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INFLUENCE OF TEMPERATURE ON THE EXTRACTION OF URANIUM(VI) AND PLUTONIUM(IV) FROM NITRIC ACID INTO n-DODECANE BY DI(2-ETHYLHEXYL)SULPHOXIDE

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ABSTRACT

The influence of temperature on the extraction of uranium(VI) and plutonium(IV) from 2 M HNO_3 medium into n-dodecane by di(2-ethylhexyl)sulphoxide (DESO) was investigated as a function of temperature in the range 25–50 °C. The results show that the distribution ratios of both U(VI) and Pu(IV) considerably decrease with increasing temperature. From the distribution measurements, thermodynamic parameters such as the free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) changes associated with the formation of $UO_2(NO_3)_2 \cdot 2DESO$ and $Pu(NO_3)_4 \cdot 2DESO$ were evaluated. Extraction of both U(VI) and Pu(IV) from nitric acid by DESO is exothermic in nature and is mainly enthalpy controlled, with negative entropy changes for the relatively less hydrated UO_2^{2+} species and a small positive value for the more hydrated Pu^{4+} species.

INTRODUCTION

Recently, di(2-ethylhexyl)sulphoxide (DESO), a novel sterically hindered branched-chain neutral extractant, has been reported to be potential extracting agent for many metal cations [1–3]. Most interestingly, DESO offers a distinct advantage over other analogous high molecular weight symmetrical di-alkyl sulphoxides because of its unrestricted solubility in an aliphatic diluent like n-dodecane [1]. Data on the extraction behaviour of trace as well as macro amounts of uranium(VI) and plutonium(IV) by DESO from nitric acid aqueous media over a wide range of experimental conditions have been recently reported by us [4]. It seemed, therefore, of interest to study the effect of temperature on the extraction of uranium and plutonium from nitric acid medium by DESO. In the present study we looked at the influence of the temperature in the range 25–50 °C on the extraction of U(VI) and Pu(IV) from 2 M HNO_3 medium into n-dodecane by DESO. Using the distribution data, the enthalpy changes and the free energy and

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entropy changes associated with the extraction processes under the specified conditions are calculated.

EXPERIMENTAL

DESO (Fairfield Chem. Co., U.S.A.) was used as received. n-Dodecane (Fluka, Germany) was washed with about 1 M NaOH and 1 M HNO_3 and finally with distilled water until free from acid and then distilled. All other reagents used were of A.R. or G.R. grade.

^{239}Pu was the major constituent in the plutonium used for the extraction studies. Plutonium was purified by absorption from 7 M to 8 M HNO_3 solution on Dowex 1X4 anion exchange resin [5] followed by double peroxide precipitation. For each experiment, samples of Plutonium ($\approx 10^{-5}$ M) in ca. 2-M HNO_3 were taken from this stock and adjusted to the tetravalent state by the addition of solid sodium nitrite (ca. 0.03 M) in the presence of 0.005 M NH_4VO_3 used as the holding oxidant [6]. The tetravalency of plutonium in the aqueous phase was checked by the usual TTA (theonyl trifluoro acetone) extraction method and it was ensured that the valency did not change during extraction. ^{233}U tracer was purified by means of the TBP (tributyl phosphate) extraction method. The radiochemical purity of these tracers was ascertained by α spectrometry. Tracer levels of both plutonium and uranium were assayed by α liquid scintillation counting using the method recommended by Ihle et al. [7]. The liquid scintillator was prepared by dissolving 0.7 g of 2,5-diphenyloxazole (PPO), 0.03 g of 1,4-bis-2-(5-phenyl oxazolyl) benzene (POPOP) and 10 g of naphthalene in 100 ml of distilled dioxane.

PROCEDURE

Solutions of DESO (0.2 M) diluted with n-dodecane, were equilibrated three times with an equal volume of 2 M HNO_3 aqueous solution. Equal volumes (generally 0.5 ml) of 2 M HNO_3 containing the tracer and 0.2 M DESO in n-dodecane, were pipetted into ground-glass-stoppered equilibration tubes and subsequently equilibrated for 1 h in a thermostatted water bath adjusted to the desired temperature to within $\pm 0.1°C$. 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_M) of the metal ions, defined as

$$D_M = \frac{\text{total concentration of metal ion in the organic phase}}{\text{total concentration of metal ion in the aqueous phase}}$$

was thus calculated.

All the measurements were done at least twice and the agreement in D_M values obtained was within ±2% with good material balance (> 95%).

RESULTS AND DISCUSSION

The distribution ratios obtained for U(VI) and Pu(IV) from 2 M HNO_3 aqueous medium into 0.2 M DESO/n-dodecane at different temperatures are given in Table 1 along with their extraction constants (K_U and K_{Pu}). From the data listed in Table 1 it is evident that D_M values for both U(VI) and Pu(IV) decrease significantly with increasing temperature, although the relative decrease is much smaller with Pu(IV) than that observed for U(VI). The distribution data are, therefore, in generally good agreement with similar data reported for the extraction of these actinides with other long-chain aliphatic sulphoxides [8].

The extraction equilibria for U(VI) and Pu(IV) can be represented by

$$UO_2^{2+} + 2NO_3^- + 2DESO \rightleftharpoons UO_2(NO_3)_2 \cdot 2DESO \tag{1}$$

$$Pu^{4+} + 4NO_3^- + 2DESO \rightleftharpoons Pu(NO_3)_4 \cdot 2DESO \tag{2}$$

The extraction constants can be written as

$$K_U = [UO_2(NO_3)_2 \cdot 2DESO] / ([UO_2^{2+}][NO_3^-]^2[DESO]^2) \tag{3}$$

$$K_{Pu} = [Pu(NO_3)_4 \cdot 2DESO] / ([Pu^{4+}][NO_3^-]^4[DESO]^2) \tag{4}$$

However, U(VI) and Pu(IV) in aqueous solutions are also present as species like $UO_2NO_3^+$, $UO_2(NO_3)_2$, $Pu(NO_3)^{3+}$, $Pu(NO_3)_2^{2+}$, etc. Hence, if C_M is the total concentration of the actinide in the aqueous phase, and D_M

TABLE 1

Variation in the distribution ratio (D_M) and the equilibrium constants (K_U and K_{Pu}) of U(VI) and Pu(IV) as a function of temperature [a]

Sample No.	Temperature (°C)	U(VI)		Pu(IV)	
		D_U	K_U	D_{Pu}	K_{Pu}
1	25	2.53 ± 0.03	100.2 ± 1.2	2.24 ± 0.05	790.2 ± 17.7
2	30	1.89 ± 0.01	74.9 ± 0.4	1.92 ± 0.10	677.3 ± 30.7
3	40	1.52 ± 0.01	58.7 ± 0.7	1.68 ± 0.02	545.2 ± 5.5
4	50	1.09 ± 0.04	42.1 ± 1.5	1.56 ± 0.04	506.3 ± 11.4

[a] Aqueous phase acidity: 2 M HNO_3. Extractant concentration: 0.2 M DESO/n-dodecane.

is the distribution ratio, it can be shown that

$$C_U = [UO_2^{2+}]\left(1 + \sum_1^n \beta_n [NO_3^-]^n\right) \tag{5}$$

$$C_{Pu} = [Pu^{4+}]\left(1 + \sum_1^n \beta_n [NO_3^-]^n\right) \tag{6}$$

where β_n represents the overall concentration stability constant for the compelxes of the type $UO_2(NO_3)_n^{(2-n)+}$ and $Pu(NO_3)_n^{(4-n)+}$ formed with U(VI) and Pu(IV), respectively. Hence,

$$K_U = [UO_2(NO_3)_2 \cdot 2DESO]\left(1 + \sum_1^n \beta_n [NO_3^-]^n\right)\Big/\left(C_U[NO_3^-]^2[DESO]^2\right)$$

$$= D_U\left(1 + \sum_1^n \beta_n [NO_3^-]^n\right)\Big/\left([NO_3^-]^2[DESO]^2\right) \tag{7}$$

and

$$K_{Pu} = D_{Pu}\left(1 + \sum_1^n \beta_n [NO_3^-]^n\right)\Big/\left([NO_3^-]^4[DESO]^2\right) \tag{8}$$

Values of the distribution ratio of nitric acid with DESO in n-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 DESO in the organic phase constant in the temperature range studied. The amount of nitric acid extracted into DESO was estimated from the equilibrium constant, already determined for the reaction given by eqn. (9), to be 0.40 [4].

$$H^+_{aq} + NO_3^- + DESO_{org} \rightleftharpoons HNO_3 \cdot DESO_{org} \tag{9}$$

The free DESO ($[DESO]_{free}$) was taken as the difference between the initial concentration of DESO (0.2 M) and the calculated concentration of $HNO_3 \cdot DESO$. The values of the term, $(1 + \Sigma_1^n \beta_n [NO_3^-]^n)$ were taken from Ref. 8. From the values of $(1 + \Sigma_1^n \beta_n [NO_3^-]^n)$, the values of K_U as well as K_{Pu} were evaluated assuming that the values of the activity coefficients of the various species involved in sulphoxide extraction remained unchanged at constant nitric acid and sulphoxide concentrations. Values of K_U and K_{Pu} were found to decrease considerably with increasing temperature.

Van't Hoff's equation in the form given by eqn. (10) was used to calculate the enthalpy change, ΔH, associated with the extraction process.

$$\Delta \log K_M / \Delta(1/T) = -\Delta H / 2.303\, R \tag{10}$$

Figure 1 depicts the plots of log K_M vs. $1/T$ for the extraction of U(VI) and P(IV) with DESO. These plots are fairly linear between 25 °C and 50 °C, in agreement with eqn. (10). The values of ΔH, along with their

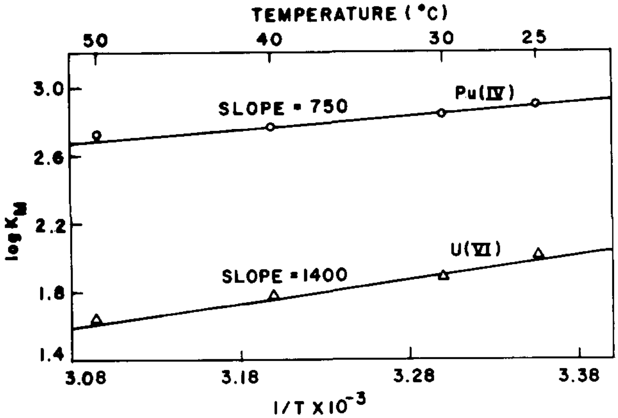

Fig. 1. Variation in log K_M with $1/T$ for U(VI) and Pu(IV) with 0.2 M DESO/n-dodecane: (△) U(VI); (○) Pu(IV).

precision, as obtained from Fig. 1 using the least-squares method, are given in Table 2. It can be seen from the data listed in Table 2 that the sulphoxide extraction of both of the actinide nitrates is exothermic in nature.

The values of ΔG and ΔS were calculated according to

$$\Delta G = -2.303\, RT \log K_M$$

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

and the results are summarized in Table 2. These parameters, 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 extractant, the contribution of the activity coefficients to the thermodynamic values should be fairly constant, rendering the values in Table 2 reliable for relative comparisons.

While the extraction of U(VI) and Pu(IV) from nitric acid into n-dodecane by DESO is favoured by high negative enthalpy change, a negative entropy change counteracts the extraction of U(VI) with DESO and both negative enthalpy and positive entropy changes seem to favour Pu(IV) extraction under similar conditions. This different behaviour can be ex-

TABLE 2

Thermodynamic parameters (ΔG, ΔH and ΔS) [a] associated with the extraction of U(VI) and Pu(IV) at 25 °C

Cation	ΔG (kJ mol $^{-1}$)	ΔH (kJ mol^{-1})	$T\Delta S$ (kJ mol^{-1})
U(VI)	-11.42 ± 0.03	-26.37 ± 2.53	-14.94 ± 1.79
Pu(IV)	-16.54 ± 0.06	-14.35 ± 2.33	2.19 ± 1.65

[a] Calculated using the least-squares method.

plained by considering the degree of hydration of the cations: U(VI) < Pu(IV). In the case of the extraction uranyl ions with DESO, because fewer water molecules are released the energy spent for the same procedure is less and hence the net enthalpy change (i.e. the energy released due to the formation of the extractable species less the energy spent in releasing the water molecules) is highly negative (-26.37 kJ mol^{-1}). Furthermore the net entropy change (i.e. the entropy gain due to release of water molecules and the entropy loss due to bonding of DESO and nitrate ions) is negative (-14.94 kJ mol^{-1}). However, in the case of tetrapositive plutonium, the energy spent in releasing the larger number of water molecules results in a net enthalpy change which is less negative (-14.35 kJ mol^{-1}) and a positive entropy change. These observations are in accord with our previously published results pertaining to the extraction of these actinide nitrates by analogous sulphoxides [8].

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