

THE EXTRACTION OF URANYL NITRATE FROM NITRIC ACID SOLUTIONS BY TRIBUTYL PHOSPHATE

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Abstract—The effects of nitric acid concentration, uranyl nitrate concentration, and temperature were investigated in order to determine the optimum conditions for the extraction of uranyl nitrate from nitric acid solutions by TBP. It is apparent from the results that greater than 97 per cent extraction is obtained when uranyl nitrate solution of less than 10 g/l. concentration and containing 6 M HNO_3 is extracted with 19 per cent TBP in kerosene at a temperature of less than 20°C.

SOLVENT extraction processes for inorganic salts have been rapidly developed in recent years. Many solvents have been tried. Of these, great interest is at present being shown in tributyl phosphate (TBP). The extraction of inorganic nitrates by TBP has been studied by many research workers,^(1,2) but comparatively little has been published on uranyl nitrate. In this paper, therefore, an account is given of the investigation of some factors affecting the extraction of uranyl nitrate from nitric acid solution in order to determine the optimum conditions.

EXPERIMENTAL

When 100 per cent TBP is used as the extraction solvent, separation of the organic and aqueous phases is difficult because the specific gravity of TBP is near to that of water. To make the separation easier it is usual to regulate the specific gravity with diluent. However, the presence of large proportions of diluent has the effect of decreasing the solubility of water in TBP, as shown by ALCOCK *et al.*,⁽²⁾ and this would probably affect the transfer of inorganic salt from aqueous phase to organic phase. The diluent most frequently employed is kerosene, and a concentration of TBP of from 20 to 40 per cent is most widely used for the extraction of inorganic salts.⁽¹⁻³⁾

The TBP was purified with 0.1 N sodium hydroxide solution exactly as described by ALCOCK *et al.*,⁽²⁾ and well washed with water. For this present study 20 volumes of water-saturated TBP was made up to 100 volumes with kerosene as diluent. This solution, because of the water content of the TBP, corresponded in TBP/kerosene ratio to one of 19 volumes of dry TBP made up to 100 volumes with kerosene, and will be referred to as "19 per cent TBP". The kerosene used was such that 25 per cent distilled between 180° and 200°C. The uranyl nitrate used was twice purified by extraction with 19 per cent TBP, being backwashed into water, and it contained 9.4 per cent moisture, as for $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

The extractions were carried out by the following procedure. 50 cm³ each of solvent and uranyl nitrate solution were put into 100 cm³ stoppered conical flasks and stood for 30 min in a water bath, thermostated at the required temperature. Then after shaking for 5 min the partition coefficient and the percentage extracted were determined. The partition coefficient is given by the ratio of the

⁽¹⁾ For example, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955*. Vols. 7 & 9, United Nations (1956); T. V. HEALY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 633 (1956); K. ALCOCK, F. C. BEDFORD, W. H. HARDWICK and H. A. C. MCKAY, *J. inorg. nucl. Chem.* **4**, 100 (1957); L. I. KATZIN, *Ibid.* **4**, 187 (1957).

⁽²⁾ K. ALCOCK, S. S. GRIMLEY, T. V. HEALY, J. KENNEDY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 39 (1956).

⁽³⁾ D. F. PEPPARD, G. W. MASON and L. J. MAIER, *J. inorg. nucl. Chem.* **3**, 215 (1956).

equilibrium concentration in the organic phase to that in the aqueous phase.⁽⁴⁾ The percentage extracted is expressed as $100x_1/x$, where x is the concentration of uranyl nitrate contained in the aqueous phase before extraction, and x_1 is that in the organic phase after extraction. Uranium was determined gravimetrically as follows: the uranyl nitrate in the organic phase was back-extracted with ammonium carbonate, the carbonate driven out by boiling, and ammonium diuranate completely precipitated with ammonium hydroxide solution and weighed as U_3O_8 after calcination.

RESULTS AND DISCUSSION

Effect of nitric acid concentration. In order to determine the optimum concentration of nitric acid which acts as salting out agent, extraction of 5 g/l. uranyl nitrate solution was carried out with 19 per cent TBP at 20°C with varying concentrations of nitric acid. The results, plotted in Fig. 1, show that the partition coefficient of uranium is a maximum at about 6 M initial nitric acid concentration.

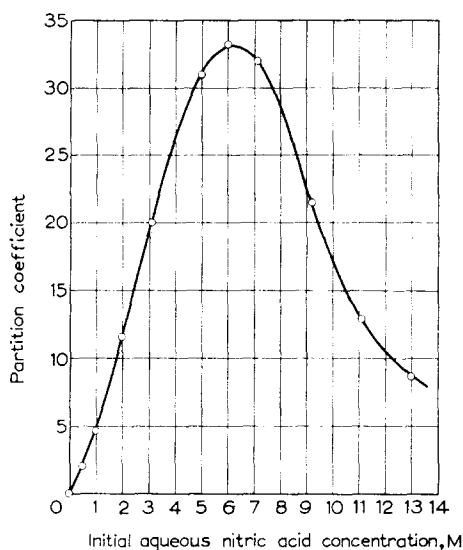


Fig. 1.—Effect of nitric acid concentration upon the extraction of uranyl nitrate by 19 per cent TBP in kerosene

Also, the partition of nitric acid in these solutions was investigated, since a compound such as $HNO_3 \cdot TBP^{(5)}$ is formed by the combination of nitric acid and TBP. The direct titration of acidity in the organic phase presented difficulty, however, because the greater proportion of the uranium is present in this phase and its precipitation at about pH4 would interfere. Consequently the acidity of the organic phase was determined by titration with alkali after addition of sodium oxalate to complex the uranium and prevent its precipitation.

The resulting extraction curve, shown in Fig. 2, corresponds closely with other published results⁽²⁾ for nitric acid alone, except that the observed extraction of nitric acid is uniformly a few per cent lower in presence of uranium. This is to be expected because part of the TBP is combined with the uranium and is not available for nitric acid extraction.

The extraction of uranyl salt into TBP is increased by the presence of the common

⁽⁴⁾ T. R. SCOTT, *Analyst*, **74**, 486 (1949).

⁽⁵⁾ R. L. MOORE, AECD-3196 (1951).

nitrate ion. However, as shown in Fig. 1, the partition coefficient curve exhibits a maximum at about 6 M nitric acid concentration. SCARGILL *et al.*⁽⁶⁾ have indicated that although the salting out effect by the nitrate ion causes the steep rise at the lower acidities, the formation of nitrate complexes and the competition by the nitric

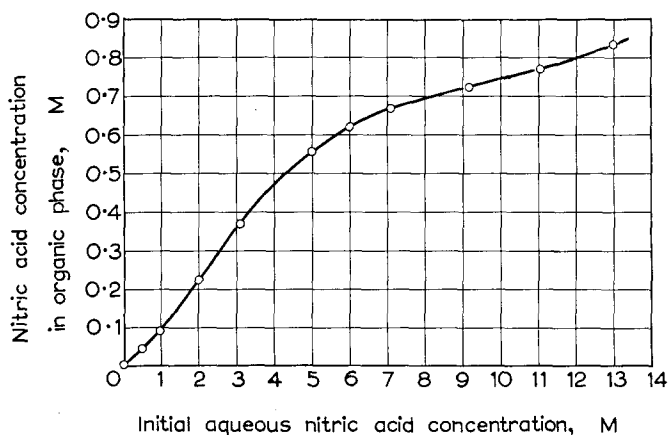


FIG. 2.—Nitric acid extraction into 19 per cent TBP in kerosene during the extraction of uranyl nitrate

acid for the available TBP check the rise at the higher acidities and often cause the partition coefficient to pass through a maximum.

Effect of uranyl nitrate concentration. Extraction of uranyl nitrate solutions of various concentrations containing 6 M nitric acid was carried out with 19 per cent TBP at 20°C. The results are shown in Table 1 where the uranyl nitrate concentration

TABLE 1.—EFFECT OF CONCENTRATION UPON THE EXTRACTION OF URANYL NITRATE

Concentration of $\text{UO}_2(\text{NO}_3)_2$ (g/l.)	Partition coefficient	Percentage extracted
1.0	60?	98.40
3.0	33.4	97.10
5.0	33.2	97.10
10.0	32.3	97.00
25	30.0	96.75
50	21.0	95.45
100	7.43	88.05
200	1.37	57.80
400	0.44	30.70
650	0.24	19.60

of 650 g/l. represents a saturated solution. These results show that greater than 97 per cent extraction can be obtained at uranyl nitrate concentrations below 10 g/l.

With the TBP-kerosene concentration employed in these experiments the amount of uranyl nitrate which combines with TBP is fixed, since the uranyl nitrate and

⁽⁶⁾ H. A. C. MCKAY. *Proceedings of the International Conference on Peaceful Uses of Atomic Energy, Geneva, 1955*. Vol. 7, p. 314. United Nations (1956); D. SCARGILL, K. ALCOCK, J. M. FLETCHER, E. HESFORD and H. A. C. MCKAY, *J. inorg. nucl. Chem.* **4**, 304 (1957).

TBP form a definite compound, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$, as suggested by MOORE.⁽⁵⁾ Therefore, when the concentration of uranyl nitrate is low the content of TBP in kerosene is more than the amount combining with uranyl nitrate and consequently its extraction will be more efficient. When the concentration of uranyl nitrate is increased towards saturation, on the other hand, the partition coefficient rapidly decreases, as shown in Table 1, owing to exhaustion of the available TBP.

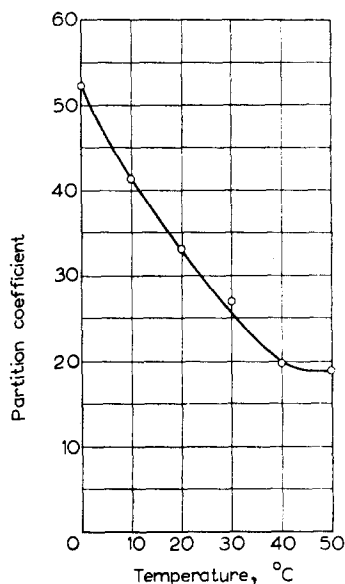


FIG. 3.—Effect of temperature upon the extraction of uranyl nitrate by 19 per cent TBP in kerosene

Effect of temperature of extraction. Extraction of 5 g/l. uranyl nitrate solution containing 6 M nitric acid was carried out with 19 per cent TBP in kerosene at temperatures of 0, 10, 20, 30, 40 and 50°C. The result is shown in Fig. 3.

Fig. 3 shows that when the extraction temperature is low the partition coefficient is large, and that it decreases with increasing temperature. Above 20°C the percentage extraction falls below 97 per cent. It is desirable therefore that the extraction of uranyl nitrate be carried out at less than 20°C.

From the foregoing results the following conclusion is drawn: when a uranyl nitrate solution of less than 10 g/l. concentration containing 6 M nitric acid is extracted with 19 per cent TBP in kerosene at below 20°C, greater than 97 per cent extraction is obtained.

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