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SOME STUDIES ON THE EFFECT OF TEMPERATURE ON THE EXTRACTION OF U(VI) AND Np(IV) FROM NITRIC ACID BY LONG-CHAIN AMINES

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ABSTRACT

The effect of temperature on the extraction of U(VI) and Np(IV) by trilaurylamine (TLA) and Aliquat-336 in Solvesso-100 from aqueous nitric acid was studied. The results show that the distribution coefficient of Np(IV) decreases with increasing temperature. From these data the enthalpy change (ΔH) for the extraction of Np(IV) was calculated and was found to be -8 to -9 kcal mole^{-1}. An attempt was also made to calculate the free energy (ΔG) and entropy change (ΔS) associated with the extraction of Np(IV). In the case of U(VI), however, the temperature had very little influence on the distribution coefficient values

INTRODUCTION

The long-chain amines offer several advantages for their use in the separation and purification of actinides. As temperature is known to influence the extraction behaviour of metal ions it was considered of interest to study the effect of temperature on the extraction of actinides by long-chain tertiary and quaternary amines. Only a couple of such data for actinides–amine systems are reported in the literature [1,2]. The present paper reports the data obtained on the extraction of U(VI) and Np(IV) by trilaurylamine (TLA) and Aliquat-336 in Solvesso-100 from aqueous nitric acid as a function of temperature. Attempts have been made to calculate some of the thermodynamic parameters associated with the extraction process from the data obtained.

EXPERIMENTAL

Materials

Neptunium-237, ^{238}Np and ^{233}U were obtained and purified as described earlier [3]. TLA, Aliquat-336 and Solvesso-100 obtained from K and K Lab., General Mills, U.S.A. and Esso Standard Co., Holland, respectively, were used as received. All other chemicals used were of A.R. grade.

Procedure

Neptunium-237 was spiked with ^{238}Np to facilitate the estimation of Np by gamma counting. Ferrous sulphamate (~0.01 M) was used as holding reductant to keep Np as Np(IV). Equal volumes of the aqueous nitric acid of the desired concentration containing either Np(IV) or U(VI) and the amine solution in Solvesso-100 of the desired concentration were pipetted into ground glass stoppered equilibration tubes. The tubes were immersed for half-an-hour in a thermostated water bath kept at the desired temperature and subsequently were equilibrated in the water bath for 30 min. The temperature of the bath was maintained within ±0.1°C. At the end of the equilibration, suitable aliquots from both phases were pipetted out for the radioassay of the actinide ion. Neptunium was estimated by gamma counting of ^{238}Np using NaI(Tl) detector coupled with a single channel analyser. ^{233}U was assayed by alpha liquid scintillation counting. The experiments were done in triplicate and the agreement between the values of distribution coefficient was normally better than ±2%.

RESULTS AND DISCUSSION

The effect of temperature on distribution coefficients (K_d)

The distribution coefficient data obtained for the extraction of U(VI) into 20% TLA and Aliquat-336 from 2 M nitric acid at various temperatures are

TABLE 1

Variation of distribution coefficient of U(VI) between nitric acid and amine–solvesso-100 with temperature

HNO_3 = 2 M, Amine = 20 volume %.

Temp. (°C)	K_d	
	TLA	Aliq-336
10	0.78	1.53
20	0.79	1.56
30	0.81	1.58
40	0.80	1.62
50	0.83	1.71
60	0.84	1.94

TABLE 2

Variation of distribution coefficient of Np(IV) between nitric acid and TLA-Solvesso-100 with temperature

HNO_3 (M)	TLA (v%)	K_d				
		20°C	30°C	40°C	50°C	60°C
1	1	0.14	0.077	0.047	0.027	
	5	3.88	2.43	1.50	0.079	
	10	16.30	11.10	6.51	3.51	
2	1	0.36	0.22	0.14	0.094	0.061
	5	8.20	5.44	3.60	2.22	1.47
	10	32.50	20.90	14.20	10.40	7.40
4	1	0.46	0.28	0.18	0.12	0.082
	5	9.20	6.60	4.30	2.81	1.94
	10	36.20	25.80	16.32	11.12	7.76

given in Table 1. It can be seen from the data that the distribution coefficient of U(VI) is almost independent of temperature.

The data on Np(IV) as a function of temperature with different concentrations of amines and nitric acid are given in Tables 2 and 3. The data show that the distribution coefficient of Np(IV) decreases with increasing temperature at all the concentrations of amines and nitric acid used here. This is similar to the observation reported by Danesi et al. [1] for the extraction of Pu(IV) into Alamine-336.

TABLE 3

Variation of distribution coefficient of Np(IV) between nitric acid and Aliq-336–Solvesso-100 with temperature

HNO_3 (M)	Aliq-336 (V%)	K_d			
		30°C	40°C	50°C	60°C
1	0.05	0.647	0.415	0.270	0.146
	0.10	2.05	1.31	0.82	0.44
	0.50	20.45	13.38	9.44	4.78
2	0.05	0.66	0.43	0.28	0.17
	0.10	2.0	1.31	0.88	0.59
	0.50	30.5	21.2	13.90	9.1
4	0.05	0.42	0.25	0.15	0.09
	0.10	1.47	0.91	0.55	0.33
	0.50	23.3	15.1	9.80	6.20

Calculation of the enthalpy change associated with the extraction of Np(IV)

The data obtained were used to calculate enthalpy change (ΔH) associated with the extraction process. The equilibrium for the extraction of Np(IV) into TLA from nitrate medium can be given by

$$Np^{4+}_{(a)} + 4\,NO^-_{3_{(a)}} + 2\,TLA \cdot HNO_{3_{(o)}} \rightleftharpoons Np(NO_3)_6(TLA\,H^+)_{2_{(o)}} \tag{1}$$

the equilibrium constant for which can be expressed by

$$K = \frac{[Np(NO_3)_6(TLA\,H^+)_2]}{[Np^{4+}][NO_3^-]^4[TLA \cdot HNO_3]^2} \tag{2}$$

A similar equilibrium reaction can be written for Aliquat-336.

The various species of Np(IV) present in the aqueous solutions are Np^{4+}, $Np(NO_3)^{3+}$, $Np(NO_3)_2^{2+}$ etc. If C_{Np} is the total concentration of Np(IV) in the aqueous phase at equilibrium it can be shown that

$$C_{Np} = [Np^{4+}]\left(1 + \sum_1^n \beta_n [NO_3^-]^n\right) \tag{3}$$

where β_n represents the overall concentration stability constant for formation of the n^{th} complex $Np(NO_3)_n^{(4-n)+}$ given by

$$Np^{4+} + n\,NO_3^- \overset{\beta_n}{\rightleftharpoons} Np(NO_3)_n^{(4-n)+} \tag{4}$$

From eqns. (2) and (3) it follows that

$$K = \frac{K_d\left(1 + \sum_1^n \beta_n [NO_3^-]^n\right)}{[NO_3^-]^4[TLA \cdot HNO_3]^2} \tag{5}$$

where K_d is the distribution coefficient of Np(IV).

A few distribution coefficient data for the extraction of nitric acid into TLA were obtained at room temperature and 50°C which showed that the extraction of nitric acid is almost independent of temperature. This may be true in the case of quaternary amines also. It is, therefore, reasonable to assume that equilibrium concentration of nitrate ion in the aqueous phase and of the $TLA \cdot HNO_3$ in the organic phase remain constant over the temperature range studied. If the value of the term $(1 + \sum_1^n \beta_n [NO_3^-]^n)$ does not change significantly over the temperature range studied, the Van 't Hoff's equation in the form given by eqn. (6) can be used to calculate the overall enthalpy change ΔH associated with the extraction of Np(IV)

$$\frac{\Delta \log K_d}{\Delta(1/T)} = \frac{-\Delta H}{2.303\,R} \tag{6}$$

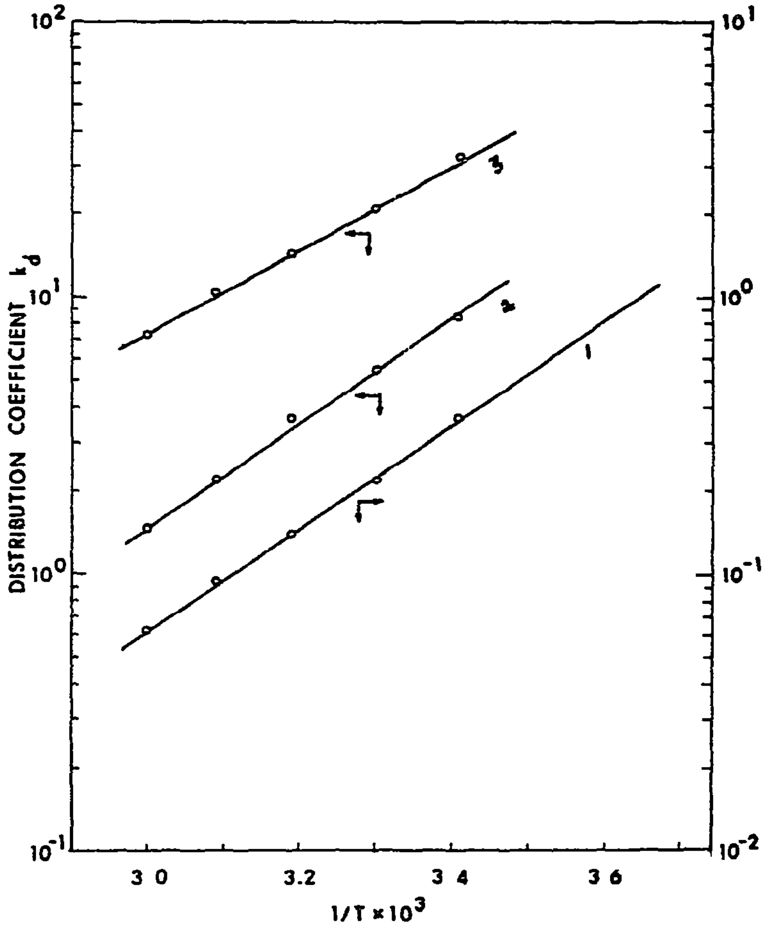

Fig. 1. Variation of distribution coefficient of Np(IV) with temperature from 2 M nitric acid, (1) 1%, (2) 5%, (3) 10%TLA in Solvesso-100.

TABLE 4

Enthalpy changes for the extraction of Np(IV) into amine/Solvesso-100 from aqueous nitric acid

HNO_3 (M)	$-\Delta H$ (kcal $mole^{-1}$)					
	TLA (V %)			Aliq-336 (V %)		
	1	5	10	0.05	0.1	0.5
1	9.88	8.53	9.1	8.55	8.83	7.45
2	8.60	8.42	7.32	9.20	8.20	8.05
4	8.51	8.03	7.63	10.31	9.99	9.50

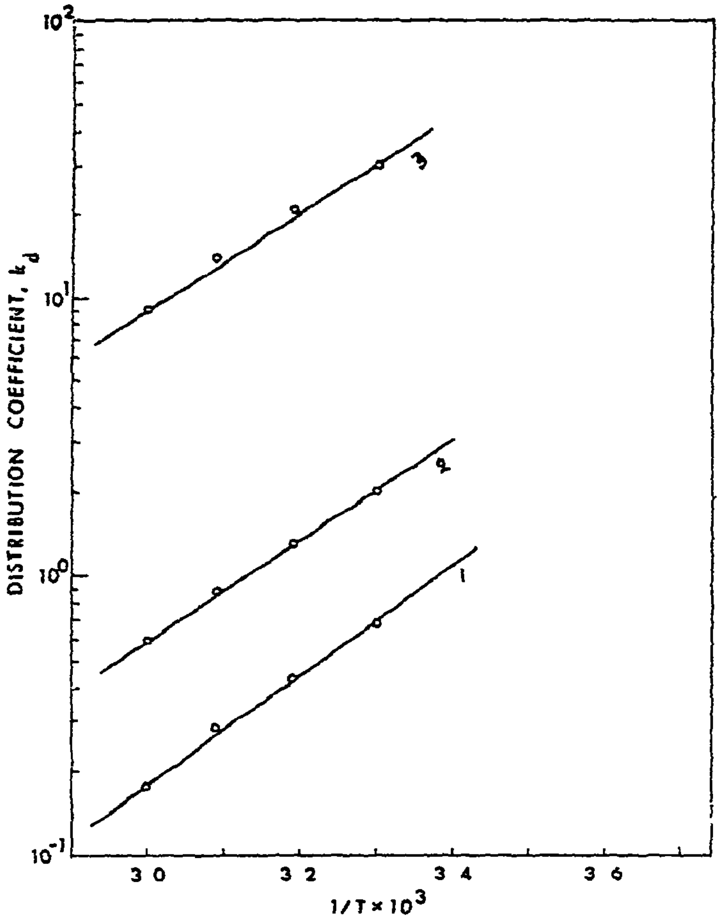

Fig 2. Variation of distribution coefficient of Np(IV) with temperature from 1 M nitric acid. (1) 0 05%, (2) 0.1%, (3) 0.5% Aliquat-336 in Solvesso-100.

The log K_d of Np(IV) vs. $1/T$ were plotted at all the concentrations of amines and nitric acid and were found to be straight lines. Typical plots for TLA and Aliquat-336 are shown in Figs. 1 and 2, respectively. The values of ΔH calculated using eqn. (6) are given in Table4. It is seen that the extraction of Np(IV) from different nitric acid and amine concentrations is exothermic. Besides, the ΔH values are approximately constant both for TLA as well as for Aliquat-336 the value being about -8 to -9 kcal mole^{-1}. The present value of ΔH for Np(IV) compares well with the ΔH value ($\Delta H = -8.2$ kcal mole^{-1}) reported by Danesi et al. [1] for the extraction of Pu(IV) into Alamine-336. From their data it can be inferred that approximately the same ΔH value is obtained for the extraction from 4, 5.4 and 9 M nitric acid and this, too, is similar to the ΔH value obtained for Np(IV) in the present work.

It has been reported that enthalpy changes associated with ion-exchange are generally small [5]. The amine extraction is analogous to ion-exchange and thus the same may be applicable here also. As the ΔH value is almost the same for different concentrations of tertiary as well as quaternary amines it appears that the extracted metal species interactions in the organic phase are small.

Calculation of free energy (ΔG) and the entropy (ΔS) changes associated with the extraction of Np(IV) by TLA

The calculation of free energy and entropy changes associated with eqn. (1) is possible only when the value of K is known. Attempts were made to calculate these values for Np(IV) from 2 N nitric acid at 30°C with TLA. The value of $(1 + \sum_1^n \beta_n[\mathrm{NO}_3^-]^n)$ was determined by the method suggested earlier [4] to enable the calculation of K using eqn. (5). This involves the measurement of distribution ratio values for Np(IV) from perchloric and nitric acids by TTA. If K_d^0 and K_d are the distribution ratio values respectively for the same concentration of $HClO_4$ and HNO_3 it can be shown that

$$\frac{K_d^0}{K_d} = \left(1 + \sum_1^n \beta_n[\mathrm{NO}_3^-]^n\right) \tag{7}$$

provided that the nitrate complexes of Np(IV) are not extracted into TTA and that the activity coefficients remain the same both in perchloric and nitric acids. The former assumption is known to be valid [6]. The values of $(1 + \sum_1^n \beta_n[\mathrm{NO}_3^-]^n)$ obtained by this method are given in Table 5. Using these values from eqn. (7) the values of K were calculated (eqn. (5)) assuming that the activity coefficients of various species involved in TLA extraction of Np(IV) remain unchanged at constant nitric acid and TLA concentrations. Further, the values of free energy (ΔG) and entropy change (ΔS) were

TABLE 5

Determination of $(1 + \sum_1^n \beta_n[\mathrm{NO}_3^-]^n)$

Acid (M)	TTA (M)	K_d of Np(IV) HClO$_4$ (K_d^0)	K_d of Np(IV) HNO$_3$ (K_d)	$K_d^0/K_d = (1 + \sum_1^n \beta_n(\mathrm{NO}_3^-)^n)$
1	0.075	10.9	2.2	4.95
2	0.15	7.96	0.54	14.8
4	0.30	7.72	0.093	83.4

TABLE 6

Summary of K, ΔG, ΔH and ΔS associated with the extraction of Np(IV) with TLA
$HNO_3 = 2$ M; temp. = 30°C

TLA (%)	K	$-\Delta G$ (kcal mole^{-1})	$-\Delta H$ (kcal mole^{-1})	$-\Delta S$ (e.u.)
1	1319	4.33	8.60	14.1
2	1305	4.32	8.42	13.5
10	1253	4.30	7.32	9.98

calculated using the following equations

$$\Delta G = -RT \ln K \qquad (8)$$

$$\Delta G = \Delta H - T\Delta S \qquad (9)$$

The values thus calculated are summarised in Table 6.

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