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ENRICHMENT OF URANIUM ISOTOPES BY CATION-EXCHANGE CHROMATOGRAPHY OF URANIUM(IV)-MALIC ACID AND -LACTIC ACID COMPLEXES

TAKAO OI, YOICHI SAKUMA and MAKOTO OKAMOTO*

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152 (Japan)

and

MASUNOBU MAEDA

Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466 (Japan)

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SUMMARY

Cation-exchange chromatography was carried out for the systems uranium(IV)-malic and -lactic acid at various temperatures in order to determine the direction of uranium isotope enrichment and the $^{235}\text{U}/^{238}\text{U}$ single-stage separation coefficient, ϵ . Uranium-235 was depleted at the front of the elution curves and enriched at the rear, in contrast to the behaviour found in uranium(VI) systems. The ϵ values for the two systems at a given temperature were consistent with each other. The ϵ value decreased with increasing temperature.

INTRODUCTION

In previous papers^{1,2} we described the $^{235}\text{U}/^{238}\text{U}$ isotope fractionation by cation-exchange chromatography of uranium(IV)-sulphate and -citrate complexes and compared the results with those obtained for uranium(VI) systems³. In both the uranium(IV) systems the depletion of ^{235}U occurred at the front of the elution curves and the enrichment at the rear. This trend was contrary to that found in the uranium(VI) systems. No difference in the single-stage separation coefficient, ϵ (defined by eqn. 4), at a given temperature was observed between the uranium(IV) systems, while in the uranium(VI) systems the ϵ value increased with increasing formation constant of the uranium(VI)-ligand complex. In the uranium(IV)-citric acid system the ϵ value decreased with increasing temperature.

In order to confirm the previous results^{1,2} and to gather more information concerning uranium isotope fractionation in systems involving uranium(IV) complex formation, we have now studied the cation-exchange chromatography of the two systems uranium(IV)-malic acid and -lactic acid, to which sulphuric acid and potassium sulphate are added to reduce the oxidation rate of uranium(IV) and to lower the pH of the eluent.

EXPERIMENTAL

Reagents

The ion-exchange resin was a high porosity, strong acid cation-exchange resin PK-1 (100–200 mesh) supplied by Asahi Chemical Industry. The stock solution of uranium(IV) was prepared by dissolving natural uranium metal (atomic ratio $^{235}\text{U}/^{238}\text{U} = 0.007280 \pm 0.00004$) in concentrated HCl and filtering off the residue. All other reagents used were of analytical grade.

Columns

The columns used were of the same type as that illustrated in ref. 1. They were of pressure-resistant Pyrex glass, (inner diameter, 1 cm; resin bed length, 110 cm) surrounded by a jacket through which thermostatted water was circulated. In chromatographic experiments three columns were connected in series by PTFE tubes having (1 mm I.D.).

Chromatographic procedures

The cation-exchange resin packed in the columns was pre-treated with 2 *M* H_2SO_4 and 1 *M* HCl to convert it completely into the hydrogen form, and then washed thoroughly with distilled water. The first column was charged with a measured volume of uranium(VI) solution to form a band of suitable length (20–50 cm). Chromatography was then carried out by continuously feeding an eluent to the column using a constant-flow-rate peristaltic pump. The displacement rate of the band was kept at about 1 cm/h. The effluent from the bottom of the third column was collected in fractions of about 1.5 ml. The concentration of the uranium(IV) in each fraction was determined by a colorimetric method and the isotopic analysis of uranium was carried out on a Varian Mat CH 5 mass spectrometer³. Prior to the isotopic analysis, sample fractions were pre-treated as follows. Uranium(IV) in the fractions was oxidized to uranium(VI) by addition of concentrated HCl and H_2O_2 , and then passed through an anion-exchange resin column to remove K^+ , SO_4^{2-} , malate and lactate ions. Uranium(VI) chloride eluted from the column was converted into U_3O_8 at around 1050°C. The oxide was then dissolved in concentrated HCl to prepare a sample for mass spectroscopic analysis.

RESULTS AND DISCUSSION

Influence of eluent composition on the displacement process and single-stage separation coefficient

First we attempted to determine the optimum eluent composition for displacement chromatography. Since no data on the complex formation of uranium(IV) with malic and lactic acids are available, it is impossible to estimate the concentrations of the complexes at a given solution composition. However, in view of the complex formation equilibria between uranium(IV) and citric acid and their displacement chromatographic processes achieved successfully in the range pH 1–1.3², it is expected that the equilibria of uranium(IV) with malic and lactic acids would be predominant also in the region pH 1–2, where the displacement chromatography would be performed. Thus, chromatographic experiments were attempted in this pH range

TABLE I

EXPERIMENTAL CONDITIONS AND RESULTS FOR CHROMATOGRAPHY OF URANIUM(IV)-MALIC ACID COMPLEXES

Compositions: load solution, 0.1 M UCl_4 + 0.9 M H_2L + 0.18 M H_2SO_4 ; eluent, 0.8 M H_2L + 0.1 M K_2L + 0.18 M K_2SO_4 . L^{2-} = malate ion.

Run No.	Volume of load solution (ml)	Eluent pH	Observation	$\epsilon \times 10^5$	Illustration
M1	75	0.95	Continuous band broadening		
M2	85	1.36	Displacement chromatography	6.2	Fig. 1
M3	190	1.95	Displacement chromatography	6.1	
M4	230	2.29	Precipitation at rear of band		

by changing the pH of the eluent by addition of HCl, the composition of the eluent being kept constant. The displacements of the uranium bands were about 340 cm in all cases. The temperature of the eluents was maintained at 50°C.

Uranium(IV)-malic acid system. The experimental conditions and results for this system are collected in Table I. In run M1 continuous band broadening occurred during displacement. In runs M2 and M3 relatively clear displacement chromatograms were obtained. As an example, the elution curve for run M2 is shown in Fig. 1. In run M4 precipitation of uranium(IV) was observed at the rear of the uranium(IV) bands.

Uranium(IV)-lactic acid system. The experimental conditions and results for this system are collected in Table II. In run L1 the uranium(IV) band continued to

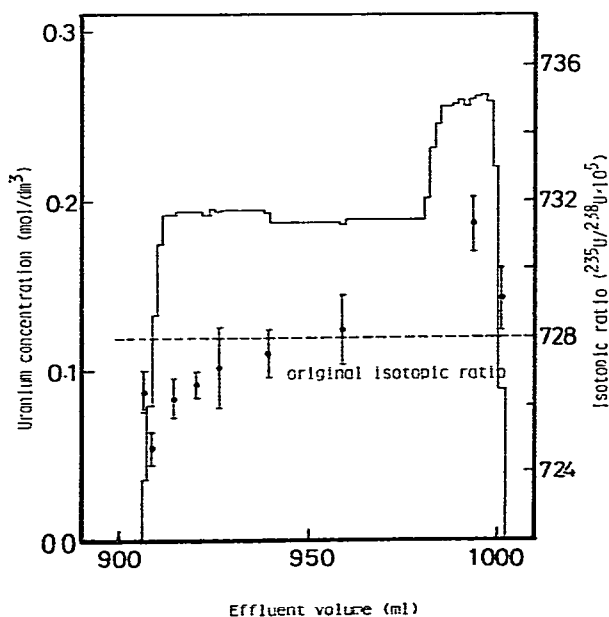


Fig. 1. Elution graph and isotopic ratio for run M2.

TABLE II

EXPERIMENTAL CONDITIONS AND RESULTS FOR CHROMATOGRAPHY OF URANIUM(IV)-LACTIC ACID COMPLEXES

Compositions: load solution, 0.11 M UCl₄ + 1.5 M HL + 0.1 M H₂SO₄; eluent, 1.3 M HL + 0.2 M KL + 0.1 M KL + 0.1 M K₂SO₄. L⁻ = lactate ion.

Run No.	Volume of load solution (ml)	Eluent pH	Observation	$\varepsilon \times 10^5$	Illustration
L1	40	0.95	Continuous band broadening		
L2	55	1.37	Displacement chromatography	7.2	
L3	60	1.70	Displacement chromatography	6.7	
L4	75	2.09	Displacement chromatography	6.3	Fig. 2
L5	110	2.87	Poor shaped chromatogram		

spread on displacement. In runs L2–L4 sharp boundaries were observed at both the front and the rear of the elution curves. As an example, the chromatogram for run L4 is illustrated in Fig. 2. In run L5 the elution curve, which showed sharp boundaries at both ends, was of poor shape.

The above results suggest that displacement chromatography is feasible around pH 1.3–2.1 in both systems, as far as the present eluent compositions are concerned. This means that the pH range which permits displacement chromatography is wider in the present two systems than in the uranium(IV)-citric acid system

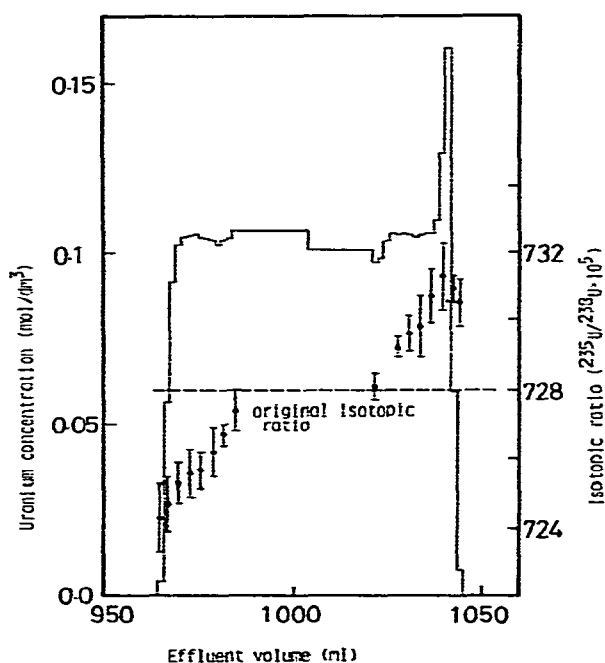
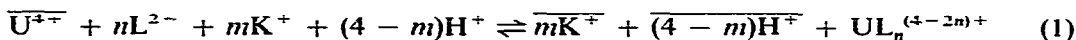


Fig. 2. Elution graph and isotopic ratio for run L4.

(pH 1–1.3)² and may partly be ascribed to the difference in complex formation equilibria.

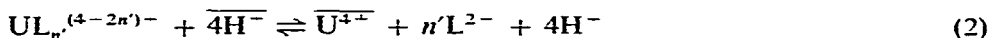
The reactions which occur in the ion-exchange column may be described as follows.

(a) At the rear boundary of the uranium(IV) band, uranium(IV) adsorbed in the resin phase is desorbed by complex formation with malate(lactate) ions in the external solution, and this desorption is accompanied by adsorption of K^+ and H^+ by the resin phase, which may be expressed by



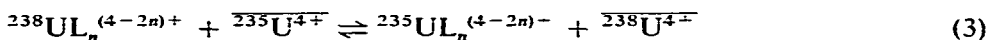
where L^{2-} denotes malate ion and the horizontal bar the resin phase.

(b) At the frontal boundary of the uranium band, uranium(IV) malate(lactate) complexes in the external solution are dissociated into uranium(IV) and less-malate(lactate)coordinated uranium(IV) species by the presence of hydrogen ions desorbed from the resin, and then these species are adsorbed by the resin, as is expressed by:



When the two reactions 1 and 2 tend to proceed to the right (which depends on the composition and the pH of the eluent), the uranium band will migrate down the column to the bottom with sharp boundaries at both edges of the band, as is shown in Figs. 1 and 2.

(c) Between the uranium(IV) malate(lactate) complexes in the external solution and the species in the resin phase, an isotopic exchange reaction occurs, which is expressed by:



The results of the isotopic analysis for the successful runs in both systems are shown in Figs. 1 and 2 as examples. It is clear that in each case ^{238}U is enriched at the front of the band, while ^{235}U is preferentially accumulated at the rear. This was also true in other runs which are not illustrated, and is consistent with results obtained in the uranium(IV)–sulphate and –citrate systems^{1,2}. However, it is contrary to the behaviour found in uranium(VI) complex formation systems³. The difference has been theoretically predicted by Kakihana⁴.

The single-stage separation coefficient, ε , is defined by

$$\varepsilon = S - 1 = \frac{[\overline{^{235}U}][^{238}U]}{[^{235}U][\overline{^{238}U}]} - 1 \quad (4)$$

where S is the single-stage separation factor, $[\quad]$ denotes the concentration of isotopes in the aqueous phase and $[\overline{\quad}]$ that in the resin phase. The separation coefficient ε can be calculated from the chromatographic data by means of the following equation⁵

$$\varepsilon = \frac{\sum f_i (R_i - R_0)}{QR_0 (1 - R_0)} \quad (5)$$

where f_i is the amount of uranium in the i th fraction, R_0 the original atomic fraction of ^{235}U , R_i the atomic fraction of ^{235}U in the i th fraction and Q the total exchange capacity of the resin bed. The ε values thus calculated are summarized in Tables I and II. It is apparent that the ε values in the malic acid system are in good agreement with each other, *i.e.*, the separation coefficient is little affected by the limited change of eluent composition in the present work. In the lactic acid system it seems that ε increases with decreasing pH, but the differences are within the experimental uncertainties. The separation coefficients $\varepsilon \approx 6 \times 10^{-5}$ at 50°C in the malic and lactic acid systems agree with those reported in the uranium(IV)–sulphate system ($\varepsilon = 5 \times 10^{-5}$ at 40°C)¹ and the uranium(IV)–citric acid system ($\varepsilon = 6 \times 10^{-5}$ at 50°C)². Thus, in contrast to uranium(VI) systems, any difference in ε among the four systems due to the difference in formation constants is not observed in the uranium(IV) systems. The separation coefficients estimated in the uranium(IV) systems are smaller than those reported for uranium(VI) systems and for electron exchange reactions between U(IV) and U(VI)⁶: they are about two thirds of those in the former systems and less than one tenth of those in the latter.

Influence of temperature on the single-stage separation coefficient

Chromatographic experiments were carried out at different temperatures with the compositions and the pH of the eluents fixed at the values for runs M2 and L3. The operating temperatures are listed in Table III. A clear displacement chromatogram was obtained in each run. Only the chromatograms at 11°C for both systems are exemplified in Figs. 3 and 4. The elution curves were influenced by the operating temperature, *i.e.*, the uranium concentrations of the effluent fractions decreased with increasing temperature. This may be mainly the result of a shift in the uranium(IV)–malate(lactate) complex formation equilibrium with temperature.

The isotopic analysis of the effluents showed that ^{235}U is depleted at the front of the bands and enriched at the rear in all the runs, the results at 11°C being illustrated in Figs. 3 and 4. This observation is in accord with that at 50°C described in the previous section. In conclusion, the direction of uranium isotope enrichment in the elution curve is not affected by a change in operating temperature.

The single-stage separation coefficients, ε , for all the runs were calculated

TABLE III

ε VALUES FOR CHROMATOGRAPHY OF URANIUM(IV)-MALIC ACID, -LACTIC ACID AND -CITRIC ACID COMPLEXES AT DIFFERENT TEMPERATURES

Temperature ($^\circ\text{C}$)	$\varepsilon \times 10^5$		
	Malic acid	Lactic acid	Citric acid
11	11.2	12.0	10.5
30	8.3	8.2	6.6
50	6.2	6.7	5.2
70	4.5	4.6	4.1

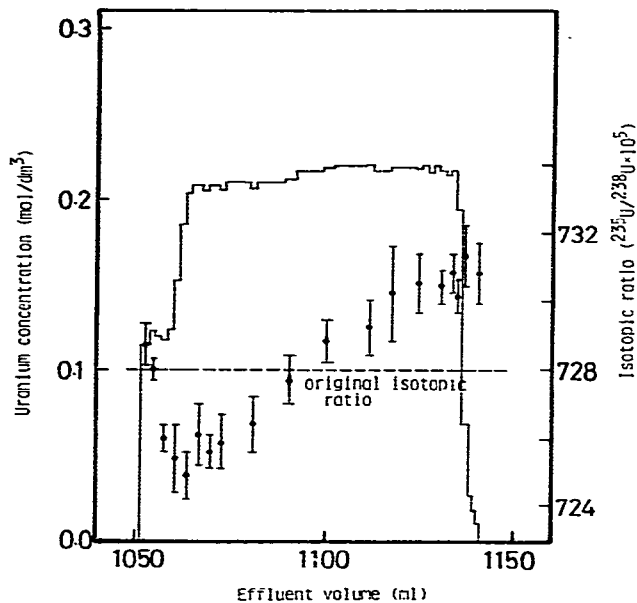


Fig. 3. Elution graph and isotopic ratio for malic acid system at 11°C.

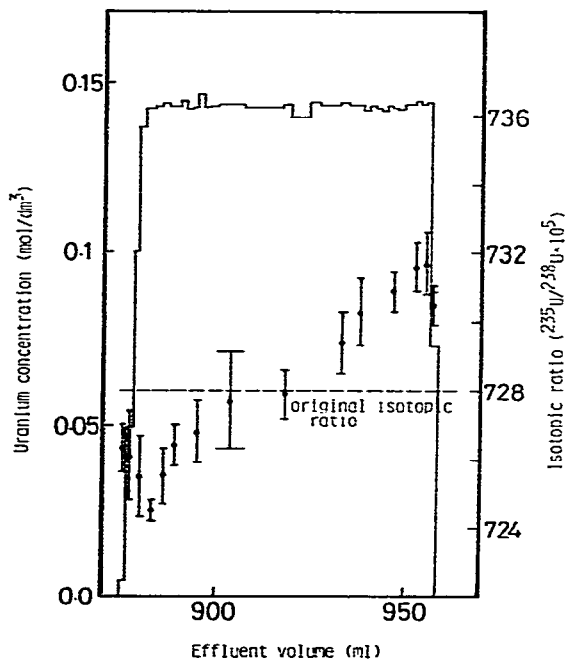


Fig. 4. Elution graph and isotopic ratio for lactic acid system at 11°C.

as described in the previous section and are collected for both systems in Table III, together with values reported for the uranium(IV)–citric acid system². It is obvious that ϵ decreases with increasing operating temperature. This trend is as predicted by the thermodynamical theory of isotope effects⁷, although no exact and quantitative interpretation is possible because the complex formation equilibria should be dependent on the operating temperature. It may be said that the ϵ values at a given temperature are little affected by the ligands, although the values for the citric acid system are the smallest among the three systems.

CONCLUSIONS

(1) Displacement chromatography in the uranium(IV)–malic acid and –lactic acid systems is feasible in a limited pH region, 1.3–2.1 with the present eluent compositions (see Tables I and II).

(2) Uranium-235 is depleted at the front of the chromatogram and enriched at the rear. This is contrary to the behaviour in uranium(VI) complex formation systems.

(3) The single-stage separation coefficient, ϵ , is little affected by the change of eluent composition at a given temperature. Its value is about 6×10^{-5} .

(4) The ϵ values in the present systems are much smaller than those reported for uranium(VI) complexation and for electron exchange reactions between U(IV) and U(VI).

(5) The ϵ value decreases with increasing temperature.

(6) Within the experimental uncertainties, the ϵ values at a given temperature are internally consistent within the uranium(IV)–citric acid, –malic acid and –lactic acid systems.

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