Study of the isotope effect in the isotope exchange reaction between Pu^{IV} and Pu^{III} by extraction redox-chromatography

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The equilibrium isotope effect in the isotope exchange reaction between Pu^{IV} extracted with tributyl phosphate and Pu^{III} in an aqueous nitric acid solution has been studied by extraction chromatography. For the $^{238/242}$Pu isotope pair the isotope separation coefficient (α) at 25 °C has been found to be 1.0022±0.0005.

Key words: plutonium, isotope effect; extraction chromatography.

Redox-chromatography has been previously used to study equilibrium isotope effects for reactions of both light atoms[1] and heavy elements, in particular, uranium[2,3] and tin.[4] The purpose of the present work was to study the isotope effects in the Pu^{IV}—Pu^{III} system. The isotope exchange was performed between Pu^{IV} extracted with tributyl phosphate (TBP) and Pu^{III} in an aqueous nitric acid solution. TBP was applied on the surface of modified (hydrophobic) silica gel. Hydroquinone was used as the reducing reagent for Pu^{IV}.

Experimental

Silica gel from which the traces of iron (fraction 0.4—0.6 mm) had been washed off was hydrophobized by treating it with dimethyldichlorosilane according to the previously described procedure.[5] Dried hydrophobic silica gel was mixed with a defined amount of TBP dissolved in CCl_4 and then was dried in a weak flow of air with stirring. The concentration of TBP on the carrier was 10 %.

An initial plutonium solution containing a mixture of α-active $^{242/238}$Pu isotopes was purified by sorption on an anion-exchanger from 7 *M* HNO_3. γ-Spectrometry showed no significant amounts of ^{241}Am in the eluate.

Isotope fractionation was performed in a glass column kept at constant temperature, 110 cm in length and with a diameter of 0.66 cm, filled with silica gel impregnated with TBP. Before the filling of the column, 0.62 mmoles of Pu^{IV} containing a mixture of $^{242/238}$Pu isotopes was extracted by the stationary phase from 3 *M* HNO_3 and 0.1 *M* N_2H_4 under static conditions. A 0.014 *M* solution of hydroquinone containing HNO_3 (3 mol L^{-1}) and N_2H_4 (0.1 mol L^{-1}) was applied to the bottom part of the column using a peristaltic pump at a rate of 0.3 mL min^{-1} cm^{-2}. The temperature of the extraction-chromatographic column was maintained at 25 °C.

The concentration of plutonium in the eluate was determined by radiometry. The isotope composition of plutonium was analyzed using an α-spectrometer. Targets for the analysis were prepared by electrochemical application of a sample on disks of stainless steel according to the previously described procedure.[5] The α-spectra of $^{242/238}$Pu were measured on a Nokia LP 4900 B multichannel analyzer equipped with a semiconducting detector with a resolution of 40—50 keV. The isotope ratios $R = {}^{242}\text{Pu}/{}^{238}\text{Pu}$ were determined from the ratio of the corresponding peak areas using a special program.[6] The statistical error for determination of R did not exceed 0.5—1.0 % in each case. The initial ratio R_0 was 0.531±0.004.

Results and Discussion

Hydroquinone is an efficient reducing reagent for Pu^{IV} (see Ref. 7). The Pu^{III} formed is virtually not extracted by TBP from 3 *M* HNO_3. Therefore, passing a hydroquinone solution through a Pu^{IV}-containing extraction-chromatographic column results in the efficient reducing re-extraction of plutonium. The presence of Pu^{III} in the eluate is confirmed by spectrophotometry by the appearance of the characteristic absorption bands in the 550—630 nm range. The "tail" part of the plutonium elution curve is presented in Fig. 1. The plutonium concentration in the eluate is almost equivalent to that of Pu^{III}.

The values of the isotope ratios of plutonium in the samples collected from the "tail" part of the elution curve and the values for the observed isotope effect $S = R_0/R$ are listed in Table 1.

It follows from these data that the plutonium in the "tail" part of the elution curve is enriched with a light isotope. Taking into account the procedure of the experiment, one may conclude that the light isotope ^{238}Pu is primarily concentrated in the plutonium that is in a higher oxidation state.

The isotope separation coefficient (α) was calculated from the Spedding equation:[8]

$$\alpha = 1 + \Sigma q_i(R_i - R_0)/QR_0(1 - R_0),$$

where q_i and Q are the content of plutonium in the *i*-th fraction of the eluate and the total amount of the ex-

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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1557—1558, September, 1994.

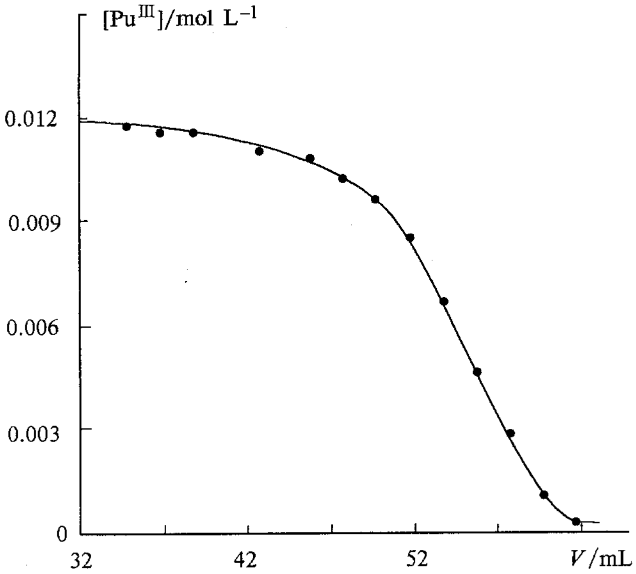

Fig. 1. "Tail" part of the elution curve for Pu^{IV} extracted with TBP on hydrophobic silica gel. HNO_3 (3 mol L^{-1}) + N_2H_4 (0.1 mol L^{-1}) + hydroquinone (0.014 mol L^{-1}) as the eluent. The elution rate is 0.3 mL min^{-1} cm^{-2}.

Table 1. Isotope ratios (R = ^{242}Pu/^{238}Pu) and the observed isotope effects ($S = R_0/R$)

Volume of the eluate/mL	R	S
35	0.526±0.002	1.009
39	0.528±0.002	1.006
43	0.520±0.003	1.021
48	0.523±0.002	1.015
51	0.517±0.003	1.027
55	0.514±0.003	1.033
58	0.507±0.003	1.047

tracted plutonium, respectively. The summation was performed over all of the fractions collected in the "tail" part of the elution curve.

The known values of α for the isotope exchange reactions of uranium and tin and the α value found in the present work are listed in Table 2. As follows from these data, the isotope separation coefficient in the Pu^{IV}—Pu^{III} system agrees well with the α values for the U^{IV}—U^{III} and U^{VI}—U^{IV} systems. The α values are substantially higher for the lighter tin isotopes in the Sn^{IV}—Sn^{II} isotope exchange reaction than for actinides.

It can be assumed that the isotope exchange in the system studied is determined by the isotope exchange reaction between the Pu^{IV} extracted with TBP and the Pu^{III} in an aqueous solution. The Pu^{IV}—Pu^{III} isotope exchange rate constant in the presence of TBP applied on silica gel[9] is 18—19 mol^{-1} L s^{-1} at 25 °C. Hence, under the experimental conditions, the time of the isotope half-exchange did not exceed several seconds, and the rate of the whole process is likely to be limited by the diffusion of plutonium in the film of the extragent on the silica gel surface.

Table 2. Isotope separation coefficients

System	Isotope pair	α
Pu^{IV}—Pu^{III}	^{238}Pu/^{242}Pu	1.0022±0.0005
U^{IV}—U^{III}	^{235}U/^{238}U	1.0020±1.0030*
U^{VI}—U^{IV}	^{235}U/^{238}U	1.0012±0.0004*
Sn^{IV}—Sn^{II}	^{112}Sn/^{116}Sn	1.0058±0.0009**
	^{112}Sn/^{119}Sn	1.0190±0.0018
	^{112}Sn/^{124}Sn	1.0251±0.0030

* Literature data.[10]
** Literature data.[4]

The authors are grateful to Prof. N. N. Krot for discussion of the results and valuable remarks and to V. P. Perminov for help in designing the computer programs.

This work was financially supported by the International Science Foundation (Grant MDB 000).

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Received April 29, 1994