

CHROM. 17 575

ZIRCONIUM ISOTOPE SEPARATION BY MEANS OF CATION-EXCHANGE CHROMATOGRAPHY

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(Received January 18th, 1985)

SUMMARY

The separation of zirconium isotopes has been studied by means of cation-exchange chromatography using zirconium–triammonium citrate and zirconium–diammonium citrate systems. Small but appreciable isotope fractionations were observed in both systems. In the former system, the lightest isotope ^{90}Zr was enriched at the rear part of the zirconium band, while in the latter case ^{90}Zr was depleted at the rear part. The elemental separation coefficients, ϵ , were around $1 \cdot 10^{-6}$ for the zirconium–triammonium citrate systems and around $-0.5 \cdot 10^{-6}$ for the zirconium–diammonium citrate systems. The isotope effect is discussed in terms of the hydrolysis of the zirconium species.

INTRODUCTION

Zirconium has been used as a cladding and a core component in nuclear reactors because of its low thermal neutron capture cross-section. It has five stable isotopes, ^{90}Zr (51.45), ^{91}Zr (11.23), ^{92}Zr (17.15), ^{94}Zr (17.38) and ^{96}Zr (2.80), where the numbers in parentheses are the percentage abundances^{1,2}. Among these, ^{90}Zr is the most important isotope. Its thermal neutron capture cross-section has been estimated to be 0.032 barns², but Smith³ reported a value of 0.0144 barns in 1979. The latter value indicates that enrichment of ^{90}Zr can provide an effective improvement in the neutron economy of nuclear reactors. Thus, the introduction of the enriched ^{90}Zr (over 90%) would not only conserve uranium supplies but also improve the lifetime of pressure tubes.

So far, the physical isotope separation processes, such as gaseous diffusion and ultracentrifugation, are not applicable to zirconium isotope separation, since no suitable gaseous zirconium compounds are available. In the present work, the separation of zirconium isotopes was investigated by a chemical process, ion-exchange chromatography, and the elemental separation coefficient for ^{90}Zr has been determined.

EXPERIMENTAL

Ion-exchange resin, equipment and reagents

A strongly acidic cation-exchange resin LS-6 (100–200 mesh) of highly porous type (Asahi Chemical Industry) was packed into a pressure-resistant Pyrex glass column (420 × 1 cm I.D.) having a jacket through which water was circulated for temperature control. The resin was converted into the hydrogen form by passing hydrochloric acid solution (*ca.* 2 mol/dm³) and the height of the resin bed was *ca.* 400 cm. The solutions were introduced into the column at a constant flow-rate using a single-plunger pump. The stock solution of zirconium was prepared by dissolving zirconyl chloride in water. Perchloric acid was added to prevent hydrolysis. All reagents used were of analytical grade.

Reverse breakthrough chromatography

Prior to the separation of zirconium isotopes, a series of preliminary experiments was carried out to determine the appropriate conditions, such as the nature, concentration and pH of the eluent, which enable a displacement reverse breakthrough chromatography with a sharp boundary.

On the basis of the results from these experiments, the conditions chosen were as follows: eluent, 0.1 mol/dm³ triammonium citrate or diammonium citrate, pH *ca.* 8. The resin bed was fed with 0.3 mol/dm³ zirconyl chloride solution to convert the resin into a zirconium form. After washing the bed with water, reverse breakthrough chromatography was carried out with the 0.1 mol/dm³ aqueous solution of triammonium citrate or diammonium citrate adjusted to pH *ca.* 8 with ammonium hydroxide. The effluent was collected in small fractions. Three chromatographic analyses were performed at 10, 25 and 40°C for the zirconium–triammonium citrate system, and two at 10 and 25°C for the zirconium–diammonium citrate system.

Analysis

The pH and the zirconium concentration were measured for each fraction using a pH meter and an inductively coupled plasma spectrophotometer (Shimazu, Model ICPS 50S), respectively. The proportions of the zirconium isotopes in each fraction were measured by a mass spectrometer (Varian MAT, Model CH-5) using a surface ionization technique, after the conversion of all zirconium species to zirconium sulphate. The details of these measurements have been described¹.

RESULTS AND DISCUSSION

The chromatograms obtained are illustrated in Figs. 1–5 and the experimental conditions are summarized in Table I. In these five analyses, three for the zirconium–triammonium citrate system and two for the zirconium–diammonium citrate system, almost the same values of the concentration and eluent pH were employed, while the temperature was varied.

At the rear portion of the chromatograms, displacement chromatography was realized except in No. 3 (Fig. 3). The tailing observed in the latter may arise from the instability of triammonium citrate at the relatively high temperature of 40°C. The chromatography of the diammonium citrate system at 40°C was unsuccessful, due to the instability of diammonium citrate.

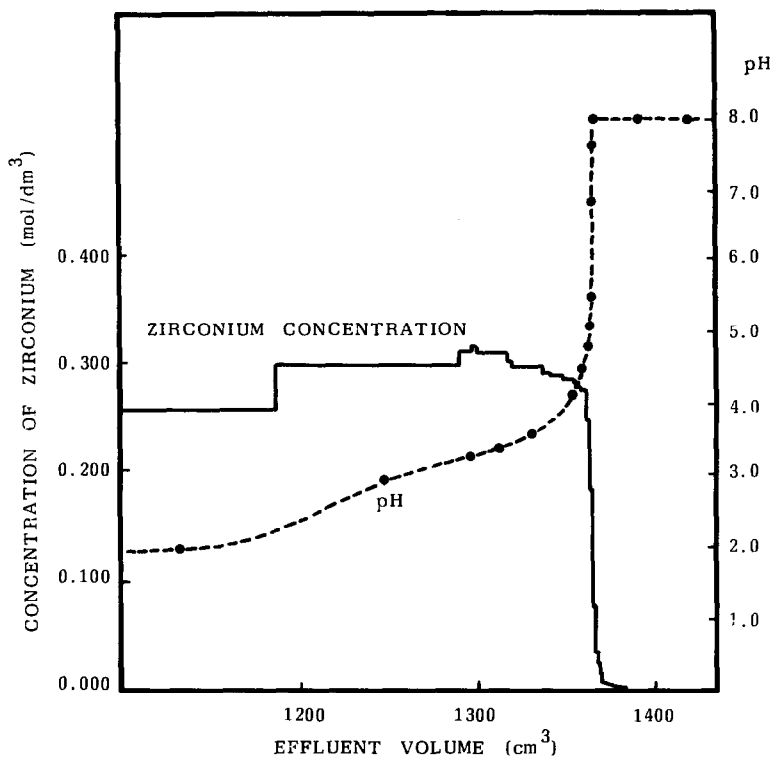
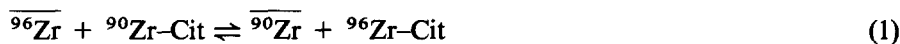


Fig. 1. Chromatogram (1) for zirconium-triammonium citrate system. Flow-rate: 6 ml/h. Temperature: 10°C.

The zirconium isotopic ratios were measured for all of the five isotopes and the $^{96}\text{Zr}/^{90}\text{Zr}$ ratios are plotted in Figs. 6–10. The isotopic ratios obtained from the triammonium citrate system, experiments 1–3, and those from the diammonium citrate system, experiments 4 and 5, are shown in Figs. 6–8 and 9, 10, respectively. The deviations of the isotopic ratios from the original ratio are small but evident in every case. In the case of diammonium citrate, the lighter isotope ^{90}Zr was depleted at the rear part of the zirconium band, while in the case of triammonium citrate, ^{90}Zr was enriched at the rear part of the band.

The isotopic exchange reaction taking place between the zirconium species in the resin phase and in the external solution phase can be expressed generally as



where the bar represents the zirconium species in the resin phase, and Zr-Cit the zirconium citrate complex existing in the external solution phase. The experimental results indicate that in the triammonium citrate system the heavier isotope ^{96}Zr was preferentially retained in the zirconium citrate complex in the external solution phase, while in the diammonium citrate system the lighter isotope ^{90}Zr was enriched in the zirconium citrate complex in the solution phase. In other words, the equilibrium constant of the above isotopic exchange reaction is larger than unity in the case of

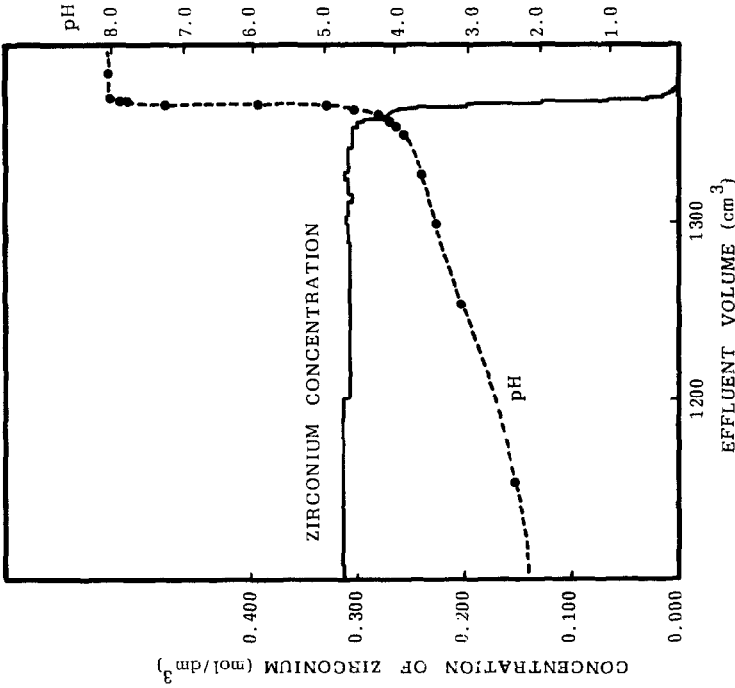


Fig. 2. Chromatogram (2) for zirconium-triammonium citrate system. Flow-rate: 4 ml/h. Temperature: 25°C.

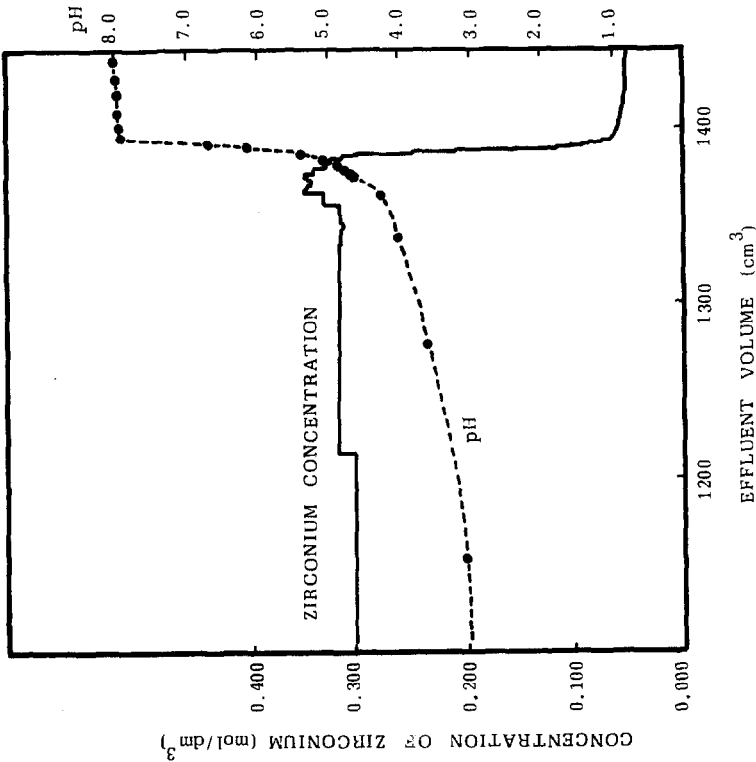


Fig. 3. Chromatogram (3) for zirconium-triammonium citrate system. Flow-rate: 6 ml/h. Temperature: 40°C.

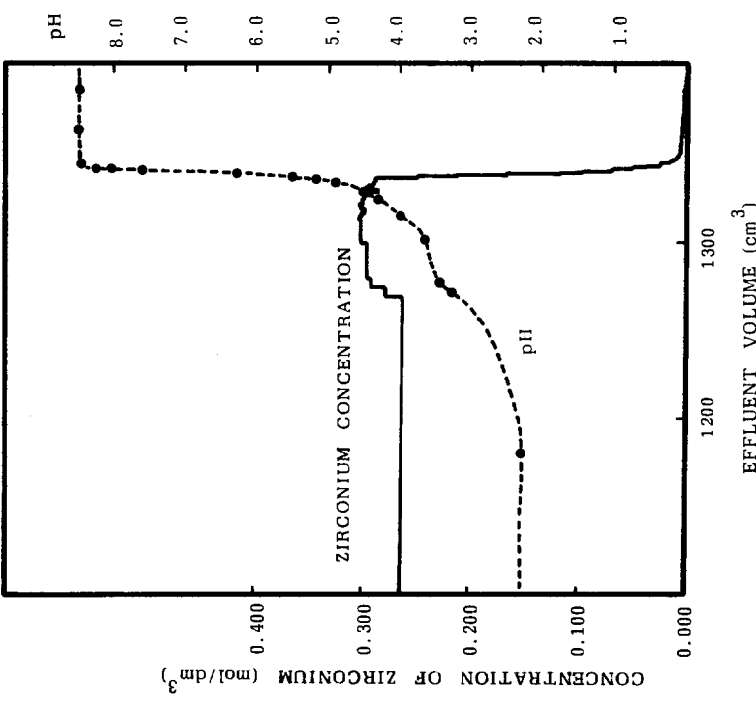
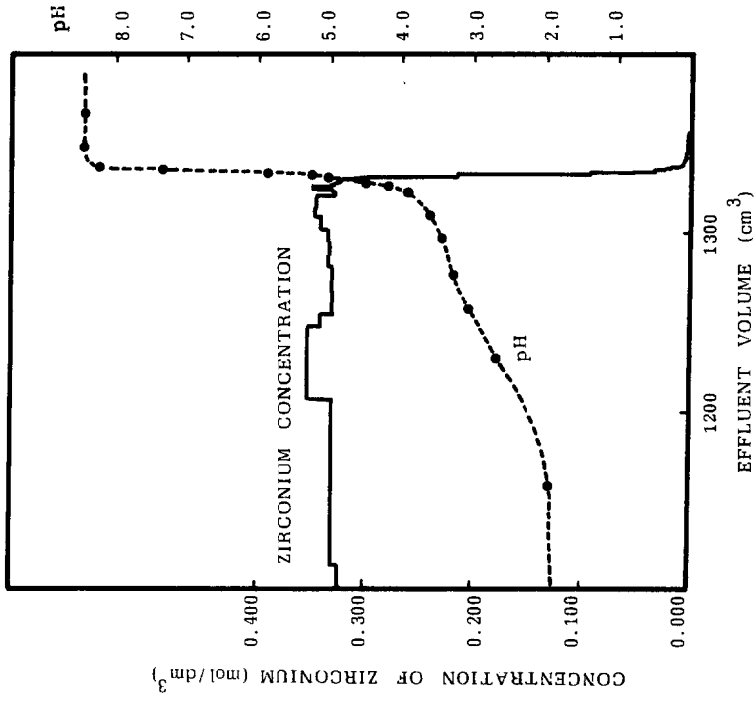


Fig. 4. Chromatogram (4) for zirconium-diammonium citrate system. Conditions as in Fig. 1.

Fig. 5. Chromatogram (5) for zirconium-diammonium citrate system. Flow-rate: 6 ml/h. Temperature: 25°C.

TABLE I

EXPERIMENTAL CONDITIONS FOR REVERSE BREAKTHROUGH CHROMATOGRAPHY ON LS-6 CATION-EXCHANGE RESIN

	<i>Experiment</i>				
	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>
Bed height (H ⁺ , cm)	411	400	400	400	431
Eluent	Triammonium citrate, 0.1 mol/dm ³ , aqueous solution			Diammonium citrate, 0.1 mol/dm ³ , aqueous solution	
pH of eluent	8.1	8.1	8.2	8.5	8.45
Eluent flow-rate (ml/h)	6.0	4.0	6.0	6.0	6.0
Temperature (°C)	10	25	40	10	25

the triammonium citrate system, but smaller than unity in the case of the diammonium citrate system.

The most interesting and important point is that the direction of enrichment of the zirconium isotopes is opposite in the two systems. The influence of the temperature on the magnitude and direction of the isotope effect was not significant under the present experimental conditions.

The isotope effect was evaluated as the elemental separation coefficient, ε , defined as

$$\varepsilon = s - 1 = \frac{[\text{}^{90}\text{Zr}][\text{}^{91-96}\text{Zr}]}{[\text{}^{90}\text{Zr}][\text{}^{91-96}\text{Zr}]} \quad (2)$$

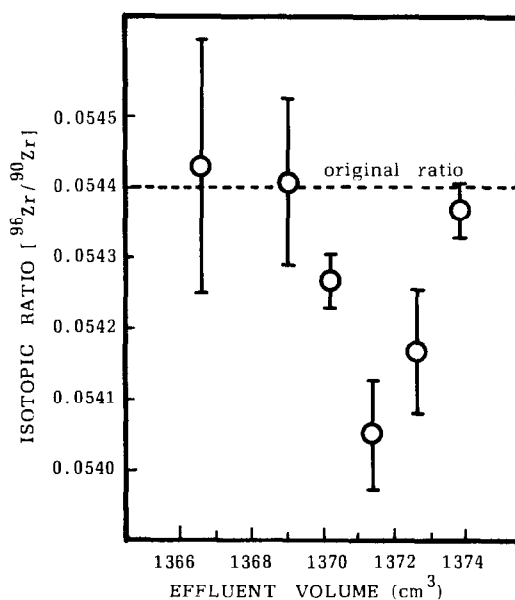


Fig. 6. Isotopic ratio ${}^{96}\text{Zr}/{}^{90}\text{Zr}$ obtained from the chromatogram in Fig 1. The 95% confidence limits are indicated.

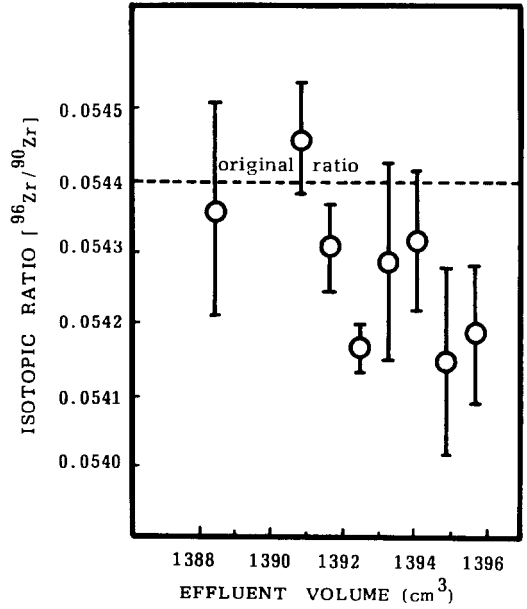
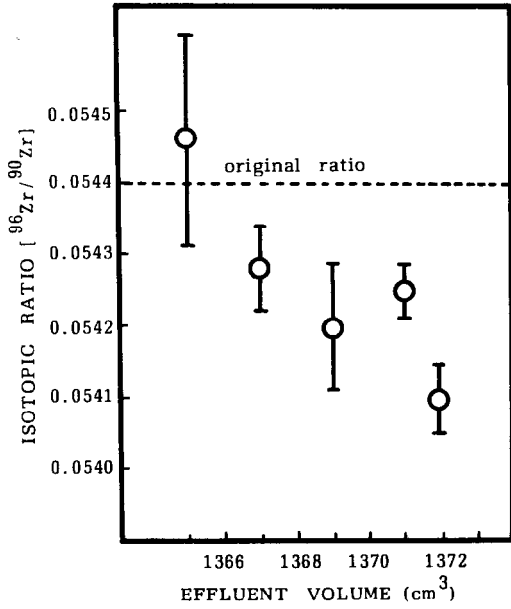


Fig. 7. Isotopic ratio ⁹⁶Zr/⁹⁰Zr obtained from the chromatogram of Fig. 2. Details as in Fig. 6.

Fig. 8. Isotopic ratio ⁹⁶Zr/⁹⁰Zr obtained from the chromatogram of Fig. 3. Details as in Fig. 6.

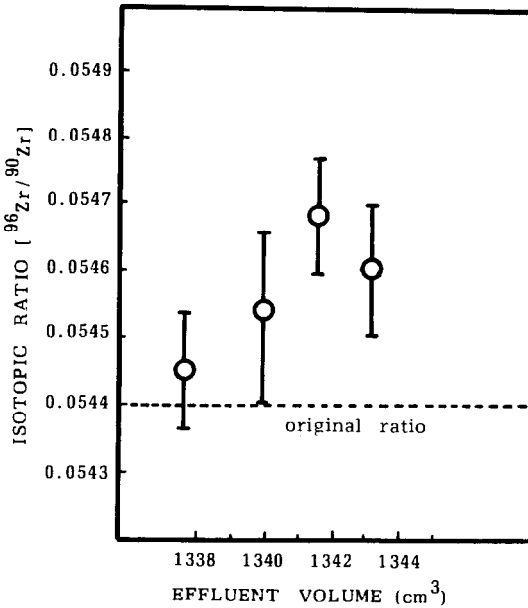


Fig. 9. Isotopic ratio ⁹⁶Zr/⁹⁰Zr obtained from the chromatogram of Fig. 4. Details as in Fig. 6.

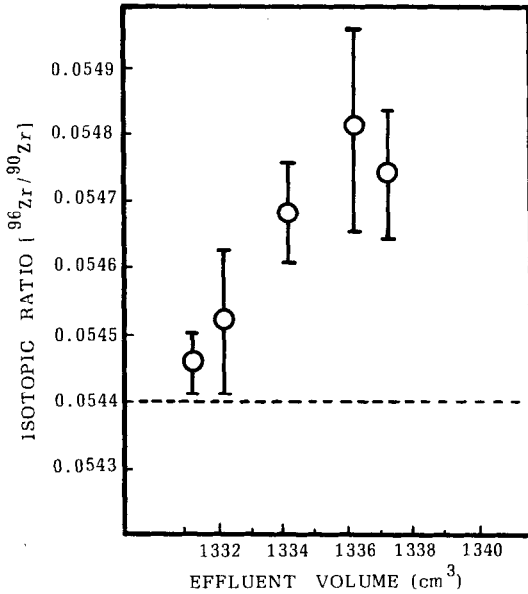


Fig. 10. Isotopic ratio $^{96}\text{Zr}/^{90}\text{Zr}$ obtained from the chromatogram of Fig. 5. Details as in Fig. 6.

where s is the single-stage separation factor, $[]$ denotes the concentration of the isotopes in the solution phase and $\overline{[]}$ the concentration of the isotopes in the resin phase. The elemental separation coefficient was calculated from the analytical data using the following equation^{4,5}

$$\varepsilon = \frac{\sum f_i (R_i - R_0)}{Q R_0 (1 - R_0)} \quad (3)$$

where f_i is the amount of zirconium in the i th fraction, R_0 the original atomic fraction of ^{90}Zr , R_i the atomic fraction of ^{90}Zr in the i th fraction and Q the total exchange capacity of the resin bed. Table II tests the values of ε thus calculated. The values are much smaller than those for the uranium isotopes obtained by similar ion-exchange chromatographic processes using uranyl or uranous complex-formation re-

TABLE II
ELEMENTAL SEPARATION COEFFICIENTS, ε

Experiment No.	ε	Temperature ($^{\circ}\text{C}$)
1	$9.5 \cdot 10^{-7}$	10
2	$1.6 \cdot 10^{-6}$	25
3	$8.7 \cdot 10^{-7}$	40
4	$-4.6 \cdot 10^{-7}$	10
5	$-4.5 \cdot 10^{-7}$	25

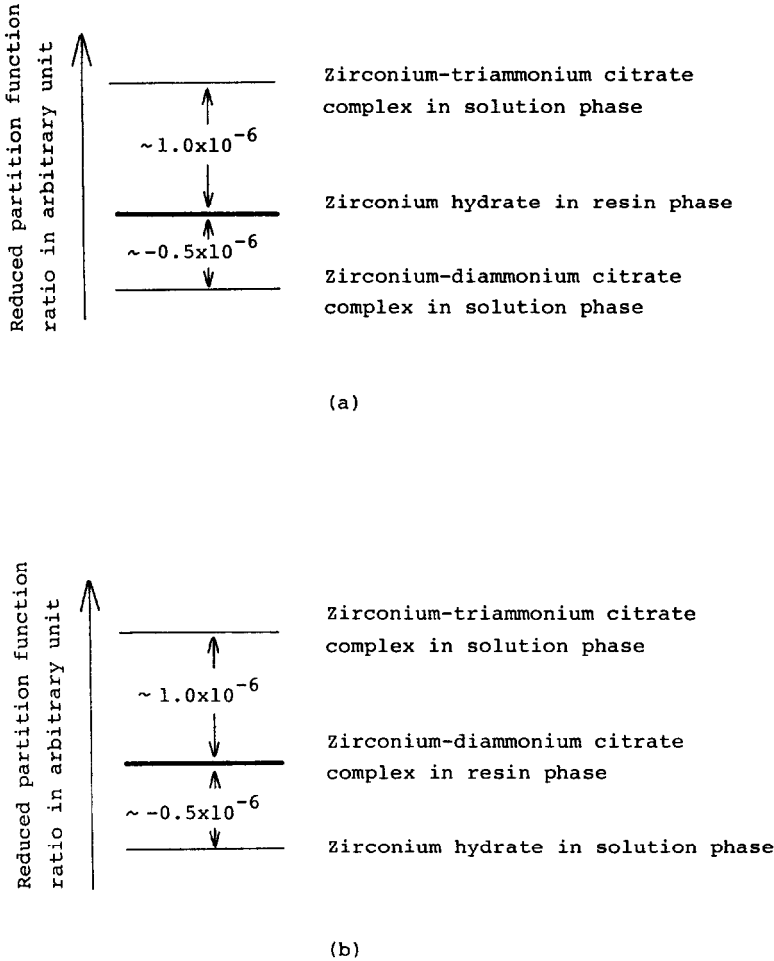


Fig. 11. The relationships between reduced partition function ratios and the elemental separation coefficients.

actions⁶⁻⁹. The negative sign for the diammonium citrate system originates from the definition of eqn. 3, as expected from the experimental results.

The isotope effect is caused by the difference between the reduced partition function ratios of the species distributed in the two phases, *i.e.*, the resin phase and the external solution phase in the present case. Its magnitude, in terms of the elemental separation coefficient, can be expressed as a function of the reduced partition function ratios and the mole fractions of the species^{10,11}

$$\epsilon = s - 1 = \Sigma \Sigma f_n X_n - \Sigma \Sigma \bar{f}_m \bar{X}_m \tag{4}$$

where f_n, \bar{f}_m represent the reduced partition function ratios of the concerned species in the external solution phase and the resin phase, and X_n, \bar{X}_m the corresponding

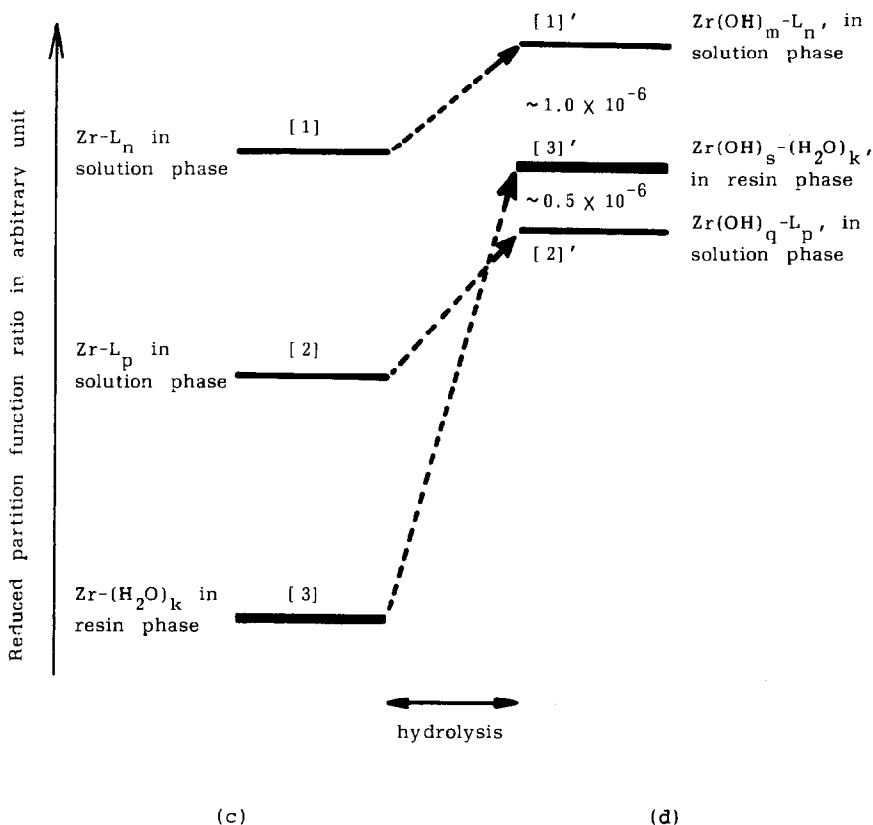


Fig. 12. The relationships between reduced partition function ratios and the elemental separation coefficients, without (c) with hydrolysis (d).

mole fractions of these species. To simplify the discussion, it is assumed for the present zirconium systems that each phase contains only one kind of species. This may be a good approximation in some chromatographic separation processes^{5,10-13}.

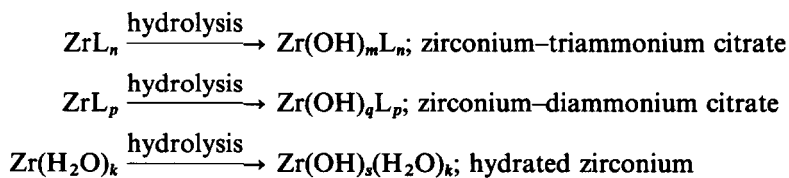
Under this assumption, the mole fractions are unity, and thus the elemental separation coefficient is considered to be the difference between the reduced partition function ratios of the species. In order to interpret the inversion of the direction of the isotope effect, we propose three possible cases for the sequence of the reduced partition function ratio as shown in Fig. 11a and b, and Fig. 12d.

In the first two proposed cases (Fig. 11a and b), the centre levels exhibit reference states for the isotope effect. Case a in Fig. 11 would be possible if the direction of the isotope effect could be physico-chemically reversed between the zirconium-triammonium citrate complex and the zirconium-diammonium citrate complex. This condition is, however, hardly expected in the light of many experimental and theoretical studies on isotope separations using complex-formation reactions⁵⁻²⁰; the reduced partition function ratio is generally shifted to the same direction on complex formation. Thus the case a is not reasonable. Case b in Fig. 11 would be acceptable only when the zirconium-diammonium citrate complex is in the resin

phase, not in the external solution phase. Consequently, this case is also not possible. The third case is illustrated in Fig. 12. Without hydrolysis of the zirconium species, the relationship between the reduced partition function ratios may be as in case c. Here the isotope effects correspond to the differences between the levels, e.g., [3] – [1] for the zirconium–triammonium citrate system and [3] – [2] for the zirconium–diammonium citrate system. This case is most likely when the previous reports on uranium isotope effects found in the uranyl–acetate system and others are considered^{9,17,19,20}. However, it cannot explain the present inversion of the direction of the zirconium isotope effect.

Zirconium, is generally considered to be hydrolyzed in aqueous solutions. Upon hydrolysis, the levels of the reduced partition function ratios in case c in Fig. 12 should be shifted upward as in d. The magnitudes of the shifts for the two zirconium citrate complexes seem to be comparable and smaller than the shift for the hydrated zirconium ion.

The natures of the three zirconium species become similar upon hydrolysis



where L represents the citrate ligand and the subscripts the number of ligands coordinated. The intervals between the levels become smaller as the result of the formation of the hydrolyzed species and this mechanism can lead to the unexpected small isotope effect found in the present study. According to the present experimental results, the relationship between the reduced partition function ratios can be understood in terms of the case d in Fig. 12. The level appropriate to the hydrolyzed species of the hydrated zirconium ion should be placed between those of the other two zirconium citrate species.

On the basis of the above hypotheses, the very small isotope effect and the change in direction of the isotope effect can be explained. To date, we have very little information on the chemistry of zirconium, especially in aqueous solutions. Thus further investigations should be carried out including some spectrometric measurements of zirconium species in the aqueous phase.

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