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The effect of temperature on the extraction of plutonium(VI) from nitric acid into dodecane by di(2-ethylhexyl)sulphoxide

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Abstract

The effect of temperature on the extraction of plutonium(VI) into dodecane by di(2-ethylhexyl)sulphoxide (DEHSO) has been investigated as a function of temperature in the range 25–50 ° C using a wide range of concentrations of both nitric acid as well as DEHSO. The results show that the distribution ratios of plutonium(VI) considerably decrease with increasing temperature. From the variation of the distribution ratio (D_{Pu}) with temperature, the thermodynamic parameters such as the free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) changes associated with the formation of $\mathrm{PuO_2(NO_3)_2 \cdot 2DEHSO}$ have been evaluated following a least squares method. Extraction of plutonium(VI) from nitric acid by DEHSO is invariably exothermic in nature and is mainly enthalpy controlled, the entropy change counteracting in all cases. Values of ΔH are not much affected by increase in nitric acid concentration. Negative values of ΔS are indicative of a smaller entropy gain due to loss of hydration water molecules compared to entropy loss due to complex formation.

INTRODUCTION

The use of symmetrical dialkyl sulphoxides as potential metal extractants has aroused much interest in recent years [1–3]. Among them, di(2-ethylhexyl)sulphoxide (DEHSO), a novel sterically-hindered branched-chain neutral extracting agent, has been recently explored for the extraction of uranium [4,5]. This prompted us to initiate a programme for the selective extraction of uranium, plutonium and americium and their separation from some long-lived fission product contaminants from aqueous nitric acid media over a wide variety of conditions [6,7]. Optimum conditions such as aqueous phase acidity, time of equilibration, sulphoxide concentration, strippant and effect of commonly associated diverse ions have been investigated in detail for the extraction–separation of trace as well as macro amounts of uranium and plutonium. Relatively, few data have been reported so far, particularly pertaining to the study of the effect of temperature on the extraction of actinides by this extractant. A knowledge of the extraction behaviour as a function of temperature is of the utmost

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use in the optimization of conditions (i.e. temperature, concentration of extractant and acid) for the selective extraction of one metal in the presence of others. For instance, Danesi et al. [8] have indicated the possibility of improving the plutonium/uranium separation by a suitable choice of temperature. Of late, results of a systematic study describing the influence of the temperature on the extraction of uranium(VI) as well as plutonium(IV) from 2 M HNO_3 aqueous medium into dodecane by DEHSO have been reported by us [9]. In continuation of our work, it seemed therefore worthwhile to examine the effect of temperature on the extraction of plutonium(VI) using a wide range of concentrations of nitric acid and DEHSO. Using the distribution data, the enthalpy changes as well as the free energy and entropy changes associated with the plutonyl ion extraction process under the specified conditions are calculated. Data so obtained can be used to ascertain what modifications and adjustments should be incorporated to improve the efficiency and selectivity of such sulphur-based solvating extractants. In addition, the collection of additional data would enable an understanding of the factors involved in the influence of temperature on partitioning of hexavalent plutonium between the aqueous and organic phases.

EXPERIMENTAL

DEHSO obtained from Fairfield Chem. Co., U.S.A., was used after treatment with excess of 11 M nitric acid in order to oxidize any sulphide present as impurity. The mixture so obtained was treated with NaOH and then washed with distilled water until free from alkali. The product obtained was then distilled at reduced pressure (0.4 mmHg) and the middle fraction distilling at around 140 ° C was collected and used for the experiments. The DEHSO product obtained as above was found to be more than 99.6% pure from non-aqueous titration in acetic anhydride medium [10]. Dodecane, procured from Fluka, Germany, was washed with about 1 M NaOH and 1 M nitric acid and finally with distilled water until free from acid and then distilled. The middle fraction collected in the range 215–216°C was used throughout the present study. All other reagents used were of AR or GR grade.

Plutonium-239 was the major constituent in the plutonium used for the extraction studies. Plutonium was purified by absorption from 7 M to 8 M nitric acid solution on Dowex 1X4 anion exchange resin [11] followed by double peroxide precipitation. Tracer plutonium (in about 2 M nitric acid) for each experiment was taken from this stock and adjusted to the hexavalent state by the addition of solid AgO (about 0.03 M) in the presence of 0.005 M sodium bromate used as the holding oxidant. Hexavalency of plutonium in the aqueous phase was checked by the usual TTA extraction method and it was ensured often that it did not change during extraction.

Radiochemical purity of the radiotracer was ascertained by alpha spectrometry. Tracer level of plutonium was assayed by alpha liquid scintillation counting using the method recommended by Ihle et al. [12]. The liquid scintillator was prepared by dissolving 0.7 g 2,5-diphenyloxazole (PPO), 0.03 g 1,4-bis-2-(5-phenyloxazolyl)benzene (POPOP) and 10 g naphthalene in 100 ml of distilled dioxane.

Procedure

Solutions of standard DEHSO, diluted with dodecane, were equilibrated three times with an equal volume of aqueous nitric acid solution of the desired molarity. Equal volumes (generally 0.5 ml) of an aqueous nitric acid solution containing plutonium-239 tracer and the extractant (DEHSO/dodecane) were pipetted into ground-glass-stoppered equilibration tubes and subsequently equilibrated for nearly 1 h in a thermostated water bath adjusted to the desired temperature to within ±0.1°C. The phases were allowed to settle for about half an hour and finally suitable aliquots from the two phases were pipetted for radioassay. The distribution ratio (D_{Pu}) of plutonium defined as

$$D_{\mathrm{Pu}} = \frac{\text{total concentration of plutonium in the organic phase}}{\text{total concentration of plutonium in the aqueous phase}}$$

was thus calculated.

All the measurements were done at least in duplicate and the agreement in D_{Pu} values obtained was within $\pm 2\%$ with good material balance ($> 95\%$).

RESULTS AND DISCUSSION

Effect of temperature on D_{Pu}

Data on D_{Pu} obtained for the extraction of plutonium(VI) from varying aqueous nitric acid concentrations with 0.2, 0.5 and 1.1 M DEHSO, dissolved in dodecane, at various temperatures in the range 25–50°C are summarized in Table 1. From these results, it is evident that the D_{Pu} values significantly decrease with increasing temperature under all sets of conditions investigated. This pattern of dependence on temperature is in fine accord with those results already reported in the literature concerning the extraction of actinides by several other neutral solvating extractants, including long-chain aliphatic sulphoxides [13–16]. Values of D_{Pu} invariably increase with increasing nitric acid concentration at a particular temperature, although the relative increase is higher at both 0.5 and 1.1 M DEHSO concentrations.

TABLE 1

Variation of D_{Pu} of Pu(VI) between aqueous nitric acid and DEHSO/dodecane as a function of temperature

(Nitric acid)	Distribution ratio D_{Pu}			
	25 °C	30 °C	40 °C	50 °C
0.2 M DEHSO				
1.0	0.20	0.16	0.14	0.11
2.0	0.30	0.26	0.20	0.16
3.0	0.32	0.31	0.25	0.20
4.0	0.36	0.29	0.23	0.21
5.0	0.47	0.35	0.26	0.29
0.5 M DEHSO				
1.0	1.05	0.96	0.74	0.55
2.0	1.56	1.25	1.06	0.82
3.0	1.73	1.58	1.27	1.01
4.0	1.86	1.80	1.35	1.20
5.0	2.06	2.15	1.69	1.30
1.1 M DEHSO				
1.0	4.56	4.44	3.27	2.60
2.0	5.75	5.20	4.97	4.09
3.0	6.56	6.21	5.25	4.87
4.0	8.39	7.74	6.69	4.61
5.0	8.94	8.18	7.42	5.73

The extraction equilibrium for plutonium(VI) can be represented by

$$PuO_2^{2+}{}_a + 2NO_3^-{}_a + x\,DEHSO_o = [PuO_2(NO_3)_2 \cdot x\,DEHSO]_o \qquad (1)$$

where subscripts a and o refer to the species present in aqueous and organic phases, respectively.

The extraction constant can be simply written as

$$K_{Pu} = [PuO_2(NO_3)_2 \cdot x\,DEHSO]_o / \left([PuO_2^{2+}]_a [NO_3^-]_a^2 [DEHSO]_o^x\right) \qquad (2)$$

based on the assumption that the various activity coefficients for a given concentration of DEHSO and nitric acid are constant.

Plutonium(VI) in aqueous solution is also present as species such as PuO_2^{2+}, $PuO_2(NO_3)^+$ and $PuO_2(NO_3)_2$. Hence, if C_{Pu} is the total concentration of plutonium(VI) in the aqueous phase, and D_{Pu} is the distribution ratio, it can be shown that

$$C_{Pu} = [PuO_2^{2+}]\left(1 + \sum_1^n \beta_n [NO_3^-]^n\right) \qquad (3)$$

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

$$PuO_2^{2+} + nNO_3^- \overset{\beta_n}{\rightleftharpoons} \left[PuO_2(NO_3)_n^{(2-n)+}\right]$$

Hence

$$K_{\mathrm{Pu}} = \left[\mathrm{PuO_2(NO_3)_2}(x\,\mathrm{DEHSO}) \times \left(1 + \sum_{1}^{n} \beta_n [\mathrm{NO_3^-}]^n\right) \Big/ C_{\mathrm{Pu}} [\mathrm{NO_3^-}]^2 [\mathrm{DEHSO}]^x \right]$$

$$= D_{\mathrm{Pu}} \left(1 + \sum_{1}^{n} \beta_n [\mathrm{NO_3^-}]^n\right) \Big/ [\mathrm{NO_3^-}]^2 [\mathrm{DEHSO}]^x \qquad (4)$$

Values of the distribution ratio of nitric acid with DEHSO in dodecane were measured at two temperatures and were found to remain constant, thus keeping the equilibrium concentrations of nitrate ion in the aqueous phase and free DEHSO in the organic phase constant in the temperature range studied. The amount of nitric acid extracted into DEHSO was estimated from the equilibrium constant, already determined for the reaction given by eqn. (5), to be 0.40 [6].

$$\mathrm{H^+ + NO_3^- + DEHSO = HNO_3 \cdot DEHSO} \qquad (5)$$

The free DEHSO, $[\mathrm{DEHSO}]_{\mathrm{free}}$, was taken as the difference between initial concentration of DEHSO and the calculated concentration of $\mathrm{HNO_3 \cdot DEHSO}$. A plot at constant nitric acid concentration (2 M nitric acid) of

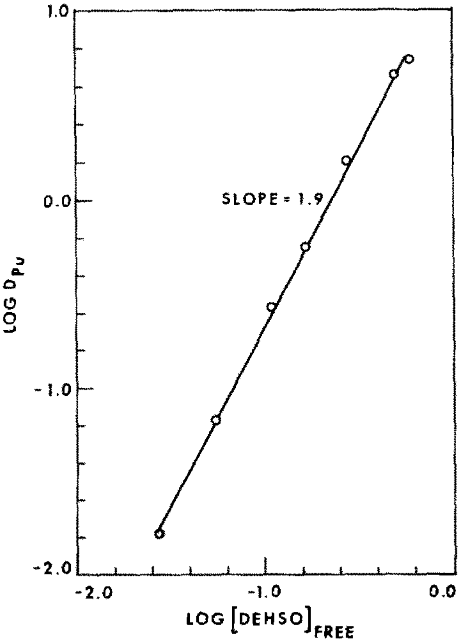

Fig. 1. Plot of extraction of Pu(VI) into dodecane by DEHSO from 2 M nitric acid as a function of free DEHSO concentration. Temperature, 25°C.

log D_{Pu} versus log $[DEHSO]_{free}$ at 25 °C was found to be a straight line with slope x equal to approximately 2 (Fig. 1) which indicated that plutonium(VI) is mainly extracted as a disolvate, presumably of the type $PuO_2(NO_3)_2 \cdot 2DEHSO$. The values of the term $(1+\Sigma_1^n\beta_n[NO_3^-]^n)$ have been taken from ref. 17. From the values of $(1+\Sigma_1^n\beta_n[NO_3^-]^n)$, the values of K_{Pu} were evaluated assuming that the activity coefficient values of the various species involved in sulphoxide extraction remain unchanged at constant nitric acid and sulphoxide concentrations. Values of K_{Pu} are found to considerably decrease with increasing temperature. By contrast equilibrium constants invariably increased with increasing nitric acid concentration in the aqueous phase at a particular temperature.

The van't Hoff equation in the form given by eqn. (6) has been used to calculate the enthalpy change ΔH associated with the extraction process.

$$\Delta \log K_{Pu}/\Delta(1/T) = -\Delta H/2.303R \quad (6)$$

Figure 2 depicts the plots of log K_{Pu} versus $1/T$ for the extraction of plutonium(VI) with DEHSO at all concentrations of DEHSO (0.2, 0.5, 1.1 M) and nitric acid (1–5 M). These plots are fairly linear between 25 and

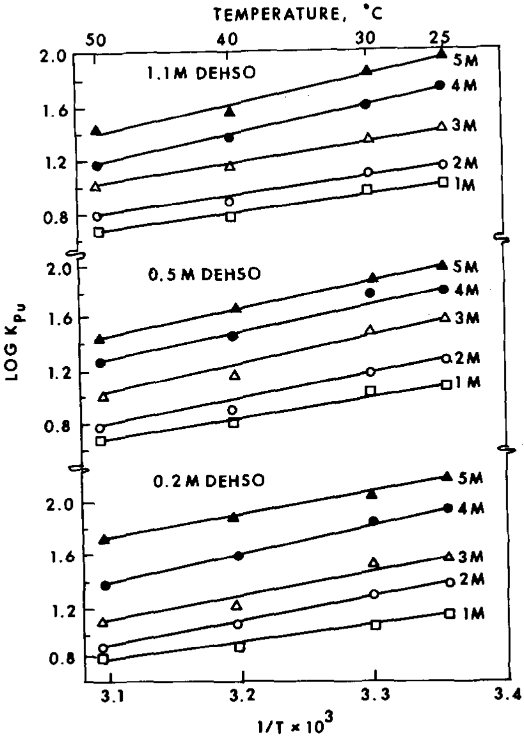

Fig. 2. Variation of log K_{Pu} with $1/T$ for the extraction of Pu(VI) by DEHSO/dodecane from nitric acid solution having different molarities.

TABLE 2

Free energy, enthalpy, and entropy changes (ΔG, ΔH, ΔS) associated with the extraction of Pu(VI) by DEHSO at 25 °C

(M) Nitric acid	Thermodynamic functions (kJ mol^{-1})		
	$-\Delta G$ [a]	$-\Delta H$ [a]	$-T\Delta S$ [a]
0.2 M DEHSO			
1	6.35 ± 0.13	25.87 ± 2.32	19.52 ± 1.27
2	7.57 ± 0.15	34.49 ± 3.09	26.92 ± 1.75
3	8.64 ± 0.17	32.11 ± 2.45	23.47 ± 1.31
4	10.79 ± 0.22	39.43 ± 1.78	28.64 ± 1.00
5	12.15 ± 0.24	31.19 ± 1.38	19.04 ± 0.91
0.5 M DEHSO			
1	5.89 ± 0.12	28.63 ± 2.24	22.74 ± 1.30
2	7.05 ± 0.14	36.25 ± 2.85	29.20 ± 1.68
3	8.68 ± 0.17	38.43 ± 2.91	29.75 ± 1.65
4	10.04 ± 0.20	36.67 ± 1.09	26.63 ± 0.67
5	11.11 ± 0.22	36.42 ± 1.97	25.31 ± 1.03
1.1 M DEHSO			
1	5.61 ± 0.11	26.75 ± 3.50	21.14 ± 1.98
2	6.41 ± 0.13	27.54 ± 2.91	21.13 ± 1.61
3	7.99 ± 0.16	28.76 ± 0.46	20.77 ± 0.38
4	9.78 ± 0.20	41.40 ± 1.05	31.62 ± 0.72
5	11.02 ± 0.22	38.68 ± 0.98	27.66 ± 0.63

[a] ΔG, ΔH and $T\Delta S$ are in kJ mol^{-1} and are calculated by the least-squares method.

50 °C in agreement with eqn. (6). The values of ΔH, along with their precision as obtained from Fig. 2 using the least-squares method, are given in Table 2. It is seen from the data in Table 2 that the sulphoxide extraction of plutonium(VI) nitrate is exothermic. The values of ΔH obtained from all the data are given in Table 2. An average value of $\Delta H = -33.51 \pm 2.25$ kJ mol^{-1} was obtained using the data at 0.2, 0.5 and 1.1 M DEHSO. At these concentrations of DEHSO, it is evident that the aqueous nitric acid concentration, in the range 1–5 M, has little effect on the values of ΔH obtained.

Effect of concentration of DEHSO and nitric acid on ΔH

It can be seen from Table 2 that the solvent extraction of plutonium(VI) by DEHSO is favoured only by high negative enthalpy change. This is in conformity with the behaviour already reported in the case of extraction of plutonyl ions with other neutral solvating extractants [17] which has been ascribed due to the extraction of the heavily hydrated $PuO_2(NO_3)$ 2DEHSO complex in the organic phase. From Table 2 it is also quite evident that the values of ΔH remain roughly unaltered with varying concentrations of DEHSO in the range 0.2–1.1 M keeping the aqueous nitric acid concentration constant. Burger [18] has suggested that the overall enthalpy change during extraction (ΔH) consists of enthalpy changes associated with (a) dehydration of PuO_2^{2+} ion (ΔH_1), (b) the complex formation of the PuO_2^{2+} ion with nitrate ions and DEHSO molecules (ΔH_2), and (c) the dissolution of the $PuO_2(NO_3)_2 \cdot 2DEHSO$ neutral complex in the organic phase (ΔH_3). The magnitude and sign of ΔH, therefore, will depend on the contributions from ΔH_1, ΔH_2 and ΔH_3. As $PuO_2(NO_3)_2 \cdot 2DEHSO$ is the only complex formed in all the instances, it can be assumed that ΔH_2 remains unchanged. At constant nitric acid concentration, ΔH_1 also remains constant irrespective of variation of the DEHSO concentration. Thus the variation of ΔH with change in DEHSO concentration is entirely due to changes in ΔH_3. The enthalpy change associated with the dissolution of the neutral complex in the organic phase (ΔH_3) is positive, since work is required to disrupt the arrangement of DEHSO and $DEHSO \cdot HNO_3$ dipoles for the dissolution of the bulky neutral complex species $PuO_2(NO_3)_2 \cdot 2DEHSO$. The amount of nitric acid in the organic phase decreases with decreasing concentration of DEHSO and hence less work would be required (ΔH_3 decreases) to disrupt the arrangement of DEHSO and $DEHSO \cdot HNO_3$ dipoles. As a result, the overall enthalpy change (ΔH) would be more exothermic at low DEHSO concentrations. No such systematic variation in the values of ΔH is, however, seen in the present study as is obvious from the data collated in Table 2.

At constant DEHSO concentration, the ΔH values remain fairly constant at different nitric acid concentrations. This trend is contrary to that observed in the case of uranium(VI) [19] where the ΔH values at constant DEHSO concentration decrease with decreasing nitric acid concentration, the decrease being attributed to the increase in the hydration of uranium(VI) ion due to increase in water activity at lower acidities. Since no trend is observed in the case of plutonium(VI), it can be inferred that the hydration of the plutonium(VI) ion is probably not influenced significantly with change in nitric acid concentration.

Values of ΔG and ΔS were calculated by following the equations

$$\Delta G = -2.303RT \log K_{Pu}$$

and

$$\Delta S = (\Delta H - \Delta G)/T$$

which are also summarized in Table 2. The thermodynamic parameter ΔG associated with the extraction of plutonium(VI) by DEHSO from varying nitric acid molarities were calculated from the values of K_{Pu} obtained at 25°C using eqn. (4). These constants computed using concentrations rather than activities of the various species involved in extraction equilibria, are not true thermodynamic quantities. Under conditions of constant concentration of acid and the extractant, the contribution of activity coefficients to the thermodynamic values should be fairly constant, rendering the values in Table 2 reliable for relative comparisons.

While the extraction of plutonium(VI) by DEHSO is favoured by high negative enthalpy change, a negative entropy change counteracts the extraction of plutonium(VI) with DEHSO. Negative ΔS may be attributed to the association of five groups to form one complex molecule. In this process, several water molecules forming the hydration sphere of PuO_2^{2+} and nitrate ions are released but they are not completely free, since in joining the bulk water, they participate in the water structure, so that their positive contribution is not fully realized [20]. These observations are in fine accord with earlier published results pertaining to the extraction of hexavalent uranium nitrate by DEHSO [9].

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