B.A.R.C.-636

B.A.R.C.-636

GOVERNMENT OF INDIA
ATOMIC ENERGY COMMISSION

EXTRACTION OF NEPTUNIUM BY TRILAURYLAMINE

by

S. K. Patil, Rajendra Swarup, M. V. Ramaniah and N. Srinivasan
Radiochemistry Division

BHABHA ATOMIC RESEARCH CENTRE
BOMBAY, INDIA
1972

B. A. R. C. - 636

B. A. R. C. - 636

GOVERNMENT OF INDIA
ATOMIC ENERGY COMMISSION

EXTRACTION OF NEPTUNIUM BY TRILAURYLAMINE

by

S. K. Patil, Rajendra Swarup, M. V. Ramaniah and N. Srinivasan
Radiochemistry Division

BHABHA ATOMIC RESEARCH CENTRE
BOMBAY, INDIA
1972

ABSTRACT

Trilaurylamine (TLA) is considered as useful solvent for the final purification of plutonium and neptunium. As TLA is considered as an alternate possible extractant for the final purification of plutonium and neptunium at Tarapur Reprocessing Plant under construction, it was considered necessary to study the optimum conditions for the extraction of neptunium using TLA.

Experiments were carried out on the extraction of Np(IV) into 20% TLA in Solvesso-100. The dependence of the extraction of Np(IV) on (a) nitric acid concentration from 1-8M, (b) neptunium concentration from 1-25 ug/ml (c) uranium concentration ranging from 0 - 300 mg/ml, has been studied. The extraction of Np(IV) from 3M nitric acid using varying concentration of TLA was studied and the log-log plot of distribution coefficient vs TLA concentration was found to be a straight line with slope 2. The effect of diluent on the extraction of Np(IV) into TLA was also studied.

The stripping of neptunium from the TLA phase was found quite satisfactory with a mixture of 1.5M sulphuric acid and 0.5M nitric acid, 1M formic or acetic acid and 0.5M perchloric acid.

EXTRACTION OF NEPTUNIUM BY TRILAURYLAMINE

by

S. K. Patil, Rajendra Swarup, M. V. Ramaniah and N. Srinivasan*

1. INTRODUCTION

Long-chain high molecular weight amines found a wide application in nuclear process chemistry for the selective extraction of metal ions, purification of fertile and fissile materials from irradiated fuels and isolation of trans-plutonium elements. Amine extraction of acids and of metal ion complexes was first reported by Smith and Page in 1948[1]. In 1957, Sheppard[2] demonstrated the high extraction power of a tertiary amine for Np(IV) and Pu(IV) nitrates. Wilson[3] extended Sheppard's study and his work aroused widespread interest in plutonium(IV) nitrate extraction with tertiary amines, especially trilaurylamine.

Trilaurylamine (TLA) is considered as useful solvent for the final purification of plutonium and neptunium. The chief advantages of using TLA as an extractant are (i) high selectivity in extracting neptunium and plutonium from nitric acid medium over a large range of acidities (ii) high extracting power at lower acidities as compared to most other amines[4-6] (iii) adequate decontamination from impurities (iv) favourable chemical and physical properties such as high boiling and freezing points, low density, low solubility in water and good resistance to acid and radiation (v) availability in relatively pure form in large quantities.

---

*Fuel Reprocessing Division

Because of its remarkable properties, trilaurylamine was used as an extractant for the final purification of plutonium in the reprocessing plants at Marcoule[7] and at Cap de la Hague[8]. Champion and Chesne[9] reported the extraction of Np(IV) by TLA in n-dodecane from nitric acid and the stripping by sulphuric acid - nitric acid. Recently Bathellier and Coworkers[10] described a counter-current process for the co-extraction of neptunium and plutonium by 20% TLA in dodecane from the wastes of the irradiated fuel processing plants. They also studied the separation of neptunium and plutonium by selective extraction of neptunium into TLA[11].

2. PRESENT WORK

As TLA is considered as an alternate possible extractant for the final purification of plutonium and neptunium at Tarapur Reprocessing Plant under construction, it was therefore considered necessary to study the optimum conditions for the extraction of neptunium using TLA. From a literature survey on the extraction properties of TLA[12], it was found that aromatic solvents are by far the most suitable diluents for the amine compared to aliphatic solvents because of the higher solubilities of amine salts and the metal complex in the former solvents. In the present study, Solvesso-100 was used as the diluent as this is likely to be used at Tarapur Plant. This report describes the following aspects of the Np(IV) - TLA extraction system:-

1. Effect of the TLA concentration

2. Effect of nitric acid on the TLA extraction of Np(IV)

3. Effect of uranium(VI) concentration on the extraction of Np(IV) by TLA

4. Effect of diluent

5. Stripping of neptunium(IV) from TLA phase by complexing agents such as (1) sulphuric acid and nitric acid mixture (2) formic acid (3) acetic acid and (4) perchloric acid

3. EXPERIMENTAL

3.1. Materials

Neptunium-237 was obtained from Oak Ridge National Laboratory, USA in the form of NpO_2 which was purified[13], [14]. Neptunium-239 was separated each time from irradiated natural uranium by TTA extraction. TLA obtained from K & K Laboratories Inc., USA was used without further purification as it was found to be of sufficiently high purity[15]. Solvesso-100 was supplied by "Esso Standard Company", Holland. Stock solution of uranium(VI) nitrate was prepared by dissolving nuc? r pure uranium oxide in A.R. nitric acid and the uranium content was estimated volumetrically[16] and spectrophotometrically[17]. The acidity of the uranyl solution was determined after complexing uranium with oxalate[18]. All the other chemicals and reagents used were of A.R grade except ferrous sulphamate which was prepared from commercial grade chemicals by the method described by Buchanan[19].

3.2. Procedure

Neptunium-237 was purified from its daughter nuclide ^{233}Pa by TTA extraction of the latter from 7M nitric acid solution. Neptunium-239 was added

to it in order to facilitate the estimation of neptunium by gamma ray counting. Ferrous sulphamate (0.1 M) was used as a holding reductant to keep neptunium as Np(IV). In all the experiments the ^{237}Np concentration was kept at about 2-3 µg per ml. 20% TLA in Solvesso-100 (v/v) was used in all the experiments.

3.3. Extraction Experiments

A suitable aliquot of the Np(IV) tracer was added to a 5 ml of aqueous phase containing the desired concentration of nitric acid and 0.1 M ferrous sulphamate. An equal volume of 20% TLA in Solvesso-100 pre-equilibrated with nitric acid of the required concentration was added and was then shaken for 10 minutes using a Vortex mixer. It was centrifuged and aliquots from both the phases were counted in a well-type NaI(Tl) γ -scintillation counter.

3.4. Stripping Experiments

Neptunium(IV) was extracted into 20% TLA in Solvesso-100 from 2 M nitric acid solution. 2 ml of the organic phase was contacted with 2 ml of the aqueous phase containing the stripping agent of known concentration and 0.01 M ferrous sulphamate (Fe^{++} was added to ensure the tetravalency of neptunium during stripping) and was shaken by slow rotation for one hour since this time was found to be adequate in attaining the equilibrium. Aliquots from both the phases were counted at the end of equilibration.

4. RESULTS AND OBSERVATIONS

4.1. Extraction

Preliminary experiments showed that the oxidation state of neptunium did not change from Np(IV) during its extraction into TLA when either 0.01 or

0.1 M ferrous sulphamate was used as holding reductant. This was checked by testing the oxidation state of neptunium in the aqueous phase before and after the extraction by TLA using TTA extraction method. It was recently reported[15] that the extraction of Pu(IV) into TLA was slow and the equilibrium was attained only after 10 minutes although it was observed by Rolandi et al that the equilibrium was attained in about a minute[20]. It was therefore considered desirable to verify this. The kinetics of extraction of Np(IV) was followed in 3 M nitric acid the results of which showed that the equilibrium was attained in 1-2 minutes. However, the equilibration was carried out for 10 minutes in all the extraction experiments. The distribution coefficient value obtained by taking Np(IV) activity in either phase was found to be the same indicating the reversibility of the system. The distribution coefficient of Np(IV) was also found to be independent of the neptunium concentration in the range 1-25 μg/ml showing that only mononuclear species are involved in the system.

4.2. Effect of TLA Concentration

The extraction of Np(IV) from 3 M nitric acid with varying concentration of TLA was studied. The log-log plot of the distribution coefficient versus TLA concentration was found to be a straight line with a slope of 2 (Fig. 1). Stevenson and Paige[21] suggested the extraction of neptunium by TLA takes place presumably via the formation of an adduct according to equation (1).

$$2[R_3NH^+NO_3^-] + Np(NO_3)_4 \rightleftharpoons (R_3NH)_2Np(NO_3)_6 \quad \ldots\ldots \quad (1)$$

This may also take place according to equation (2).

$$[Np(NO_3)_6^{2-}] + 2[R_3NH^+NO_3^-] \rightleftharpoons (R_3NH)_2Np(NO_3)_6 + 2NO_3^- \quad \ldots (2)$$

Both these mechanisms suggest that the distribution coefficient of Np(IV) varies with the second power of TLA concentration as found experimentally.

4.3. Effect of Nitric Acid Concentration

Apart from some results obtained for plutonium by Coleman[22], Van Geel[23] and Kumar et al[24], no quantitative data are available on the extraction of the actinides, particularly neptunium for the system TLA-Solvesso-100 HNO_3-H_2O. The variation of the distribution coefficient of Np(IV) with the nitric acid concentration is shown in Fig. 2. The values for Pu(IV) for the same system taken from literature[23] are also plotted for comparison. A broad maximum around 4M HNO_3 was observed for both neptunium and plutonium. However, values for Pu(IV) are higher than for Np(IV) by a factor of 4-5 at all the acidities. This agrees with the trend of the results obtained by Kedar et al[25] for Np(IV) and Pu(IV) with TOA in xylene. The decrease of extractability at the higher acid concentration may be attributed to the formation of the higher complex or uncharged complex metal acids of the type $H_2Np(NO_3)_6$. The decrease might at least partly be also due to the decrease of nitrate ions at higher concentration of nitric acid or due to the competing effect of the nitric acid present in the organic phase.

4.4. Effect of Uranium Concentration

As the feed solution for the final purification of neptunium in the Purex process is likely to contain some uranium(VI) (approximately of the order of 3 g/l), it was considered necessary to study the effect of U(VI) concentration

on the distribution coefficient of Np(IV). The distribution coefficient of Np(IV) was determined as a function of U(VI) concentration (0-300 g/l). The data given in Table 1 show that the distribution coefficient of Np(IV) decreases with increasing U(VI) concentration. This trend is similar to that observed in the extraction of Pu(IV) with different amines[26,27]. The distribution coefficient of U(VI) in 20% TLA in Solvesso-100 from 2 M nitric acid was reported to be about 1[23]. The extracted uranium decreases the concentration of free TLA available for the extraction of neptunium which results the decrease of Np(IV) distribution coefficient with increasing uranium concentration as observed.

4.5. Effect of Diluent

It is known that the diluents have pronounced effect on the extraction of elements[28]. The variation of the distribution coefficient with the diluent was attributed by Taube[29] to the change in the diluent polarity. The distribution coefficient data for Np(IV) obtained by using different diluents for TLA are summarised in Table 2 and are compared with similar literature data for Np(IV) and Pu(IV). It can be seen that diluents have pronounced effect on the extraction of both neptunium and plutonium as expected (Fig. 3).

4.6. Stripping

Since the distribution coefficient of Np(IV) into TLA is fairly high even from dilute nitric acid solution the stripping of neptunium from TLA phase by reducing the aqueous nitric acid concentration is not practicable. Therefore complexing agents were used to study the feasibility of using these

reagents to strip neptunium from TLA. Chesne' et al[30] recommended a mixture of 1.5M sulphuric acid and 0.07M nitric acid for stripping the plutonium into the aqueous phase from TLA phase. Souka[31] reported the possibility of using formic acid as a stripping agent for plutonium whereas Coleman[32] and Haeffner[33] proposed acetic acid for the same purpose. Experiments were carried out using all these stripping agents as well as perchloric acid and the results are summarised in Tables 3 and 4. It can be seen from these data that all the reagents strip Np(IV) from TLA almost quantitatively. The effective stripping of Np(IV) by perchloric acid may be due to the high extractability of ClO_4^- ion into TLA because of its poor hydration. Acetic and formic acids probably behave as bidentate ligands and form complexes with Np(IV) which may be only cationic and are not extracted by TLA.

REFERENCES

1. Smith, E.L. and Page, J.E., J. Soc. Chem. Ind. Lond., 67, 48 (1948).
2. Sheppard, J.C., USAEC Report HW-51958 (1957).
3. Wilson, A.S., Proc. 2nd UN Int. Conf. PUAE, 17, 348 (1958)
4. Vaughen, V. and Mason, F.A., USAEC Report TID-12665 (1960)
5. Coleman, C.F., Nucl. Sci. Eng., 17, 274 (1963).
6. Baroncelli, F., et al., Nucl. Sci. Eng., 17, 298 (1963).
7. Chesne' A., Koehly, G. and Bathellier, A., Nucl. Sci. Eng., 17, 557 (1963)
8. Duboz, M., Energie Nucleaire, 7, (4), 228 (1965).
9. Champion, J. and Chesne', A., CEA-R-2607 (1964).
10. Gourisse Par D. and Bathellier, A., Radiochim Acta., 13 (4) 187 (1970).

11. Bathellier, A et al., ibid., 13 (4) 191 (1970).

12. Wilson, A.S., HW-68207 (1961).

13. Patil, S.K., et al - BARC/I-140 (1971).

14. Moore, F.L., Anal. Chem., 29, 1941 (1957).

15. Srinivasan, N., et al., BARC-374 (1968).

16. Vogal, A.I., "Text Book of Quantitative Inorganic Analysis", 3rd Ed. p.333 (1961).

17. ORNL Master Analytical Manual TID-7015, Method No. 1-215212

18. ORNL Master Analytical Manual TID-7015, Method No. 9-042200

19. Buchanan, R.F., et al., Talanta, 6, 173 (1960).

20. Rolandi, G., et al, NP - 14945 (1964).

21. Stevenson, C.E., and Paige, D.M., React. Fuel Process. Tech., 10 (3), 247 (1967).

22. Coleman, C.F., Atomic Energy Review, 2 (2) 3 (1964).

23. Van Geel, J.N.C., Thesis "Recovery of Pure Plutonium by Extraction with Trilaurylamine and Direct Precipitation", Laboratories for Industrial Development of Eurochemic, Mol. Belgium (January, 1968).

24. Kumar, S.V., Kapoor, S.C., and Jain, S.P., BARC-476 (1970).

25. Kedar, W.E., et al, Nucl. Sci. Eng., 17, 287 (1963).

26. Wilson, A.S., Proc. 2nd Int. Conf. (UN) PUAE Geneva, 17, 348 (1958).

27. Baroncelli, F., Scribona, G., and Zifferero, M., Radiochim. Acta., 1, 75 (1963).

28. Brown, K.B., et al., Ind. Eng. Chem., 50, 1756 (1958).

29. Taube, M., J. Inorg. Nucl. Chem., 12, 174 (1959).

30. Cheene', A., Kohely, G., and Bathellier, A., "Solvent Extraction Chemistry" symposium, Gatleinberg, Tenn. Oct. 23-26 (1962).

31. Souka, N., Radiochim. Acta., 13 (2) 71 (1970).

32. Coleman, C.F., USAEC Report ORNL-CF-61-5-74 (1961).

33. Haeffner, E., Hulgran, A., and Larson, A., Proc. Third Int. Conf. Geneva, 10, 370 (1965).

34. Bathellier, A., et al., CEA-R-2594 (1964).

Table - 1

EFFECT OF URANIUM(VI) CONCENTRATION ON THE EXTRACTION OF Np(IV) BY 20% TLA IN SOLVESSO-100 FROM 2 M NITRIC ACID

U(VI) (mg/ml)	0	5	10	15	30	50	100	150	200	250	300
Distribution coefficient of Np(IV)	84.2	67.1	57.4	48.0	33.7	12.6	7.4	5.5	4.3	3.5	2.7

Table - 2

EFFECT OF DILUENT ON THE EXTRACTION OF Np(IV) BY TLA
CONCENTRATION OF TLA - 20% (v/o)

Conc. of HNO_3, M	Kd							
	Xylene		Solvesso-100		Shell sol-T		Dodecane ++	
	Np(IV)	Pu(IV)*	Np(IV)	Pu(IV)**	Np(IV)	Pu(IV)†	Np(IV)	Pu(IV)
1	29.7	216	34.7	180	116.8	690	60	450
2	70.0	275	84.2	300	227.1	888	140	780
3	82.6	311	90.4	400	250	984	220	900
4	86.4	262	92.2	450	258.2	1051	300	1000

* - Reference 15
** - " 23
† - " 24
++ - " 34

Table - 3

STRIPPING OF Np(IV) FROM TLA PHASE BY SULPHURIC ACID AND NITRIC ACID MIXTURE

Aqueous phase - Sulphuric acid + nitric acid with 0.01 M Ferrous Sulphamate

Organic phase - 20% TLA in Solvesso-100 with Np(IV)

H_2SO_4, M	HNO_3, M	Distribution coefficient of Np(IV)
0.2	1.8	6.6
0.5	1.5	1.17
0.8	1.2	0.36
1.0	1.0	0.18
1.5	0.5	0.014
2.0	0	0.005

Table - 4

STRIPPING OF Np(IV) FROM TLA PHASE BY FORMIC, ACETIC AND PERCHLORIC ACIDS

Aqueous phase - Formic, acetic and perchloric acids with 0.01 M ferrous sulphamate

Organic phase - 20% TLA in Solvesso-100 with Np(IV)

Concentration of the acid, M	Distribution coefficient of Np(IV)		
	Formic acid	Acetic acid	Perchloric acid
0.2	-	-	0.0125
0.5	-	-	0.0032
1.0	0.00252	0.00691	0.00125
1.5	-	-	0.00063
2.0	0.00227	0.005	0.00030
3.0	0.00187	0.00464	-
4.0	0.00215	0.00395	-
5.0	0.00242	0.00429	-

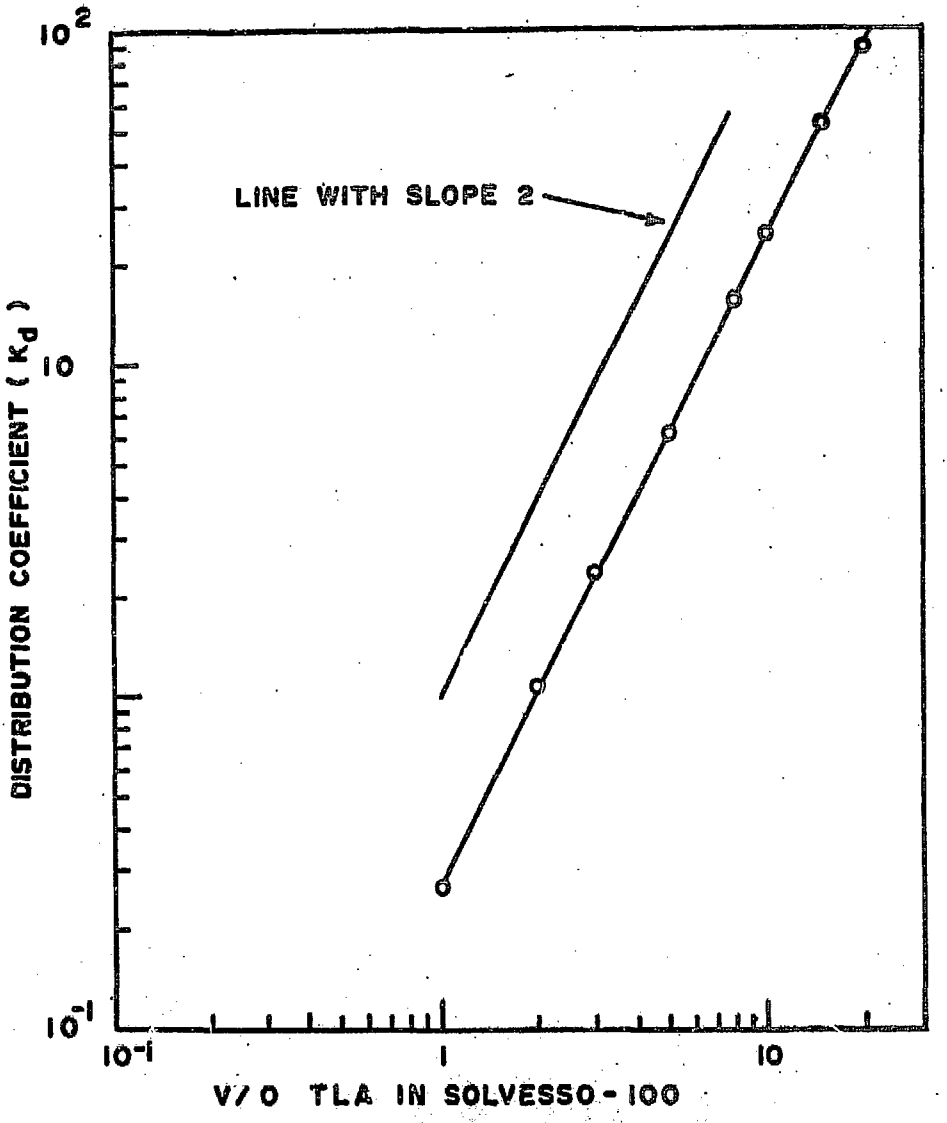

FIGURE-1. DISTRIBUTION RATIOS FOR EXTRACTION OF Np(IV) FROM 3M HNO_3 Vs COCENTRATION OF TLA IN SOLVESSO-100.

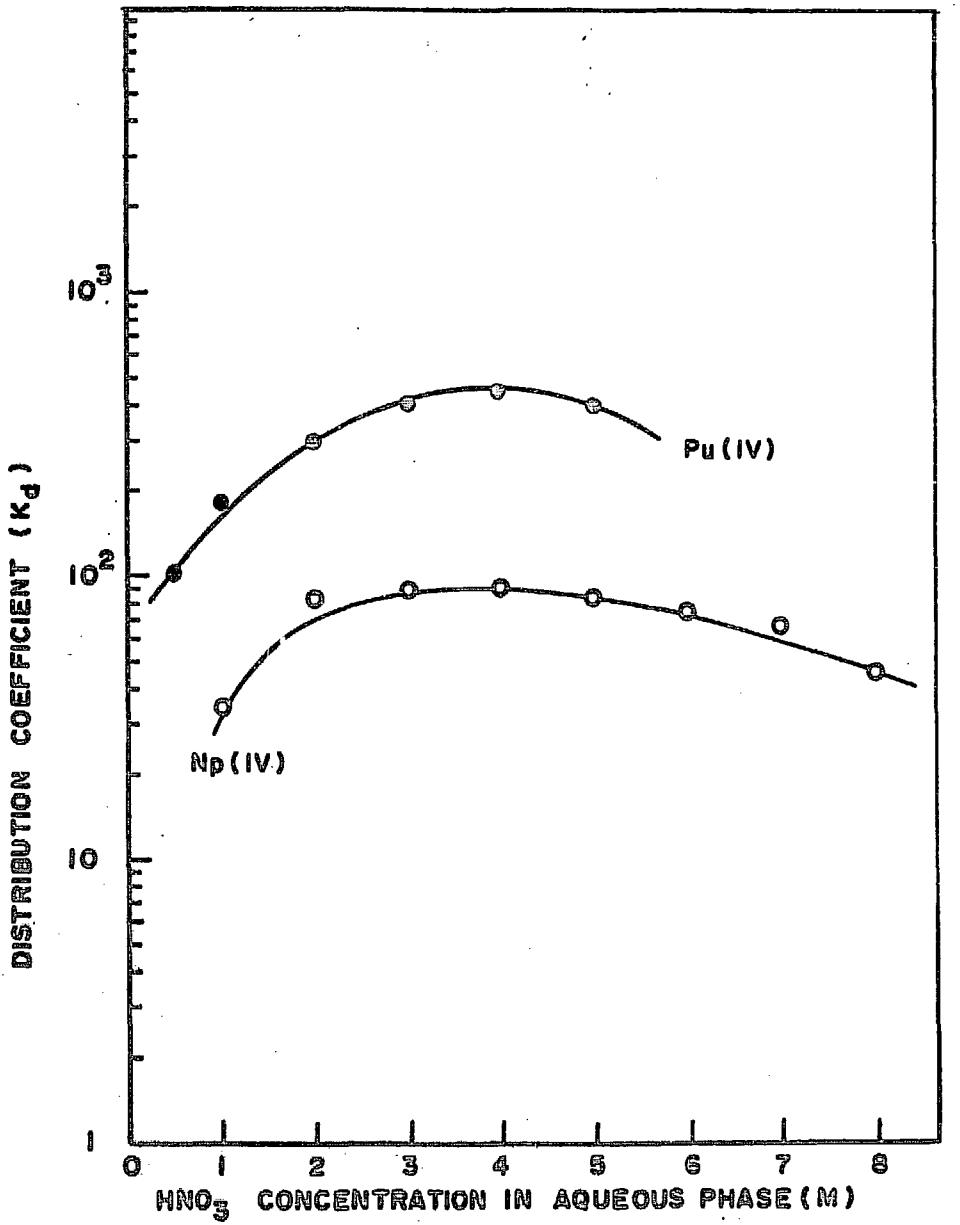

FIGURE-2. VARIATION OF K_d OF Np(IV) AND Pu(IV) BY 20% TLA IN SOLVESSO-100 WITH NITRIC ACID CONCENTRATION.

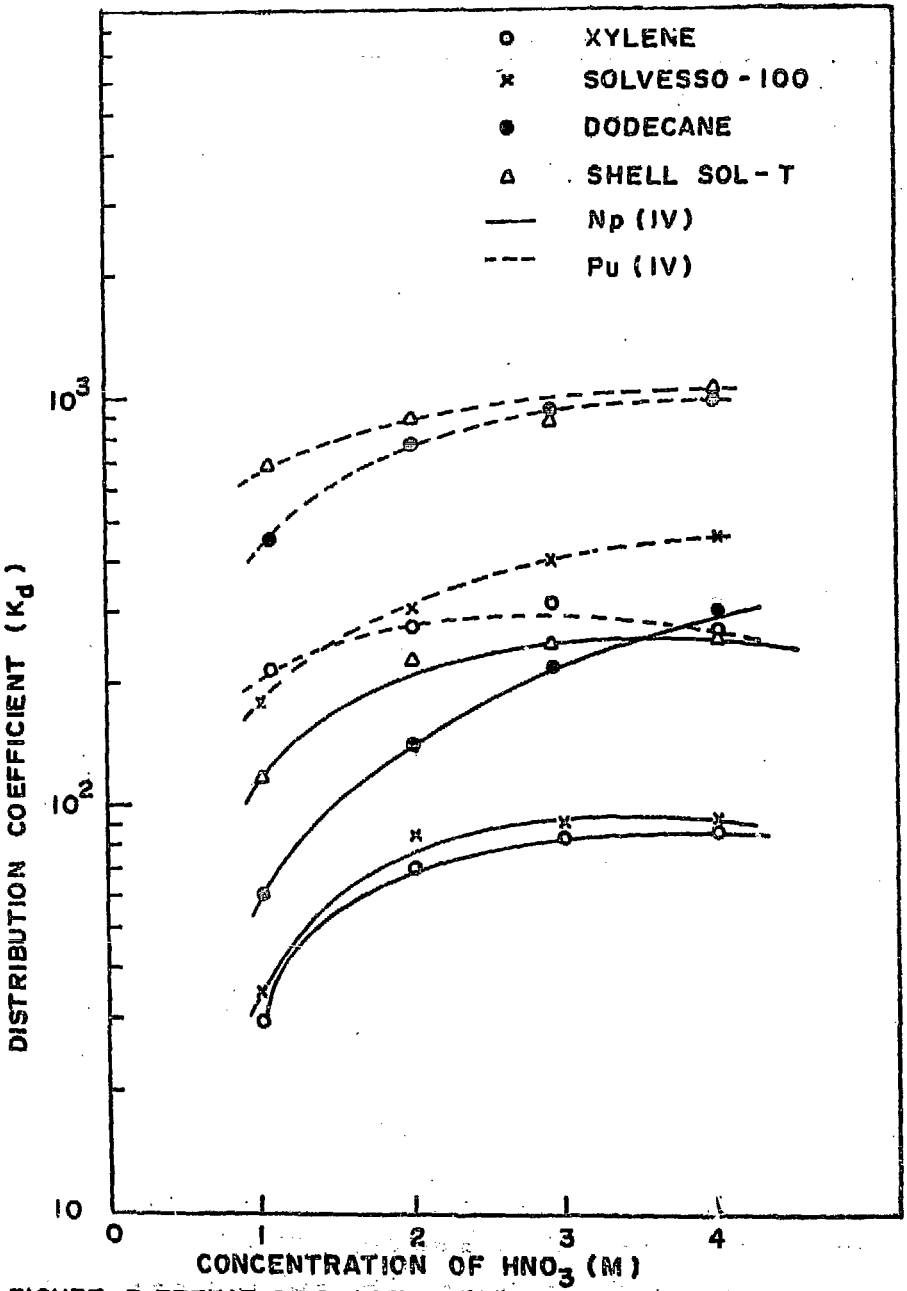

FIGURE-3. EFFECT OF DILUENT ON THE EXTRACTION OF Np(IV) AND Pu(IV) INTO 20 % TLA.