of benzene.

Uranium was determined spectrophotometrically by the thiocyanate method [5,6]. Only the water phase which contained the smallest fraction of U was analysed, whereas the uranium content of the TBP phase was obtained as the difference between the initially added uranium concentration (0.1 M) and that found in the aqueous phase.

HNO$_3$ was determined by titration with NaOH.

The α activity of Pu was measured by an argon-methane proportional counter. By means of the TEG-method [7] dry, thin samples were obtained.

The β, γ counting of ^{140}La, ^{106}Ru (^{106}Rh) and ^{234}Th (UX$_1$) was made on dry samples, whereas ^{89}Sr was measured with a liquid counter. In order to increase the sensitivity of the determinations at very low and at very high distribution ratios, the volume ratio V_{TBP}/V_{aq} was varied, *i.e.* for $q_{Sr} \leq 10^{-2}$ $V_{TBP}/V_{aq} = 5$, for $q_{Th} \geq 10^2$ $V_{TBP}/V_{aq} = 0.1$. In the latter case, the small amount Th in the water phase was concentrated by a hydroxide precipitation with La as carrier thus increasing the counted activity.

For the determination of Zr and Nb separately in a mixture of both of them, the following procedure was used. By means of a lead absorber (200 mg/cm^2) the β-activity was filtered away and the total γ-activity of the solution of ^{95}Zr (0.40 MeV β,; 0.71 MeV γ) + ^{95}Nb (0.15 MeV β, 0.76 MeV γ) was determined from measurements on dry samples. The fraction of γ-activity contributed by ^{95}Zr on this solution was determined by precipitating [8] the zirconium as BaZrF$_6$ and counting the precipitate through the same absorber; inactive zirconium was added as a carrier. From an average of four determinations 37.5 % of the total γ-activity was ascribed to ^{95}Zr. For the ratio $R = I_{Zr}/I_{Nb}$ we then calculate the value 0.60.

In the distribution experiments, the total γ-activity of each phase was determined (I_{TBP} respectively I_{aq}) as well as the Zr content of the water phase ($I_{Zr\ aq}$), by measuring precipitated BaZrF$_6$. q_{Zr} was calculated from the relation

$$q_{Zr} = \frac{R}{(R+1)} \cdot \frac{(I_{TBP} + I_{aq})}{I_{Zr,aq}} - 1$$

The ratio I_{TBP}/I_{aq} was found to depend on the time of mixing and increased with time, probably because equilibrium was slowly attained for Nb. For a shaking time of 5 min the distribution ratio q_{Nb} was calculated according to

$$q_{Nb} = \frac{1}{(R+1)} \cdot \frac{(I_{TBP} + I_{aq})}{(I_{aq} - I_{Zr,aq})} - 1$$

Good material balance was obtained.

RESULTS AND DISCUSSION

The distribution curves

The distribution ratio q_M (subscript refers to the metal investigated) has been plotted against the molarity of HNO_3 in the aqueous phase at equilibrium. The curves are shown in Figs. 1—7 for initial $Ca(NO_3)_2$ concentrations of 0, 1, 2, 3 and 4 M. In all cases the distribution ratios increase with increasing $Ca(NO_3)_2$ concentration. The distribution ratios also increase with increasing HNO_3 concentration except at high $Ca(NO_3)_2$ concentrations.

The distribution of HNO_3 is presented in two different ways. Fig. 1a shows the HNO_3 concentration of the TBP phase as a function of the aqueous HNO_3 concentration. Fig. 1b shows q_H as a function of the HNO_3 concentration.
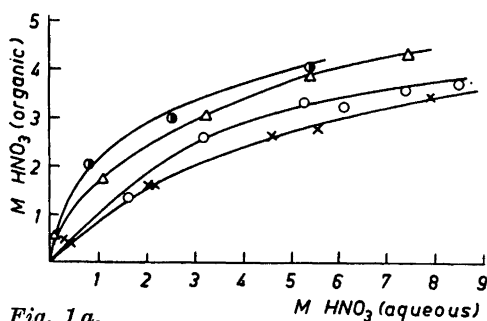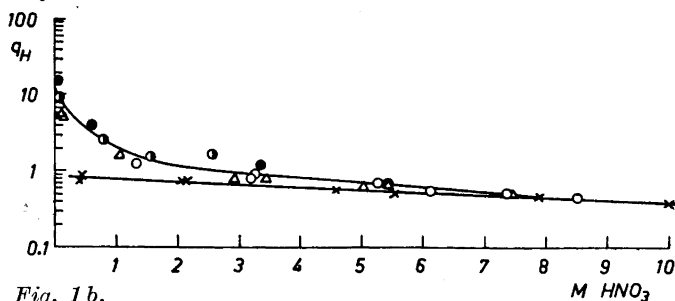

Fig. 1 a.

Fig. 1 b.

The distribution of HNO_3 as a function of the equilibrium concentration of HNO_3 in the aqueous phase in two different graphical representations. Concentrations of initial $Ca(NO_3)_2$: ● 4M, ◑ 3 M, △ 2 M, ○ 1 M, × no $Ca(NO_3)_2$ present.

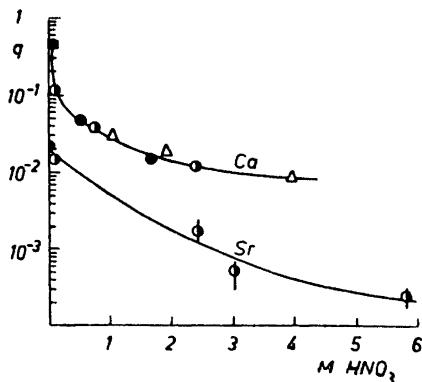Fig. 2. The distribution ratio q of calcium and strontium as a function of the equilibrium concentration of HNO_3 in the aqueous phase. Concentrations of initial $Ca(NO_3)_2$: ● 4 M, ◑ 3 M, △ 2 M.
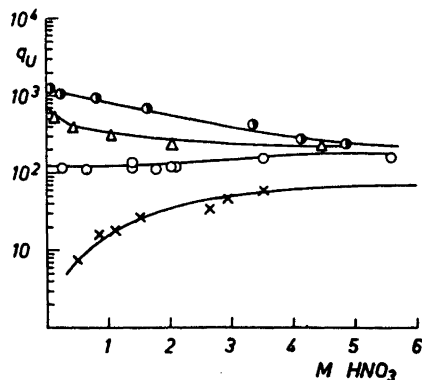
Fig. 3. The distribution ratio q_U of hexavalent uranium as a function of the equilibrium concentration of HNO_3 in the aqueous phase. Concentration of initial $Ca(NO_3)_2$: ◑ 3 M, △ 2 M, ○ 1 M, × no $Ca(NO_3)_2$ present.

These results can be compared with some data available in the literature. The distribution curve of HNO_3 with no $Ca(NO_3)_2$ present (Fig. 1a) agrees closely with that determined by Alcock et al.[10] It is noteworthy that at low HNO_3 concentration our results agree better with their calculated curve for a 1:1 complex of $HNO_3 \cdot TBP$ than their experimental data do[Ref. 10, Fig. 4]. Peppard et al.[11] report the extraction of Th and Zr into 100 % TBP from HNO_3 solutions containing no $Ca(NO_3)_2$. Their results for Th agree
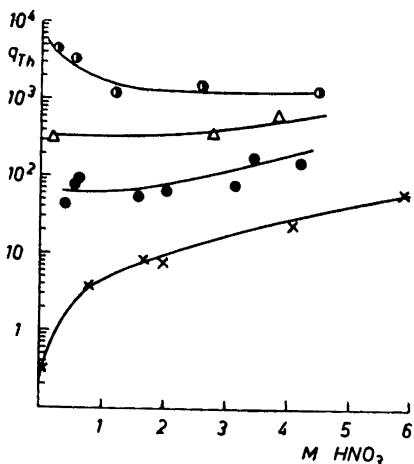

Fig. 4. The distribution ratio q_{Th} of thorium as a function of the equilibrium concentration of HNO_3 in the aqueous phase. Concentration of initial $Ca(NO_3)_2$: ◑ 3 M, △ 2 M, ● 1 M, × no $Ca(NO_3)_2$ present.
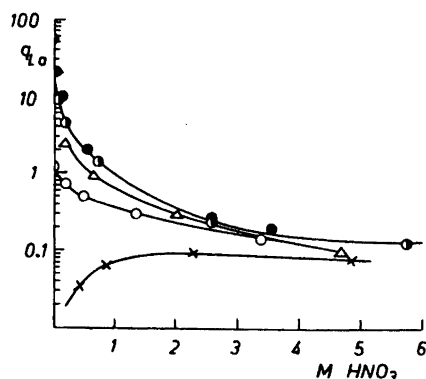
Fig. 5. The distribution ratio q_{La} of lanthanum as a function of the equilibrium concentration of HNO_3 in the aqueous phase. Concentration of initial $Ca(NO_3)_2$: ● 4 M, ◑ 3 M, △ 2 M, ○ 1 M, × no $Ca(NO_3)_2$ present.
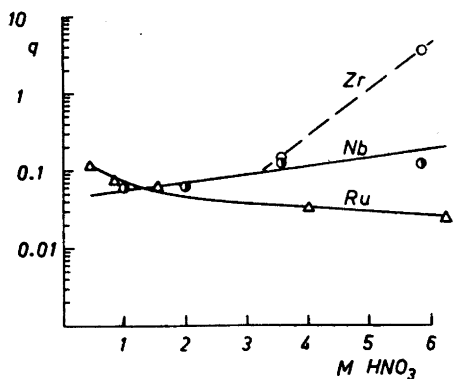
Fig. 6. The distribution ratios of ruthenium △, zirconium ○ and niobium ◑ as a function of the equilibrium concentration of HNO₃ in the aqueous phase. No Ca(NO₃)₂ present.

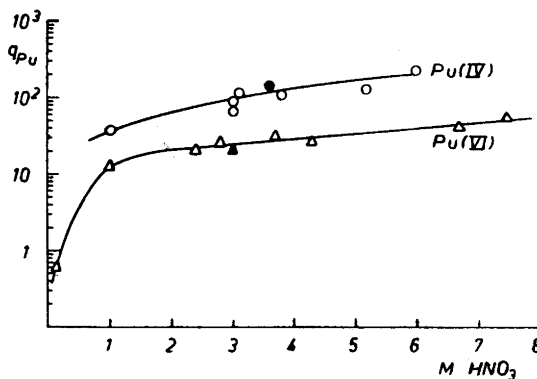*Fig. 7.* The distribution ratio q_{Pu} of tetravalent and hexavalent plutonium as a function of the equilibrium concentration of HNO₃ in the aqueous phase. No Ca(NO₃)₂ present. Plutonium pretreated with 10 M HNO₃ ○, NaNO₂ ●[cf. Ref. 9], BrO₃⁻ ▲, and S₂O₈²⁻ △.

with the present work except for high acidities where we obtain a lower value of q_{Th}. The presence of $H_2C_2O_4$ in our stock solution of Zr probably explains our lower value of q_{Zr} compared with Peppard's (*cf.* Bruce [12] who shows the effect of $H_2C_2O_4$ on q_{Zr}). Scadden and Ballou [13] report the extraction of Zr and Nb from HNO₃ solutions into 100 % TBP. Their data are, however, for TBP as received, which yields quite different results because of small impurities of hydrolysis products as, *e.g.*, dibutylphosphate (DBP). Peppard *et al.*[14] report $q_{La} = 0.33$ for 100 % TBP and an aqueous phase 15.6 M in HNO₃, a value which is of the same order as that determined here *.

The extraction mechanism

It can be shown [15] that if a metal M (charge N+) is extracted as a nitrate complex into TBP, the distribution Q_M of the metal between the two phases should follow eqn. (1), if only mononuclear complexes of the type $M(NO_3)_n(TBP)_s^{N-n}$ are formed (neglecting waters of hydration).

$$Q_M = \frac{\sum\limits_{0}^{s} \lambda_{Ns} \varkappa_{Ns} \{NO_3^-\}^N \{TBP\}^s}{1 + \sum\limits_{1,1}^{ns} \varkappa_{ns} \{NO_3^-\}^n \{TBP\}^s} \qquad (1)$$

Here { } are used to indicate activities, which all refer to the aqueous phase; $\varkappa_{ns}$ is defined as the complexity constant and λ_{Ns} as the distribution constants of the uncharged complexes $M(NO_3)_N(TBP)_s$. If the concentration of all

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* *Note added in proof.* D. Scargill *et al.*[21] report q_{La} for 100 % TBP and varying HNO₃ solutions in close agreement with our data.

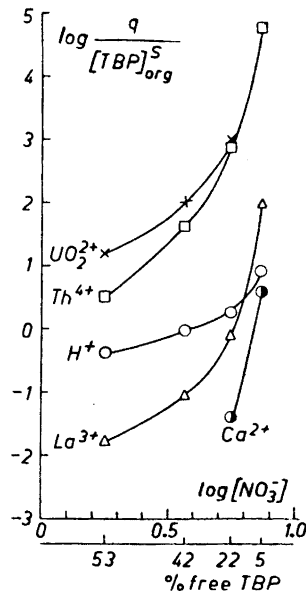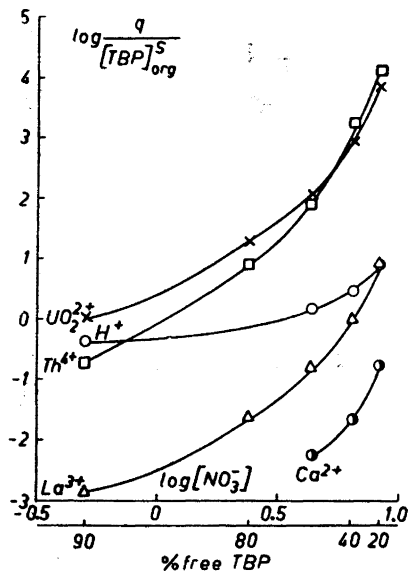**Fig. 8.** The variation of log $\dfrac{q}{[TBP]^S_{org}}$ with the nitrate concentration for constant $[HNO_3]_{(aq)} = 0.5$ M.

Fig. 9. The variation of log $\dfrac{q}{[TBP]^S_{org}}$ with the nitrate concentration for constant $[HNO_3]_{(aq)} = 2$ M.

complexes of M in the aqueous phase is small compared to the concentration of M^{N+}, the second term in the denominator of eqn. (1) can be neglected. If it is further assumed that only one complex of M is extracted, *e.g.* $M(NO_3)_N$ $(TBP)_S$, eqn. (1) can then be rewritten (using [ ] for concentration):

$$\log \frac{q_M}{[TBP]^S_{org}} - (N+1) \log f_\pm + \log \frac{f_{MC}}{f^S_{TBP}} = N \log [NO_3^-]_{aq} + \log K \quad (2)$$

Here all constants are included in K. The activity factor $f_\pm$ refers to the metal nitrate in the aqueous phase, f_{MC} to the metal complex and f_{TBP} to the free TBP in the organic phase; for 100 % TBP we define $f_{TBP} = 1$; f_{MC} is also $= 1$ in this case since the organic phase is infinitely dilute with respect to the metal complex. Q_M in eqn. (1) has been substituted by q_M to indicate that the distribution ratio in eqn. (2) refers to the concentration of the metal.

If the concentrations of the species present in large (molar) amounts are unaltered throughout the experiments, the activity factors can usually be regarded as constant. It is seen from eqn. (2) that a plot of log $q_M/[TBP]^S_{org}$ against log $[NO_3^-]_{aq}$ should then give a straight line of slope N. Such plots have been made in Figs. 8 and 9.

The q-values corresponding to different $Ca(NO_3)_2$ concentrations were taken from Figs. 1—5 at a constant acidity of 0.5 M and 2 M. $Ca(NO_3)_2$ was assumed to be completely

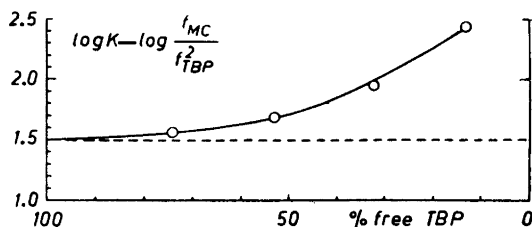Fig. 10. Plot for $UO_2(NO_3)_2$ of $\log$ $(q \cdot [TBP]_{org}^{-2}[NO_3^-]^{-2} \cdot f_{\pm}^{-3}) = \log K - \log \dfrac{f_{MC}}{f_{TBP}^2}$ at varying concentration of free TBP in the organic phase. Cf. equation 2, p. 1178.
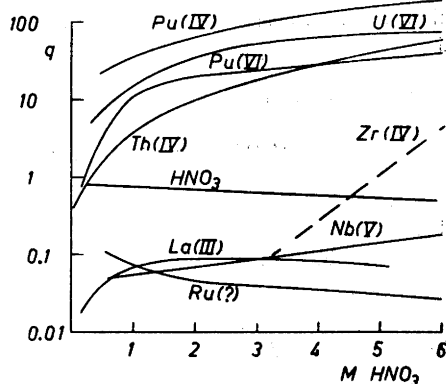
Fig. 11 The distribution ratios of the investigated metal ions and HNO_3 as a function of HNO_3 in the aqueous phase, when no $Ca(NO_3)_2$ is present.

dissociated in HNO_3 solutions <2 M, whereas a small correction for undissociated HNO_3 at high NO_3^- concentrations has been made [16].

The concentration of free, uncomplexed TBP in the organic phase, $[TBP]_{org}$, was calculated by subtracting the TBP bound to HNO_3[10] and to metal complexes [17,18] (see below) from the original TBP concentration ($[TBP]_{org,init}$) according to the equation

$$[TBP]_{org} = [TBP]_{org,init} - [HNO_3]_{org} - \Sigma S[M(NO_3)_N]_{org} \qquad (3)$$

which is valid if HNO_3 and $M(NO_3)_N$ are bound to a constant number (1 or S, respectively) of TBP molecules in the organic phase. $[TBP]_{org,init} = 3.4$ M when 100 % TBP is equilibrated with water and 3.2 M when at equilibrium with 2 M HNO_3[22] due to a small volume change.

S has been taken from investigations by McKay et al. for the complexes $UO_2(NO_3)_2 \cdot 2TBP$ [17,18], $Th(NO_3)_4 \cdot 2TBP$ [17,18], $La(NO_3)_3 \cdot 3TBP$ [18], $Ca(NO_3)_2 \cdot 3TBP$ [18] and $HNO_3 \cdot TBP$ [10].

It is seen from Figs. 8 and 9 that a straight line is not obtained in any case; all curves (except for HNO_3) start at low NO_3^- concentrations with a slope $< N$ and end up with a slope $> N$. Apparently it is impossible to adequately describe the systems without considering activity factors (the ionic strength of the aqueous phase varies from 3 to 12 molar, or 0.5 to 8 molal, and the concentration of free TBP from 90 to only 10 %).

The activity factors are only known for one of the metal complexes in these systems. They have been determined by McKay [19] for $UO_2(NO_3)_2$ in solutions of $Ca(NO_3)_2$; these activity factors include possible complex formation between UO_2^{2+} and NO_3^- ions in the aqueous phase. Introducing these values for $f_{\pm}$ in eqn. (2), one can calculate $\log K - \log f_{MC}/f_{TBP}^2$ as a function of $[TBP]_{org}$; this has been graphed in Fig. 10 where, on the abscissae, % free TBP is given instead of molarity. With increasing percentage of

TBP, the concentration of HNO_3 as well as of the metal complex in the organic phase decreases. By extrapolating the curve in Fig. 10 to 100 % TBP, we thus obtain log $K = 1.5$, since by definition $f_{TBP} = 1$ and also $f_{MC} = 1$.

It can easily be shown that this K is the equilibrium constant for the reaction

$$UO_2^{2+}{}_{(aq)} + 2NO_3^-{}_{(aq)} + 2\ TBP_{(org)} = UO_2(NO_3)_2(TBP)_{2(org)}$$

It follows from Fig. 10 that the vertical distance between the curve and the horizontal line represented by log K must be equal to log f_{MC}/f_{TBP}^2. For 13 % free TBP one obtains $f_{MC}/f_{TBP}^2 = 0.1$. It can be deduced from this ratio that one or both of the activity factors f_{MC} and f_{TBP} must deviate from 1 by a factor of at least 2. Much greater variations have in fact been shown by McKay to exist for solutions of TBP, though in his case the solutions consisted of mixtures of highly polar TBP and HNO_3 in a solvent (kerosene) of low dipole moment *; in our case, when all components most probably are very polar, the change in the activity factors is expected to be smaller, which is in agreement with the findings.

The deviation of the curves in Figs. 8 and 9 from straight lines may not solely be due to variations in activity factors. Since at high NO_3^- concentrations a considerable part of the TBP is tied up in complexes with HNO_3 and $M(NO_3)_N$, it seems probable that the HNO_3 and metal complexes here are deficient in TBP. This is definitely indicated by the result in Fig. 9, where the TBP concentration according to eqn. (3) is < 0 at the highest NO_3^- concentration. It can also be seen from Fig. 1a that the ratio $[HNO_3]_{org}/[TBP]_{org}$ exceeds 1 (*i.e.* $[HNO_3]_{org} > 3.4$ M) at high values of HNO_3, indicating that HNO_3 is extracted in other forms than the complex $HNO_3 \cdot TBP$. This means that eqn. (3) is no longer correct; the concentration of free TBP is probably somewhat higher. The consequence of this is that the ordinate values log $q/[TBP]_{org}^N$ in Figs. 8 and 9 should be lowered, and the higher the NO_3^- concentration is the greater the decrease, which would give the curves a less steep slope at high values of log $[NO_3^-]$. It should further be noted that the formation of complexes of M in the aqueous phase (*i.e.* $[M^{N+}] \not\gg \overset{n,s}{\underset{1,1}{\Sigma}} [M(NO_3)_n$ $(TBP)_s]_{aq}$) will lead to the same consequence, *i.e.* to a less steep slope of the curves at high NO_3^- concentrations. Thus, *e.g.*, Ahrland [20] has shown that in 2 M NO_3^- about 50 % of U(VI) is in the form of $UO_2NO_3^+$. It therefore seems incorrect to explain the deviation from straight lines in Figs. 8 and 9 solely as due to variations in activity factors. Certainly part of the deviations are due to the formation of more than one type of complex for HNO_3 and for the metals in the organic as well as in the aqueous phase.

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* It should be observed that in Ref.[10] another reference state for the activity factor of TBP is used, *i.e.* $f_{TBP} = 1$ for 0 % TBP in 100 % kerosene.

Fig. 12. The distribution ratios of the investigated metal ions and HNO_3 as a function of HNO_3 in the aqueous phase. Concentration of $Ca(NO_3)_2$: 3 M. (The curves for Pu(VI) and Pu(IV) have been extrapolated assuming Pu(VI) parallels U(VI) and Pu(IV) parallels Th(IV)).
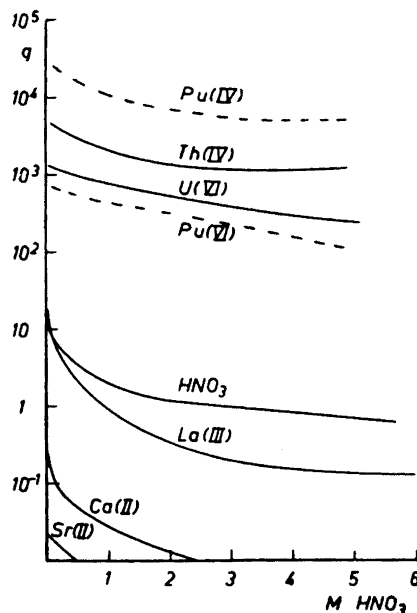
Separation of uranium and plutonium from other metals.

The distribution curves for the different metals and HNO_3 are given in Fig. 11 for no $Ca(NO_3)_2$ present, and in Fig. 12 for 3 M $Ca(NO_3)_2$. The dashed curves for Pu(IV) and Pu(VI) in Fig. 12 are calculated on the assumption that $q_{Pu(IV)}$ changes approximately like q_{Th}, and $q_{Pu(VI)}$ like $q_{U(VI)}$, when going from 0 M to 3 M $Ca(NO_3)_2$ solutions. Similar curves for 1, 2 and 4 M $Ca(NO_3)_2$ can be obtained from Figs. 2—7.

By comparing Figs. 11 and 12 it is seen that the distribution factors increase with increasing $Ca(NO_3)_2$ concentration, and that this increase is greatest for the tetravalent and hexavalent actinides. As a consequence of this, highly salted aqueous solutions and pure TBP would seem to be a suitable system for separating Th, U and Pu from the other metals. Now it is a well-known fact that the best separation between two metals *e.g.* M_1 and M_2, is obtained if $q_{M_1} = q_{M_2}^{-1}$ at equal phase volumes. If M_1 represents Th, U or Pu, and M_2 represents the other metals, it can be seen from Fig. 12 that this optimum relation between q_{M_1} and q_{M_2} cannot be obtained with 3 M $Ca(NO_3)_2$ solutions. In fact, it is difficult to obtain an organic phase containing Th, U and Pu, which is free of the other metals. It can therefore be concluded that 3 M $Ca(NO_3)_2$ solutions are not suitable for separating U and Pu from the fission products.

In certain instances it may be of importance to determine small amounts of plutonium or uranium in aqueous solutions very dilute with respect to these elements. If the aqueous phase then is strongly salted, as with $Ca(NO_3)_2$, and mixed with a small volume of pure TBP, practically all Pu(IV), Pu(VI)

and U will move over into the organic phase. This concentration of Pu and U which may amount to a factor of 50, will make it easier to analyse for these metals.

It is seen from Fig. 11 where no $Ca(NO_3)_2$ is present that between 1 and 3 M HNO_3 the difference in distribution ratios between the tetravalent or hexavalent actinides and the other metals is about a factor 100. The conditions for separating U and Pu from the fission products (F.P.) at equal phase volumes are here optimum $(q_U \approx q_{Pu} \approx q_{F.P.}^{-1})$. It can be calculated[1] that in a counter-current extraction with 3 extraction stages and 3 stripping stages, about 99.9 % of Pu(IV), Pu(VI) and U are extracted, with a decontamination factor from the fission products investigated in Fig. 11 of the order of 10^6.

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