Thermochimica Acta, 47 (1981) 277—286
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

THE EFFECT OF TEMPERATURE ON THE EXTRACTION OF PLUTONIUM(VI) FROM NITRIC ACID BY TRI-*n*-BUTYL PHOSPHATE

M.S. SAJUN, V.V. RAMAKRISHNA and S.K. PATIL *

Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085 (India)

(Received 16 February 1981)

ABSTRACT

The extraction of Pu(VI) from varying concentrations of nitric acid into TBP in dodecane was studied at different temperatures in the range 20—60°C. From the distribution coefficient data, the enthalpy changes for the extraction of Pu(VI) under different conditions were determined. All the data obtained showed that the extraction of Pu(VI) from nitric acid into TBP is exothermic in nature. An attempt was made to evaluate the thermodynamic free energy and entropy changes.

INTRODUCTION

The data reported in the literature [1—3] reveal wide discrepancies for the distribution of traces of Pu(VI) between tri-*n*-butyl phosphate (TBP) and aqueous nitric acid. The fluctuations in the distribution coefficient (K_d) values of Pu(VI) were attributed [4] to several factors, e.g. the presence of ^{241}Am, the daughter product of ^{241}Pu, as an impurity; the existence of other oxidation states of plutonium, especially Pu(IV); the use of plutonium concentration too high to be regarded as trace concentration; solvent impurities like mono- and di-butyl phosphoric acids; and errors in plutonium counting by α-planchetting for aqueous and organic phases.

The effect of temperature on the extraction of various actinide ions from aqueous nitrate medium by TBP has been studied by several workers. A systematic study on the extraction of actinide ions by TBP and the variation of the distribution coefficients with temperature was initiated in this laboratory and some of the results obtained have been reported previously [5—7]. In continuation, the effect of temperature on the extraction of Pu(VI) by TBP in *n*-dodecane was studied and the data are reported here. From these data, the enthalpy changes associated with the extraction of Pu(VI) under the specified conditions have been calculated. An attempt was also made to calculate the free energy and entropy changes associated with the extraction of Pu(VI).

---

* To whom correspondence should be addressed.

EXPERIMENTAL

Materials

Plutonium, mainly ^{239}Pu, was purified by thenoyltrifluoroacetone (HTTA) extraction of Pu(IV) from 1 M nitric acid and subsequent back-extraction of the extracted Pu(IV) into 8 M nitric acid. Traces of HTTA dissolved in the aqueous phase were removed by scrubbing the back-extracted Pu(IV) solution with benzene. TBP was purified by the method given by Alcock et al. [8]. *n*-Dodecane, supplied by K&K Laboratories, U.S.A., was used without any purification. Scintillation grade PPO, POPOP and naphthalene were used for preparing the liquid scintillator solutions. A.R. dioxan was refluxed over sodium hydroxide pellets and distilled prior to use [9]. All other chemicals used were of A.R. grade.

Procedure

A suitable aliquot of purified plutonium in 8 M nitric acid was fumed to near dryness with a few drops of perchloric acid to destroy any fluoride and organic matter extracted into nitric acid during back-extraction. To this, a few drops of dilute nitric acid followed by 5 mg of AgO were added to oxidize plutonium to Pu(VI). Excess AgO was destroyed by heating under an IR lamp. The Pu(VI) stock thus prepared was added to the desired concentration of nitric acid containing ~0.01 M potassium dichromate or ~0.01 M ceric ammonium nitrate serving as the holding oxidant. It was observed that when potassium dichromate was used as holding oxidant for Pu(VI) at 0.25 M and 0.50 M nitric acid, the distribution coefficient values were abnormally high. It has been reported [10] that at low acidities, uranium is extracted from chromic acid solutions as UO_2CrO_4, and the K_d values for uranyl chromate are about 1000 times greater than those for uranyl sulphate. A similar behaviour may be expected for Pu(VI), and the abnormally high K_d values obtained may be due to the extraction of PuO_2CrO_4. However, when ceric ammonium nitrate was used as holding oxidant for Pu(VI) at 0.25 M and 0.50 M nitric acid, the K_d values were in the expected range.

Solutions of the required concentration of TBP in dodecane were prepared and pre-equilibrated thrice with equal volumes of nitric acid solution of required concentration. Equal volumes (3 ml each) of aqueous nitric acid containing Pu(VI) and 2.5, 5, 15 or 30 volume % TBP in *n*-dodecane, were pipetted into ground-glass stoppered equilibration tubes. The initial aqueous phase concentration of plutonium was ~10 μg ml^{-1}. The tubes were covered with black paper to avoid possible photochemical reduction of Pu(VI) [11], sealed in polythene bags and immersed for 30 min in a thermostated water bath kept at the desired temperature, and subsequently equilibrated in the water bath for 15 min. The temperature of the bath was maintained within ±0.1°C. At the end of the equilibration, the phases were allowed to settle and suitable aliquots from both phases were withdrawn into liquid scintillation vials containing 5 ml of liquid scintillator solutions [12]. Usually 100—500 μl aliquots were pipetted. However, when the K_d value was very low, 2 ml of the organic phase were required in order to have sufficient α-activity to be measured satisfactorily, and hence the scintillator solution used was twice the normal concentration, and only 2 ml of this solution were used in liquid scintillation counting. The K_d values were always obtained in triplicate and the agreement was usually within ±2%. An excellent material balance (>95%) was also usually obtained.

RESULTS AND DISCUSSION

The effect of temperature on K_d

The distribution coefficient data obtained for the extraction of Pu(VI) from nitric acid into 2.5, 5, 15 and 30% TBP in dodecane, at various temperatures, are given in Tables 1—4, respectively. From these data, it is seen that the K_d values decrease with increasing temperature under all sets of conditions studied. Thus, the data are in general agreement with those reported in the literature [5,13,14].

Calculation of the enthalpy change associated with the extraction of Pu(VI)

The equilibrium for the extraction of Pu(VI) from nitrate medium into TBP is given by

$$PuO_{2(a)}^{2+} + 2\ NO_{3(a)}^{-} + 2\ TBP_{(o)} \rightleftharpoons PuO_2(NO_3)_2 \cdot 2\ TBP_{(o)} \qquad (1)$$

where (a) and (0) refer to the species present in aqueous and organic phases, respectively. The equilibrium constant (K) for this equilibrium can be expressed by

$$K = \frac{[PuO_2(NO_3)_2 \cdot 2\ TBP]\gamma PuO_2(NO_3)_2 \cdot 2\,TBP}{[PuO_2^{2+}]\,[NO_3^-]^2[TBP]^2\gamma PuO_2^{2+}\gamma^2 NO_3^-\gamma^2 TBP} \qquad (2)$$

where the square brackets denote the concentrations and the γs are the activity coefficients of the respective species.

Assuming that the various activity coefficients for a given concentration

TABLE 1

Variation of distribution of coefficients of Pu(VI) between nitric acid and 2.5% TBP/dodecane as a function of temperature

$[HNO_3]$ (M)	Distribution coefficient (K_d)				
	20°C	30°C	40°C	50°C	60°C
0.5	0.00664	0.00512	0.00399	0.00342	0.00302
1.0	0.0255	0.0194	0.0146	0.0133	0.0109
2.0	0.0813	0.0627	0.0500	0.0393	0.0337
3.0	0.151	0.114	0.0895	0.0714	0.0525

TABLE 2

Variation of distribution coefficients of Pu(VI) between nitric acid and 5% TBP/dodecane as a function of temperature

$[HNO_3]$ (M)	Distribution coefficient (K_d)				
	20°C	30°C	40°C	50°C	60°C
0.5	0.0326	0.0251	0.0196	0.0159	0.0130
1.0	0.0939	0.0738	0.0601	0.0493	0.0416
2.0	0.275	0.222	0.180	0.148	0.121
3.0	0.453	0.356	0.282	0.224	0.182

TABLE 3

Variation of distribution coefficients of Pu(VI) between nitric acid and 15% TBP/ dodecane as a function of temperature

$[HNO_3]$ (M)	Distribution coefficient (K_d)				
	20°C	30°C	40°C	50°C	60°C
0.25	0.0671	0.0542	0.0462	0.0414	0.0428
0.50	0.170	0.139	0.115	0.101	0.104
1.0	0.510	0.426	0.366	0.317	0.279
2.0	1.27	1.10	0.958	0.820	0.717
3.0	1.90	1.62	1.37	1.14	0.978

TABLE 4

Variation of distribution coefficients of Pu(VI) between nitric acid and 30% TBP/ dodecane as a function of temperature

$[HNO_3]$ (M)	Distribution coefficient (K_d)				
	20°C	30°C	40°C	50°C	60°C
0.25	0.221	0.182	0.159	0.149	0.162
0.50	0.573	0.520	0.491	0.477	0.471
1.0	1.40	1.27	1.14	1.03	0.931
2.0	2.95	2.69	2.41	2.17	1.94
3.0	4.43	3.69	3.36	2.92	2.56

of TBP and HNO_3 are constant, eqn. (3) can be obtained from eqn. (2)

$$K' = \frac{[PuO_2(NO_3)_2 \cdot 2\ TBP]}{[PuO_2^{2+}]\,[NO_3^-]^2[TBP]^2} \tag{3}$$

where $K' \alpha K$.

The various species of Pu(VI) present in the aqueous phase are PuO_2^{2+}, $PuO_2(NO_3)^+$, $PuO_2(NO_3)_2$, ... etc. If C_{Pu} is the total concentration of Pu(VI) in the aqueous phase at equilibrium, it can be shown that

$$C_{Pu} = [PuO_2^{2+}]\left(1 + \sum_{1}^{n} \beta_n[NO_3^-]^n\right) \tag{4}$$

where β_n is the overall concentration stability constant for the complex $PuO_2(NO_3)_n^{(2-n)+}$ formed by the reaction

$$PuO_{2(a)}^{2+} + nNO_{3(a)}^- \overset{\beta_n}{\rightleftharpoons} PuO_2(NO_3)_{n(a)}^{(2-n)+} \tag{5}$$

From eqns. (3) and (4), eqns. (6) and (7) follow

$$K' = \frac{[PuO_2(NO_3)_2 \cdot 2\,TBP]\left(1 + \sum_{1}^{n} \beta_n[NO_3^-]^n\right)}{C_{Pu}[NO_3^-]^2[TBP]^2} \tag{6}$$

$$K' = \frac{K_d\left(1 + \sum_{1}^{n} \beta_n[NO_3^-]^n\right)}{[NO_3^-]^2[TBP]^2} \tag{7}$$

From the determination of the distribution ratio of nitric acid using different concentrations of TBP and nitric acid, at temperatures in the range 20—60°C, it has been reported [7] that temperature has an insignificant effect on its distribution ratio. Therefore, it is reasonable to assume that the equilibrium concentrations of nitrate ion in the aqueous phase and the free TBP in the organic phase would remain constant over the temperature range studied. If the value of the term $(1 + \Sigma_1^n\beta_n[NO_3^-]^n)$ does not change significantly with temperature in the temperature range studied, the enthalpy changes (ΔH) associated with the extraction of Pu(VI) can then be calculated using the Van 't Hoff equation in the form

$$\frac{\Delta \log K_d}{\Delta(1/T)} = \frac{-\Delta H}{2.303R} \tag{8}$$

The term $(1 + \Sigma_1^n\beta_n[NO_3^-]^n)$ was found to remain unaltered with temperature in the case of U(VI) [7]. It is assumed that a similar trend is valid for Pu(VI). The K_d data obtained at different concentrations of TBP and nitric acid are given in Tables 1—4. Log K_d values were plotted vs. $(1/T)$ and the typical plots for 1.0 M nitric acid are shown in Fig. 1. The linearity of all the plots is in agreement with eqn. (8). The values of ΔH obtained from all the data are given in Table 5. An average value of $\Delta H = -4.2$ kcal mole^{-1} was obtained using the data at 2.5 and 5% TBP. At these concentrations of TBP, it is seen that the aqueous nitric acid concentration, in the range 0.25 to 3.0 M, has practically no effect on the values of ΔH obtained.

The effect of concentration of TBP and nitric acid on ΔH

From the data presented in Table 5, it is observed that there is a significant change in ΔH values when the concentration of TBP is varied, keeping the nitric acid concentration constant. It has been reported [15] that the overall enthalpy change (ΔH) associated with the extraction consists of enthalpy changes associated with (a) the dehydration of the actinide ion (ΔH_1), (b) the formation of the neutral extractable complex of the actinide ion (ΔH_2), and (c) the dissolution of the neutral complex in the organic phase (ΔH_3). Thus, the contributions from ΔH_1, ΔH_2 and ΔH_3 influence the

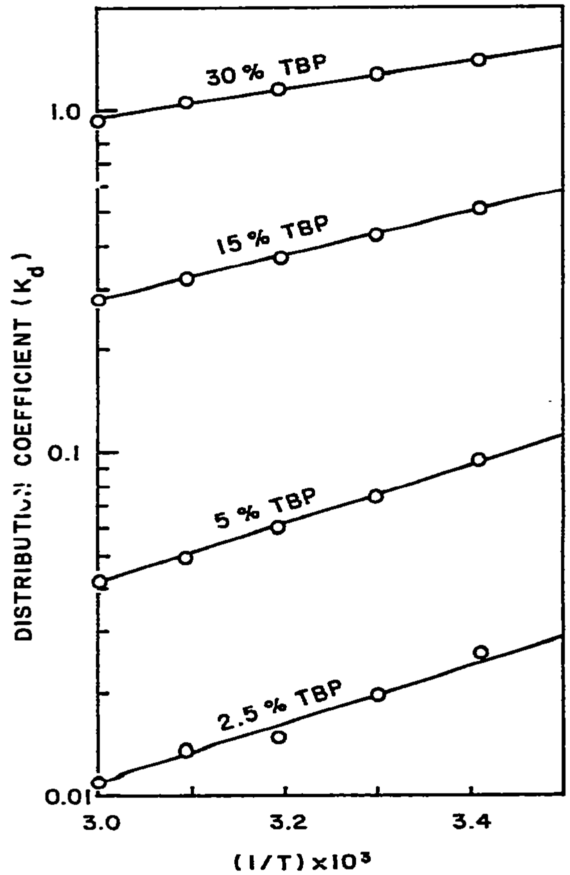

Fig. 1. Variation of the distribution coefficient of Pu(VI) with 1/T.

TABLE 5

Enthalpy values for the extraction of Pu(VI) into TBP/dodecane from aqueous nitric acid

$[HNO_3]$ (M)	$-\Delta H$ (kcal $mole^{-1}$ at different TBP %)			
	2.5	5	15	30
0.25 [a]			2.92	2.29
0.50 [a]	4.18	4.47	3.50	1.19
1.0	3.82	3.83	2.89	1.90
2.0	4.33	4.02	1.97	2.78
3.0	4.64	4.37	3.05	3.21

[a] 0.01 M $(NH_4)_2Ce(NO_3)_6$ was used as holding oxidant.

magnitude as well as the sign of ΔH. As $PuO_2(NO_3)_2 \cdot 2$ TBP is the only species formed in all the cases, one can safely assume that ΔH_2 remains unchanged. At constant HNO_3 concentration, ΔH_1 also remains constant irrespective of variation of the TBP concentration. Thus the variation of ΔH with change in TBP concentration is entirely due to changes in ΔH_3. The heat change associated with the dissolution of the neutral complex in the organic phase (ΔH_3), is positive, as work is required to disrupt the arrangement of TBP and TBP $\cdot$ HNO_3 dipoles for the dissolution of the bulky neutral complex molecule $PuO_2(NO_3)_2 \cdot 2$ TBP. The amount of nitric acid in the organic phase decreases with decreasing concentration of TBP and hence less work would be required (ΔH_3 decreases) to disrupt the arrangement of TBP and TBP $\cdot$ HNO_3 dipoles. Consequently, the overall enthalpy change (ΔH) would be more exothermic at low TBP concentrations and this is clearly observed from the data in Table 5.

At constant TBP concentration, the ΔH values remain fairly constant at different nitric acid concentrations. This trend is contrary to that observed in the case of U(VI) [7] where the ΔH values at constant TBP concentration decrease with decreasing nitric acid concentration, the decrease being attributed to the increase in the hydration of U(VI) ion due to increase in water activity at lower acidities. Since no such trend is observed in the case of Pu(VI), it can be inferred that the hydration of the Pu(VI) ion, is probably not influenced significantly with change in nitric acid concentration.

Determination of free energy and entropy changes associated with the extraction of Pu(VI)

The free energy associated with the extraction can be calculated from the value of K' obtained from eqn. (7). The values of $(1 + \Sigma_1^n \beta_n [NO_3^-]^n)$ can be evaluated if the values of β_1 and β_2 are known. The values of β_1 and β_2, however, are not available under the conditions used in the present work. In the case of U(VI) [16] these values were evaluated as $\beta_1 = 0.2$ and $\beta_2 = 0.05$. The value of the term $(1 + \Sigma_1^n \beta_n [NO_3^-]^n)$ was found [7] to be independent of temperature. Assuming these values to be the same for Pu(VI) and using the

TABLE 6

Values of K' with different TBP and HNO_3 concentrations (temperature = 25°C)

TBP (%)	$[HNO_3]$ (M)					
	0.25	0.50	1.0	2.0	3.0	Ref.
2.5		3.45	4.39	9.27	21.2	This work
5		4.19	4.24	8.00	16.1	This work
15	3.42	2.48	2.61	4.25	7.78	This work
30	2.90	2.28	1.87	2.54	5.03	This work
5			5.67			19
5				6.53		20
30		1.87	1.42	1.91	3.43	21
30		1.83	1.62	2.31		19

K_d values for 25°C read from the plot of log K_d vs. $1/T$, the K' values were obtained using eqn. (7) for different concentrations of TBP and nitric acid, and are given in Table 6. The K' values calculated from the values of K_d reported in the literature are also included for comparison. It can be seen from the data in Table 6 that there is good agreement between the values of K' obtained under the same conditions. The amount of nitric acid extracted into TBP was estimated assuming the equilibrium constant for the reaction given by eqn. (9) to be 0.16 [8].

$$H^+_{(a)} + NO^-_{3(a)} + TBP_{(o)} \rightleftharpoons HNO_3 \cdot TBP_{(o)} \qquad (9)$$

It has been reported that the value of this equilibrium constant ranges from 0.15 to 0.20. However, as [TBP · HNO_3] is very small, its value calculated using any value of the equilibrium constant between 0.15 and 0.20 does not change significantly. The free TBP was taken as the difference between initial concentration of TBP and the calculated concentration of TBP · HNO_3.

From the data in Table 6, it is seen that the values of K' do not remain constant and this can probably be attributed to changes in the activity coefficients of the various species involved. However, at low concentrations of nitric acid and TBP ([HNO_3] $\leqslant$ 1 M; [TBP] $\leqslant$ 5%) the values of K' are approximately constant, thereby indicating that the changes in activity coefficients are small under these conditions. An average value of $K' = 4.1$ was obtained. The values of free energy and entropy changes were calculated for 0.50 and 1.0 M HNO_3 using eqn. (10) and (11)

$$\Delta G = -2.303RT \log K' \qquad (10)$$

$$\Delta G = \Delta H - T\,\Delta S \qquad (11)$$

and these values were found to be $\Delta G = -0.840$ kcal mole^{-1} and $\Delta S = -11.3$ cal deg^{-1} mole^{-1}.

The thermodynamic values of free energy and entropy changes associated with the extraction of Pu(VI) were calculated from the value of K obtained using eqn. (2). As the concentrations of Pu(VI) in both the aqueous and organic phases are very low ($<10^{-4}$ M), γ PuO_2^{2+} and γ $PuO_2(NO_3)_2 \cdot 2$ TBP are assumed to be equal to unity. Using the values reported in the literature for γ NO_3^- [17] and γ TBP [8], the values of K were calculated and are given in Table 7. The values of K are reasonably constant for 0.50 and 1.0 M nitric acid concentrations and for TBP concentration of 2.5 and 5%, thus showing reasonable validity of the assumptions made in the calculations. The average value of K was found to be 14.3 ± 3. The free energy change (ΔG) was calculated from this value of K and was -1.58 kcal mole^{-1}. From the value of $\Delta H = -4.2$ kcal/mole^{-1} obtained using the data at 2.5 and 5% TBP, the value of ΔS was calculated to be -8.8 cal deg^{-1} mole^{-1}.

The negative entropy change obtained for the extraction of Pu(VI) may be attributed to the associaton of five groups to form one complex molecule. In this process, several water molecules from the hydration sphere of PuO_2^{2+} and NO_3^- ions are released but they are not set completely free since, in joining the bulk water, they participate in the water structure, so that their full positive contribution is not felt [18].

TABLE 7

Thermodynamic values of K for the extraction of Pu(VI) by TBP

[HNO_3] (M)	aHNO_3	[TBP] (M)	γTBP	K_d	$(1 + \Sigma_1^n \beta_n [NO_3^-]^n)$	$K = \frac{K_d(1 + \Sigma_1^n \beta_n [NO_3^-]^n)}{a^2TBP \cdot a^2HNO_3}$
0.5	0.3664	0.0844	0.78	0.00588	1.11	11.2
0.5	0.3664	0.1768	0.66	0.0289	1.11	17.6
1.0	0.7499	0.0825	0.78	0.0225	1.25	12.1
1.0	0.7499	0.1632	0.66	0.0839	1.25	16.1

ACKNOWLEDGEMENTS

Our sincere thanks are due to Dr. M.V. Ramaniah, Director, Radiological Group, for his interest in this work. One of the authors (M.S. Sajun) is grateful to the Department of Atomic Energy for the Junior Research Fellowship under the Bombay University—BARC collaboration program.

REFERENCES

1 B. Bernstrom and J. Rydberg, Acta Chem. Scand., 11 (1957) 1173.
2 T. Ishimori and E. Nakamura, Bull. Chem. Soc. Jpn., 32 (1959) 713.
3 V.I. Zemlyanukhin, G.P. Saroskina and M.F. Pushlenkov, Radiokhimiya, 6 (1964) 714.
4 L. Magon, H.A.C. McKay and A.G. Wain, J. Inorg. Nucl. Chem., 36 (1974) 3849.
5 S.K. Patil, V.V. Ramakrishna, G.V.N. Avadhany and M.V. Ramaniah, J. Inorg. Nucl. Chem., 35 (1973) 2537.
6 A. Ramanujam, V.V. Ramakrishna and S.K. Patil, J. Inorg. Nucl. Chem., 40 (1978) 1167.
7 S.V. Bagawde, P.R. Vasudeva Rao, V.V. Ramakrishna and S.K. Patil, J. Inorg. Nucl. Chem., 40 (1978) 1913.
8 K. Alcock, S.S. Grimley, T.V. Healy, J. Kennedy and H.A.C. McKay, Trans. Faraday Soc., 52 (1956) 39.
9 P. Dreze, Thesis Annex, Faculty of Science, University of Liege, Belgium, 1966.
10 V.B. Shevchenko. I.V. Shilin and Yu.F. Zhdanov, Russ. J. Inorg. Chem.. 15 (1960) 1367.
11 A.S. Ghosh Mazumdar and C.K. Sivaramakrishnan, J. Inorg. Nucl. Chem., 27 (1965) 2423.
12 H. Ihle, M. Karayannis and A. Murrenhaff, Organic Scintillators and Liquid Scintillation Counting, Academic Press, New York, 1971, p. 879.
13 E.A. Filappov, V.V. Yakshin, V.A. Belov, G.G. Arkhipova, I.S. Serebryakov and B.N. Laskorin, Dokl. Akad. Nauk, S.S.S.R., 234 (1977) 117.
14 E.A. Filippov, V.V. Yakshin, I.S. Serebryakov and B.N. Laskorin, Dokl. Akad. Nauk, S.S.S.R., 240 (1978) 1168.
15 L.L. Burger, Nucl. Sci. Eng., 15 (1963) 428.
16 Y. Marcus and A.S. Kertes, Ion Exchange and Solvent Extraction of Metal Complexes, Wiley-Interscience, New York, 1969, p. 899.
17 Y. Marcus and A.S. Kertes, Ion Exchange and Solvent Extraction of metal complexes, Wiley-Interscience, New York, 1969, p. 923.
18 Y. Marcus and Z. Kolarik, J. Chem. Eng. Data, 18 (1973) 155.
19 Wieczorek and Haas, KAPL-1002 (1954), quoted by L.L. Smith in USAEC Report, DP-700 (1962).
20 J.G. Moore, ORNL-4348 (1969).
21 M. Germain, D. Gourisse and M. Sougnez, J. Inorg. Nucl. Chem., 32 (1970) 245.