

THERMODYNAMIC STUDIES OF COMPLEX FORMATION OF  
ACTINYL IONS EXTRACTED WITH TBP FROM HYDROCHLORIC  
AND NITRIC ACIDS

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The changes of the free energy, enthalpy and entropy accompanying the extraction of the U/VI/, Np/VI/ and Pu/VI/ by TBP have been determined by the method of extraction chromatography. The results obtained indicate outer-sphere complexation.

#### INTRODUCTION

According to the complex formation - partition model of extraction proposed by Siekierski<sup>1</sup>, extracted complexes are assumed to be formed in the aqueous phase and then transferred into the organic phase. It can be assumed, that for the differences in the extraction ability of f-elements, the complex formation step is much more important than the partition step. Therefore, the changes in thermodynamic functions of extraction of actinyl ions with Z /atomic number/ reflect the changes in these of complex formation in the aqueous phase. Actinides seem

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to be especially sensitive to the changes occurring in the first hydration sphere. This is reflected e.g. in the manifestation of the double-double effect<sup>2</sup>.

Our interest in the solvent extraction of hexavalent actinides in the TBP - mineral acid systems is based on the unexpected trend of extraction coefficients along the actinide series<sup>3</sup>. General trend observed in extraction abilities with Z, is of importance when structure of extracted species is concerned.

Our previous studies have shown that the investigated inorganic ligands can be divided from this point of view into two groups. Nitrate and perchlorate form the first group, while chloride - the second one<sup>4,5</sup>. For the first group the free energy of extraction increases with Z, whereas for the system with hydrochloric acid such an increase is not observed. It was interesting therefore to evaluate the enthalpy and entropy changes with Z in order to compare the trends in these functions for both groups of inorganic ligands.

### EXPERIMENTAL

Extraction chromatography has been used because of the presence of neptunium/V/ ions and colloidal plutonium. Using this method, each oxidation state of the actinide ions can be separated as an individual chromatographic peak and elute with an appropriate volume of mineral acid.

The chromatographic columns have been prepared after the procedure described by Fidelis and Siekierski<sup>6</sup>. Because of the low values of separation factors, two types of radioactivity emitters were used. Chromatographic fractions were collected on watch-glasses and measured

twice: by ZnS/Ag and NaI/Tl crystal scintillators for alpha and gamma radiations, respectively.

In order to oxidize the actinide to the hexavalent state, the samples were ozonized for 1 h in 1M HNO<sub>3</sub> or 1M HCl solutions, respectively. The oxidation of neptunium samples was performed immediately before the experiments, because neptunyl ions are reduced easily in sunlight. Plutonyl ions are stable for at least 2 weeks.

## RESULTS AND DISCUSSION

Values of  $\ln D$  determined in various temperatures for traces of UO<sub>2</sub><sup>2+</sup>, NpO<sub>2</sub><sup>2+</sup> and PuO<sub>2</sub><sup>2+</sup> in the 0.6M HNO<sub>3</sub>-TBP and 2M HCl-TBP systems, together with the standard deviations calculated from several experimental data, are presented in Table 1. The data show linear dependence on the  $1/T$  term with slopes and intercepts presented in Table 2.

The free energy values were calculated using the equation:

$$\Delta G = -RT \ln D \quad //$$

where  $D$  are the extraction coefficients for the investigated actinides.

The enthalpy values have been determined by the temperature coefficient method. The values obtained in this way contain terms due to changes with temperature of activity coefficients of the species involved. Assuming that these changes are near the same for consecutive actinyl ions, the changes with  $Z$  in the enthalpy and entropy of extraction can be investigated. The obtained enthalpy values are presented in Table 3.

TABLE 1  
 The changes of lnD for actinyl ions extracted in the 0.6M HNO<sub>3</sub>-TBP and 2M HCl-TBP systems with temperature. Confidence level - 0.95

Temperature, °C	Nitrates			Chlorides		
	UO <sub>2</sub> <sup>2+</sup>	NpO <sub>2</sub> <sup>2+</sup>	PuO <sub>2</sub> <sup>2+</sup>	UO <sub>2</sub> <sup>2+</sup>	NpO <sub>2</sub> <sup>2+</sup>	PuO <sub>2</sub> <sup>2+</sup>
5	2.936±0.035	2.786±0.045	1.623±0.031	2.519±0.044	3.905±0.033	3.021±0.041
15	2.775±0.029	2.607±0.043	1.462±0.028	2.401±0.043	3.750±0.031	2.955±0.039
25	2.626±0.027	2.441±0.040	1.312±0.028	2.303±0.039	3.606±0.030	2.849±0.037
35	2.486±0.026	2.284±0.038	1.171±0.027	2.206±0.040	3.471±0.029	2.837±0.035
45	2.355±0.025	2.138±0.036	1.039±0.026	2.114±0.036	3.344±0.028	2.783±0.033

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TABLE 2

Slopes and intercepts for the  $\ln D = A/T + B$  relation for the systems with nitric and hydrochloric acid

Ion	Nitrates		Chlorides	
	A	B	A	B
$UO_2^{2+}$	1284.5 $\pm$ 60.1	-1.68 $\pm$ 0.21	894.9 $\pm$ 83.9	-0.69 $\pm$ 0.28
$NpO_2^{2+}$	1433.9 $\pm$ 106.2	-2.37 $\pm$ 0.35	1241.9 $\pm$ 102.4	-0.55 $\pm$ 0.33
$PuO_2^{2+}$	1292.6 $\pm$ 69.2	-3.02 $\pm$ 0.23	526.6 $\pm$ 105.9	1.13 $\pm$ 0.35

TABLE 3

The  $\Delta H^0$  values /kJ mol<sup>-1</sup>/ for the systems with nitric and hydrochloric acid

Ion	Nitrates	Chlorides
$UO_2^{2+}$	-10.68 $\pm$ 0.02	-7.77 $\pm$ 0.03
$NpO_2^{2+}$	-11.92 $\pm$ 0.03	-10.32 $\pm$ 0.03
$PuO_2^{2+}$	-10.75 $\pm$ 0.02	-4.35 $\pm$ 0.03

The corresponding entropy values, calculated using the equation:

$$\Delta G = \Delta H - T\Delta S \quad /2/$$

are presented in Table 4. As far as the entropy values are concerned, one should note the different trends in the two investigated systems. A distinct increase in en-

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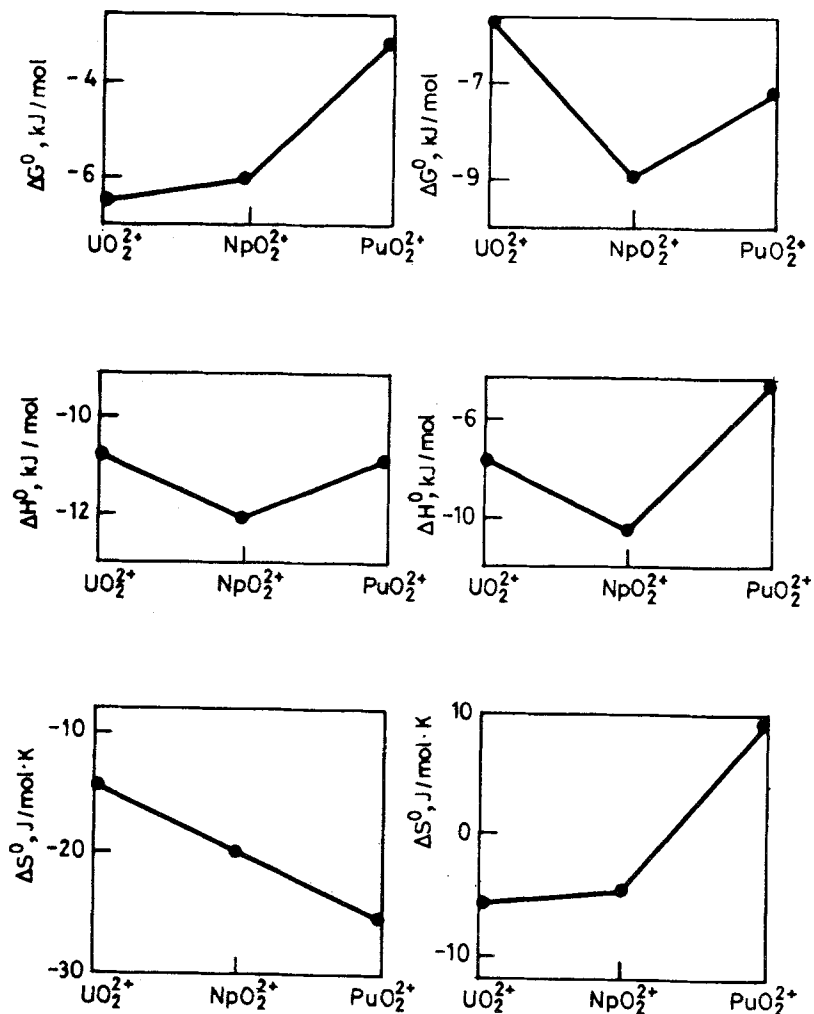


Fig. 1. Variation of the free energy, enthalpy and entropy with the atomic number of actinyl. The plots on the left concern the nitrates, and those on the right - chlorides

entropy is observed for the  $PuO_2^{2+}$  ion in case of hydrochloric acid, while in the case of nitric acid we have a smooth decrease in  $Z$ . The trends in the free energy, enthalpy and entropy changes are shown in Fig. 1. The

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TABLE 4

The  $\Delta S^\circ$  values /J mol<sup>-1</sup> K<sup>-1</sup>/ for the system with nitric and hydrochloric acid

Ion	Nitrates	Chlorides
UO <sub>2</sub> <sup>2+</sup>	-13.99±0.09	-5.80±0.10
NpO <sub>2</sub> <sup>2+</sup>	-19.70±0.12	-4.65±0.11
PuO <sub>2</sub> <sup>2+</sup>	-25.14±0.09	9.38±0.12

comparison of the investigated trends shows that the entropy term is responsible for the difference in free energy changes observed between chloride and nitrate systems<sup>5</sup>.

As far as the problem of outer - vs. inner - sphere complexation is concerned, the trend in the free energy changes along the series is of importance. The lack of the significant increase in stability with Z for both investigated systems can be assumed as an evidence that hydrated actinyl ions participate in the formation of the extracted complexes. If the extracted complexes were of the inner-sphere type, a distinct increase in stability with Z would be observed, because of the actinide contraction.

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