A Fundamental Study on Uranium Isotope Separation Using U(IV)–U(VI) Electron Exchange Reaction

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Displacement chromatography of electron-exchange reaction between U(IV) and U(VI) has been accomplished in an anion exchange resin column using Ti(III) ion as a reductant and Fe(III) ion as an oxidant. The details of the so-called redox-process for uranium isotope separation are described. The temperature dependencies of the elementary separation coefficient and the equilibrium constant of the isotope exchange reaction are discussed using the analytical data obtained by a series of separation experiments at different temperatures.

Introduction

As has been reported in a previous paper [1], an anion exchange chromatographic process using the electron-exchange reaction between uranous ion and uranyl ion has given a very large isotope effect compared with those obtained by other chemical separation processes of uranium isotopes [2–5]. In the present study, the temperature dependencies of the elementary separation coefficient and the equilibrium constant of the isotopic exchange reaction (electron exchange reaction) have been investigated as important basic data of the redox-process as a candidate of an alternative commercial process of uranium isotope separation. In addition, from the view point of engineering, the feasibility of band displacement chromatography on an anion exchange resin column has been examined for the system Ti(III)–U(VI)–Fe(III), and a long migration was carried out to confirm the steady accumulation of the elementary isotope effect along with the migration distance.

Experimental

Equipment and Reagents

Pressure-resistant Pyrex glass columns with inner diameter of 1.0 cm and overall height of 120 cm or 200 cm, and fitted with a heat exchange jacket for temperature control were used. For long distance migration, four columns were connected in series with Teflon tubes having an inner diameter of 1 mm. In Fig. 1, the column is illustrated schematically. The ion exchange resin used was a strongly basic anion exchange resin supplied by Asahi Chemical Industry. Uranyl chloride solution was prepared by eluting a cation exchange resin column of uranyl form with hydrochloric acid solution.

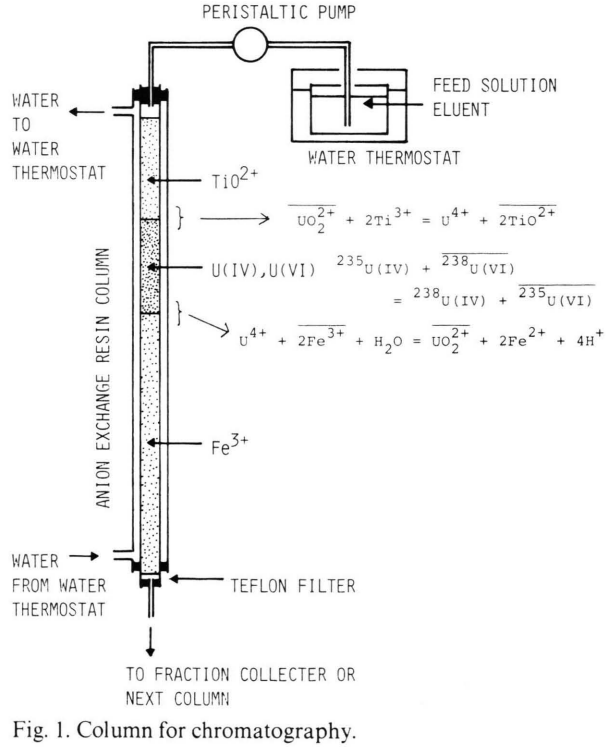

Fig. 1. Column for chromatography.

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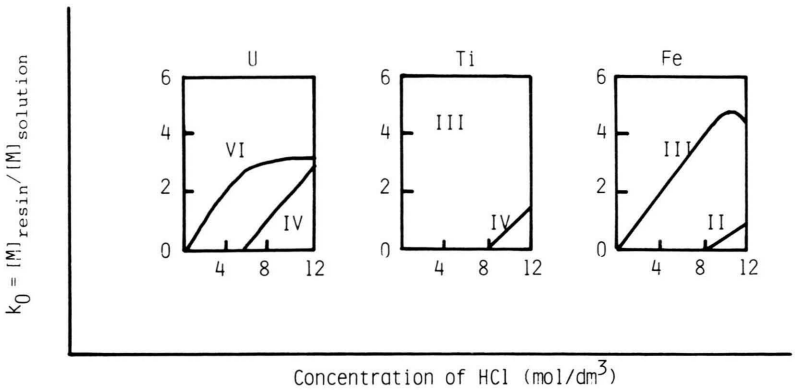

Fig. 2. Anion exchange selectivities of uranium, titanium, and iron as function of HCl concentration.

$TiCl_3$ solution was prepared by dissolving highly pure metalic titanium into concentrated hydrochloric acid. Other reagents were analytical grade.

Determination of the Concentration of Hydrochloric Acid to Realize an Ideal Electron-Exchange Chromatography

In the present electron-exchange chromatography, uranyl ion should be reduced to uranous ion by Ti^{3+} ion and the uranous ion should be oxidized to uranyl ion by Fe^{3+} ion, in the resin bed. These oxidation and reduction rections will proceed due to the differences of their redox potentials:

$TiO_2 + 4H^+ + e^- = Ti^{3+} + 2H_2O$ 0.099 V
$UO_2^{2+} + 4H^+ + 2e^- = U^{4+} + 2H_2O$ 0.330 V
$Fe^{3+} + e^- = Fe^{2+}$ 0.771 V

Another important point is the anion exchange selectivity of the species depend on the concentration of hydrochloric acid. The anion exchange selectivities of the elements are shown in Fig. 2 as functions of the concentration of hydrochloric acid [6]. The selectivity is also dependent on temperature; thus we have carried out a series of preliminary experiments to determine the ranges of the hydrochloric acid concentration and temperature in which the electron-exchange chromatography can be best realized. The results of the observations, shown in Fig. 3, indicate that the maximum concentration of hydrochloric acid to maintain ideal chromatography varies from 9 mol/dm^3 at 15 °C to 4 mol/dm^3 at 83 °C.

Goda et al., on the other hand, reported that the rate of the electron-exchange reaction is a function

Table 1. Experimental conditions.

Run No.	1	2	3*	4	5	6*
Temperature (°C)	30	50	70	70	70	87
Uranium feed solution	0.1 M UO_2Cl_2 5 M HCl 1 M $FeCl_2$**	0.1 M UO_2Cl_2 4.5 M HCl 1 M $FeCl_2$**	0.1 M UO_2Cl_2 5 M HCl	0.1 M UO_2Cl_2 3.5 M HCl 1 M $FeCl_2$**	0.1 M UO_2Cl_2 3.5 M HCl 1 M $FeCl_2$**	0.1 M UO_2Cl_2 4 M HCl
Titan eluent	0.1 M $TiCl_3$ 5 M HCl 1 M $FeCl_2$**	0.1 M $TiCl_3$ 4.5 M HCl 1 M $FeCl_2$**	0.1 M $TiCl_3$ 5 M HCl	0.1 M $TiCl_3$ 3.5 M HCl 1 M $FeCl_2$**	0.1 M $TiCl_3$ 3.5 M HCl 1 M $FeCl_2$**	0.1 M $TiCl_3$ 4 M HCl
Migration distance (cm)	185.9	184.5	100	122.6	2201	93.5
Flow rate (ml/h)	3.08	4.04	3.70	4.05	7.93	12.3
Band velocity (cm/h)	0.68	0.83	0.53	1.09	2.07	2.25

* Previous reported in [1], M: mol/dm^3.
** $FeCl_2$ is a catalyst whose effect on efficiency of separation will be described in another paper.

of hydrochloric acid concentration as shown in Fig. 4 [7, 8]; hence the concentration should be as high as possible at a given temperature. The experimental conditions selected are listed in Table 1.

Chromatography

First four reverse breakthrough experiments were carried out under different temperatures: 30, 50, 70, and 87 °C. The column was packed with the anion exchange resin and conditioned with hydrochloric acid of an appropriate concentration. Uranylchloride solution was then introduced from the top of the column until the effluent became the same as the feed solution. After that the absorbed uranyl ions were eluted containing HCl and $TiCl_3$ reductant. The effluent, which emerged from the column, was collected in small fractions.

Two band displacement experiments were carried out at 70 °C to confirm the constancy of the elementary separation coefficient and accumulation of it with increase of the migration distance. In this case, uranylchloride solution was fed to the column whose resin was equilibrated with $FeCl_3$ solution of an appropriate concentration as shown in Table 1. After forming a uranyl absorption band of a suitable length, the eluent containing $TiCl_3$ reductant was introduced into the column. According to the differences of the redox potentials and the selectivities of the species, the uranium band migrated downward with sharp front and rear boundaries. The effluent from the column was collected in small fractions.

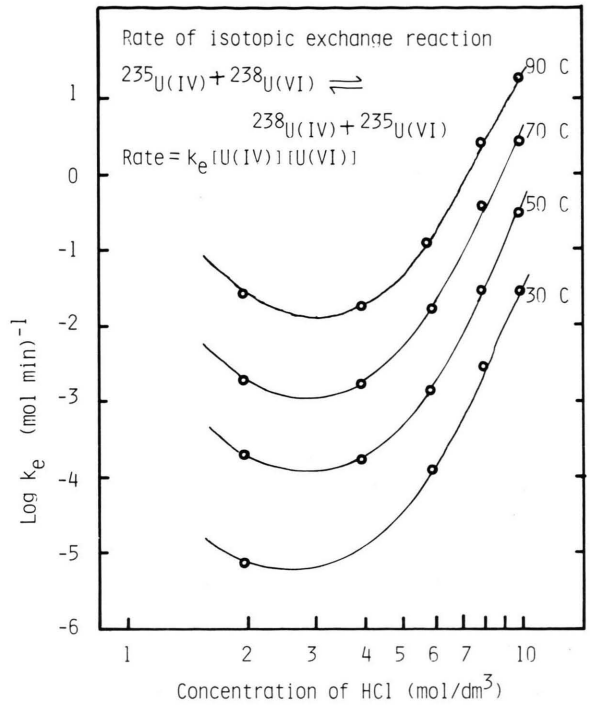

Fig. 4. Rate constant of the electron-exchange reaction as a function of HCl concentrations.

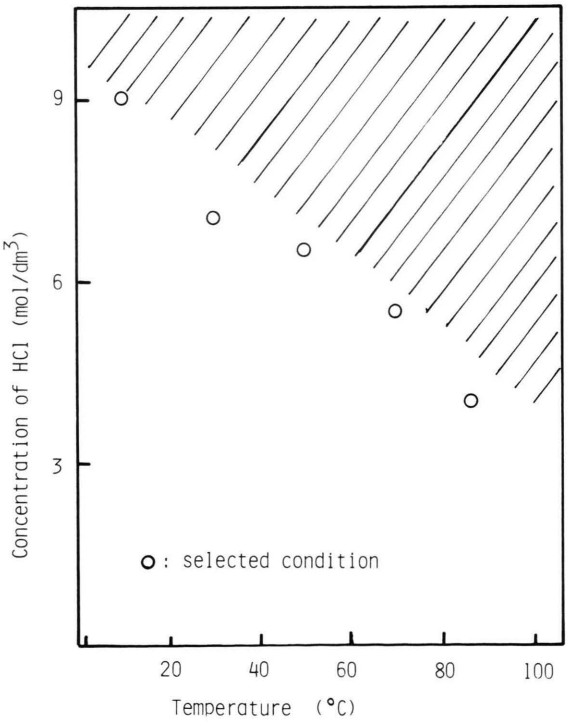

Fig. 3. Selected HCl concentrations for five temperatures. In the shaded area displacement chromatography can not be realized.

Analysis

The uranous content in the sample fractions was determined spectrophotometrically at 650 nm. The total uranium content was determined colorimetrically after the removal of co-existing metalic elements using a small cation exchange resin column. A part of the purified uranium sample was used to determine the uranium isotopic ratio, using a mass spectrometer Model Varian MAT CH-5. The uranyl content was evaluated as the difference between the total uranium and the uranous content.

Results and Discussion

Examples of the analytical results for a reverse breakthrough chromatography and a band displacement chromatography are illustrated in Fig. 5 for Run No. 2 and Fig. 6 for Run No. 5, respectively. A series of reactions took place in these chromatographic processes. At the rear boundary of the uranium band, uranyl ion in the resin phase in reduced to uranous ion by Ti(III) ion in the eluent, and the uranous ion moves downward through the solution phase. At the front boundary, the uranous ion is oxidized to uranyl ion by Fe(III) ion in the resin phase. It forms chloride complex with negative charge and is absorbed in the resin phase again. The reactions are given by following equations:

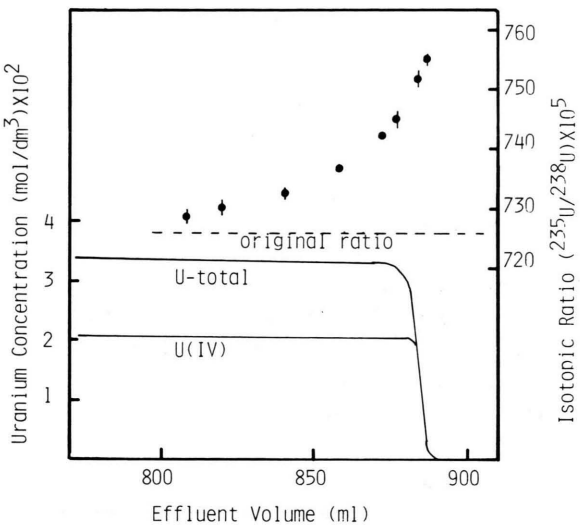

Fig. 5. Analytical results obtained by reverse breakthrough chromatography, Run No. 2.

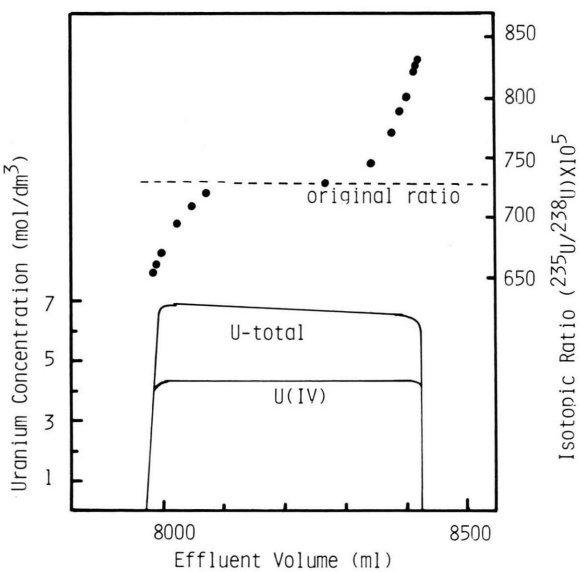

Fig. 6. Analytical results obtained by band displacement chromatography, Run No. 5. Migration length 22 m.

$$\overline{UO_2^{2+}} + 2Ti^{3+} \rightarrow U^{4+} + \overline{2TiO^{2+}} \quad (1)$$

at the rear boundary,

$$U^{4+} + \overline{2Fe^{3+}} + 2H_2O \rightarrow \overline{UO_2^{2+}}\, 2Fe^{2+} + 4H^+ \quad (2)$$

at the front boundary,

where $\overline{}$ represents the species that exist in the resin phase. When uranous ion passed through the uranium band, the following isotope exchange reaction occurred between the uranyl species in the resin phase and the uranous species in the solution phase:

$$^{235}U(IV) + \overline{^{238}U(VI)} = {}^{238}U(IV) + \overline{^{235}U(VI)}. \quad (3)$$

Reactions (1) and (3) took place in the reverse breakthrough chromatography, while in the band displacement migration, reactions (1), (2), and (3) took place. Reactions (1) and (2) should tend toward the right due to differences of the redox potentials and the concentration of the hydrochloric acid selected as mentioned above. Hence, both the reverse breakthrough migration and the band displacement migration were acomplished with satisfactory sharp boundaries as shown in Figs. 5 and 6. The isotopic ratio profiles indicate that the lighter isotope ^{235}U was enriched in the rear part of the uranium band, i.e. the equilibrium constant of the reaction (3) is larger than unity.

As shown in Fig. 6, the band displacement chromatography was successfully realized using Ti(III) and Fe(III). In addition, this band displacement chromatography was maintained stable for long distance migration, with steady accumulation of the elementary isotope effect. For instance, the maximum value of the local separation factor ($[U^{235}U/^{238}U]_l/[^{235}U/^{238}U]_0$) increased from 1.045 for 122.6 cm migration to 1.144 for 2201 cm migration (Run No. 4 and Run No. 5). The separa-

tion factor of 1.44 is remarkably larger than 1.019 obtained for the uranyl-uranylcitrate system by a cation exchange resin column using the same migration length.

Temperature Dependency of the Elementary Separation Coefficient

The elementary separation coefficient ε was calculated from the analytical data with the equation [9]

$$\varepsilon = \sum f_i(R_i - R_0)/(QR_0(1 - R_0)$$

where f_i is the amount of uranium in the i-th sample fraction, Q the total ion exchange capacity of the resin bed, R_i the atomic fraction of ^{235}U in the i-th sample fraction and R_0 the atomic fraction of ^{235}U in the original solution of uranium. The calculated values are listed in Table 2 together with the equilibrium constant K, which will be described later. These values indicate that the elementary separation coefficient in the present temperature region is essentially independent of temperature and the one found by the long migration Run No. 5 almost equals the one bound by the short distance migration Run No. 4. This constancy is an advantage of the present process.

In the present study, the equilibrium constant was determined according to th theory for two phase distribution of isotopes derived by Kakihana and Aida [10]. The separation factor (S) between two equilibrated phases is defined as

$$S = (1 + \varepsilon) = [\overline{^{235}U}][^{238}U]/[^{235}U][\overline{^{238}U}], \quad (4)$$

where the brackets denote the total amounts of the given isotopes. The right hand side of (4) can be expressed in terms of the mole fractions of the complex species and the reduced partition function ratios for the isotopic species. As shown in the previous paper [1], the elementary separation coefficient is given by the following equation in the present case:

$$\varepsilon = (K - 1)(X_{IV} - \overline{X_{IV}}),$$

where K is the equilibrium constant of (3) and X_{IV} and $\overline{X_{IV}}$ are the mole fractions of the uranous species in the solution phase and the resin phase, respectively.

Table 2. Elementary separation coefficient ε and equilibrium constant K.

Run No.	Temperature (°C)	ε	K
1	30	7.8×10^{-4}	1.0013_8
2	50	6.8×10^{-4}	1.0011_3
3	70	7.3×10^{-4}	1.0009_7
4	70	7.2×10^{-4}	1.0010_7
5	70	6.7×10^{-4}	1.0010_4
6	87	7.0×10^{-4}	1.0009_0

In the present experiment, ε is known experimentally, X_{IV} can be estimated from the analytical data and $\overline{X_{IV}}$ can be assumed to be zero with a good approximation. Thus K can be calculated. The results are listed in Table 2. K is plotted vs. the square of the reciprocal temperature in Figure 7. The graph shows a reasonably straight line crossing the zero point. This finding indicates that the temperature dependence of the equilibrium constant of the isotope exchange reaction (3) has been successfully determined.

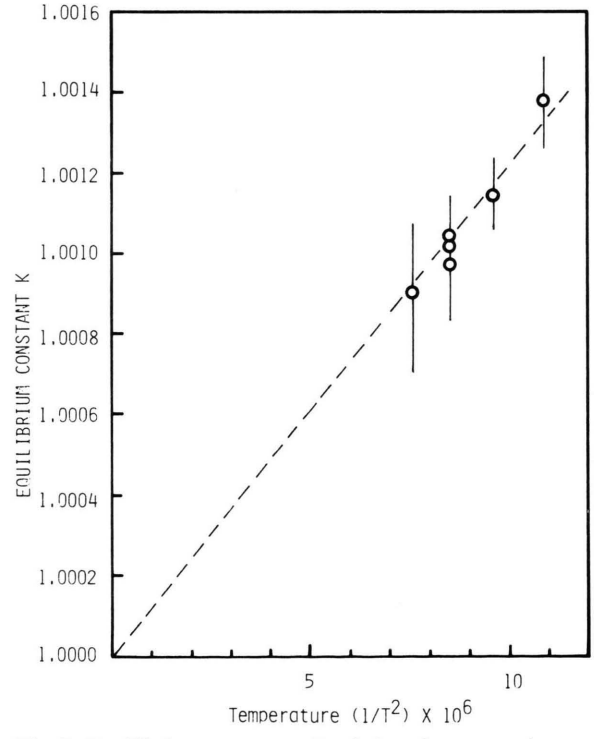

Fig. 7. Equilibrium constant K of the electron-exchange reaction vs. $1/T^2$.

Conclusion

A series of experiments for uranium isotope separation has been carried out using the electron-exchange reaction between U(IV) and U(VI). Both reverse breakthrough and band displacement chromatographies have been accomplished satisfactorily in an anion exchange resin column at different temperatures. The atomic fraction of ^{235}U was increased from its original value 0.007280 to 0.008325 by band displacement chromatography with a 22 m long migration. The elementary separation coefficient was found to be around 7×10^{-4} with no temperature dependency. On the other hand, the equilibrium constant of the electron-exchange reaction calculated from the analytical data varies from 1.0009 to 1.0014 and is proportional to the square of the reciprocal temperature.

[1] J. Fukuda, Y. Fujii, and H. Kakihana, J. Nucl. Sci. Technol. **15,** 745 (1978).
[2] H. Kakihana and Y. Fujii, Genshiryoku Koggo (Nuclear Engineering) **23,** 31 (1977).
[3] J. H. Coates, C. Frèjaques, and J. M. Leart, International Conference on Nuclear Power and Its Fuel Cycle, IAEA-Salzburg 1977, Evolution des procédés de séparation des isotopes de l'uranium en France.
[4] M. Seko, T. Miyake, and K. Takeda, Nippon Genshiryoku Gakkaishi (J. Atom. Energy Soc. Japan) **20,** 547 (1978).
[5] T. Oi, Y. Sakuma, M. Okamoto, and M. Maeda, J. Chromatography **248,** 281 (1982).
[6] E. Akatsu, JAERI-M 7168, Data of Ion Exchange.
[7] K. Gonda, Doctoral Thesis (Tokyo Institute of Technology) 1968.
[8] H. Tomiyasu and H. Fukutomi, Bull. Chem. Soc. Japan **48,** 39 (1975).
[9] H. Kakihana and T. Kanzaki, Bull. Tokyo Institute of Technology **90,** 77 (1969).
[10] H. Kakihana and M. Aida, Bull. Tokyo Institute of Technology **116,** 39 (1973).