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Anion Exchange Separation of Hard Acid-metals Using HF-H_3BO_3 Media

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The properties of HF–H_3BO_3 media and the distribution coefficients of eighteen metals have been investigated to achieve the separation of hard acid-metals by the anion exchange method. As the addition of boric acid to hydrofluoric acid solution reduces the free fluoride ion concentration to about one hundredth, it is possible to control the formation of metal fluoride complexes in a way favorable for the separation. The BF_4^- and BF_3OH^- produced in this media are adsorbed strongly to the resin and reduce the relative adsorbabilities of metal fluoride complexes remarkably. Using these properties of HF–H_3BO_3 media and the adsorbabilities of other anions, a new anion exchange method for the separation of hard acid-metals has been proposed. The new method is especially useful for the separation of titanium, zirconium, niobium, and tantalum. Distribution coefficients and elution behaviors of metal ions are not affected by the increase of the amount of metals because of the buffer action relating to the fluoride ion in HF–H_3BO_3 media.

Most ion exchange separations of hard acid-metals[1] such as titanium, zirconium, niobium, tantalum, tungsten, molybdenum, and tin have been done using anion exchange resins[2] (unless otherwise devised[3]), because these metals are easily hydrolysed in the absence of complexing agents and tend to form stable anion complexes in the presence of complexing agents.

As anion complexes of these metals have similar chemical properties, the separation of these metals is not easy, and many efforts have been attempted.[4–13] The following three points are considered to be essential for the satisfactory separation:

(1) Select a proper complexing agent forming metal complexes whose chemical properties depend on the kind of metals.

(2) Choose coexisting anions and their concentrations to control the relative adsorbabilities of metal anionic complexes on the resin.

(3) Control the concentration of complexing agents, to adjust the stage of complex formation.

As for point (1), such complexing agents as fluoride,[14,15] oxalate,[11–13] and thiocyanate[16–18] have been investigated. Fluoride has been most frequently adopted in the practical separations of hard acid-metals, probably because the stability constants of fluoride complexes depend on the kind of metals most strongly. Even in hydrofluoric acid (more than 0.1 M, 1 M=1 mol dm^{-3}), however, sufficient separation is not expected unless other anions are present, since the difference in the adsorbabilities of fluoride complexes on a fluoride-form resin are not large enough.[14]

As for point (2), such a mixed solvent as HF-HCl[4–7] or HF–HNO_3[8–10] has been proposed for the separation of hard acid-metals. The adsorbability of a chloride or nitrate ion on the anion exchange resin is much stronger than that of fluoride ion. With the strong adsorbability of chloride or nitrate, the relative adsorbabilities of metal fluoride complexes are weakened and the separation of hard acid-metals becomes possible.

As for point (3), Kraus *et al.*[19] controlled the stage of chloride complex formation by adjusting the concentration of hydrochloric acid suitably and proposed the anion exchange separation of transition metals (including a few hard acid-metals).

If one would apply point (3) to the separation of hard acid-metals in the media containing fluoride ions, the concentration of fluoride ion must be kept fairly low and constant, because these metals form fully fluorinated complexes such as ZrF_6^{2-} and TiF_6^{2-} in hydrofluoric acid more than 0.1 M. In solutions which contain fluoride ion in less than 10^{-4} M, partially fluorinated complexes such as ZrF_5^- and TiF_4 are expected to form.[3]

In hydrofluoric acid solution or HF-HCl and HF–HNO_3 mixtures, however, it is not easy to maintain the fluoride ion concentration low and constant all through the procedures, since fluoride ions may be consumed by the relatively large amounts of metal ions or supplied from metal fluoride complexes adsorbed on the resin and fluoride-form resin.

The author reported in a previous paper[3] that the fluoride ion concentration can be kept low (10^{-4} to 10^{-5} M) in HF–H_3BO_3 media according to the formation of fluoroboric acids, though the concentration of hydrofluoric acid is rather high (more than 0.1 M). In the media, the fluoride ion concentration is kept constant by the buffer action based on the dissociation of fluoroboric acids even when large amounts of metal ions are present.

In the present paper, the separation of hard acid-metals is discussed in HF–H_3BO_3 media in relation to the above mentioned properties of HF–H_3BO_3 media and the adsorbabilities of coexisting anions, while referring to points (2) and (3).

Experimental

Chemicals and Apparatus. Standard solutions of metal ions were prepared by the procedures mentioned in the previous paper.[3] Other chemicals and apparatus were also the same as used previously.

Ion Exchange Resin. A strongly basic anion exchange resin, Diaion SA ♯ 100, product of Mitsubishi Chemical Ind. Ltd. (8% DVB, 75 to 150 μm, Cl^--form) was used. After washing the resin in a column with five times volume of 3 M HNO_3 and with distilled water untill the effluent was free from nitrate ions, the resin was dried to constant weight at 70 °C and stored in a vacuum desiccator.

Determination of Distribution Coefficient. *Method I*: Fifty ml of a definite concentration of hydrofluoric–nitric acid solution or hydrofluoric–boric–nitric acid solution containing 2×10^{-4} M of a metal ion was added to a 150 ml polyethylene bottle containing 0.5 g of the dried resin. The bottle was then shaken gently for 24 h at room temperature (the equilibrium is attained within 4 h). After filtration of the resin, the metal ion concentration in the solution was determined by a suitable method as previously described.[3]

The distribution coefficient, K_d, was determined by the following equation:

$$K_d = (\text{Amount of metal ion in resin/Amount of metal ion in solution}) \times (\text{ml of solution/g of resin}) \quad (\text{ml/g})$$

Method II: Fifty ml of 0.2 M hydrofluoric acid solution containing 2×10^{-4} M of a metal ion was added to a 150 ml polyethylene bottle containing 0.5 g of the dried resin. The bottle was then shaken for 24 h at room temperature. After discarding the solution the resin was washed with 10 ml of 10^{-2} M HF, and 50 ml of a definite concentration of HF–HNO_3 solution or HF–H_3BO_3–HNO_3 solution was added to the bottle. Subsequent procedures were the same as in Method I.

Column Operation. About 4 g of the dried resin in NO_3^--form which had been swelled with distilled water was packed in a polyethylene column (8 mm$\phi\times$180 mm) and the column was conditioned with about 50 ml of 0.2 M HF. After addition of a test solution containing 1 mg of a metal ion in 0.2 M HF, an eluent of a definite composition was passed through the column. The effluent was collected with a fraction collector and the concentration of the metal ion in each fraction was determined by the methods previously mentioned.[3]

Results

The following experimental results were obtained in solutions containing more than 10^{-2} M in HNO_3 in order to prevent the hydrolysis of hard acid-metals, unless otherwise mentioned.

Distribution Coefficients. Distribution coefficients K_d of Ti(IV), Zr(IV), Nb(V), and Ta(V) were investigated by Method I in solutions which contained various concentrations of hydrofluoric acid (C_{HF}) both in the presence and in the absence of 0.5 M H_3BO_3. The results are illustrated in Fig. 1.

The K_d values of these metals in HF–H_3BO_3 media are smaller than those in HF. In both media, the K_d values of these metals are increased with the increase of C_{HF} up to 10^{-2} M. In solutions containing more than 10^{-2} M of HF, the K_d in HF–H_3BO_3 media are decreased with increasing C_{HF}, whereas those in HF are almost unchanged with C_{HF}. The K_d values in both media at any C_{HF} decrease with increasing nitric acid concentration (C_{HNO_3}).

The K_d values obtained by Method II are similar to those by Method I as shown in Fig. 2.

The K_d of other metals in HF–H_3BO_3 media containing HNO_3 are presented in Table 1. In the third and fourth columns in Table 1, K_d in solutions containing various concentrations of H_3BO_3 ($C_{H_3BO_3}$) and 0.1 M HF, and K_d in solutions containing various C_{HF} and 0.5 M H_3BO_3 are listed.

At constant C_{HF} (column 3 in Table 1), the K_d of W(VI), Nb(V), Hf(IV), Zr(IV), Mo(VI), Ti(IV), and Sn(IV) remarkably decrease when the $C_{H_3BO_3}$ is changed from 10^{-2} to 0.1 M. The decrease of K_d of Ta(V) with increasing C_{HF}, however, is not noticeable.

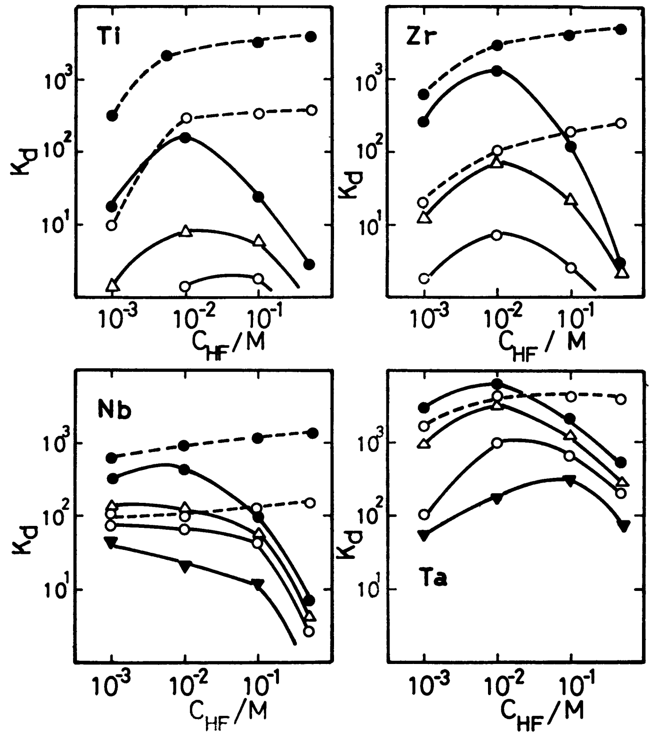

Fig. 1. Distribution coefficients of Ti(IV), Zr(IV), Nb(V), and Ta(V) in HF and HF–H_3BO_3 media containing HNO_3.
HF–0.5 M H_3BO_3–HNO_3 (——), HF–HNO_3 (------). C_{HNO_3}; ●: 10^{-2} M, △: 0.03 M, ○: 0.1 M, ▼: 0.3 M.

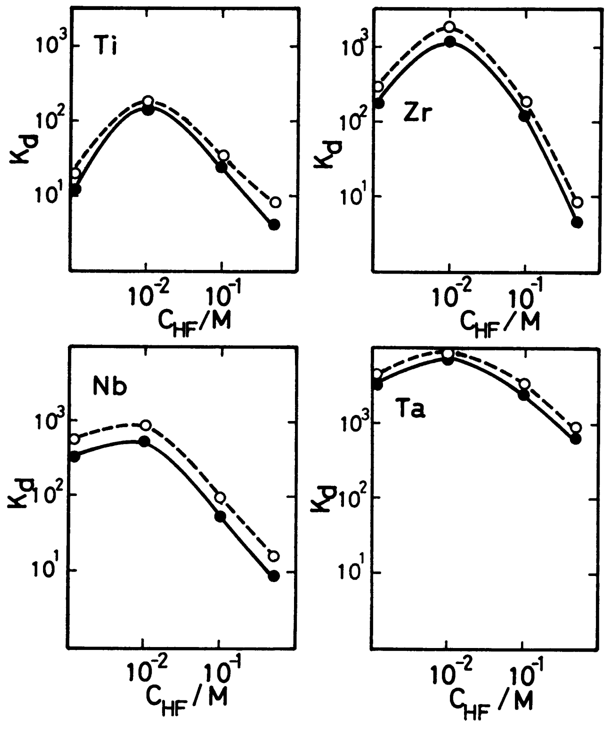

Fig. 2. Effect of equilibrating method on K_d of Ti(IV), Zr(IV), Nb(V), and Ta(V) in HF–0.5 M H_3BO_3–10^{-2} M HNO_3.
—●—: Method I, ---○---: Method II.

TABLE 1. ANION EXCHANGE DISTRIBUTION COEFFICIENTS OF METAL IONS IN $HF–H_3BO_3$ MEDIA CONTAINING HNO_3

Ion	$[HNO_3]$/M	0.1 M $HF–H_3BO_3$					$HF–0.5$ M H_3BO_3			
		$[H_3BO_3]$/M					[HF]/M			
		0	10^{-3}	10^{-2}	0.1	0.5	10^{-3}	10^{-2}	0.1	0.5
Ta(V)	10^{-2}	$>5\times10^3$	5×10^3	4.1×10^3	2.4×10^3	2.3×10^3	3.3×10^3	5×10^3	2.3×10^3	606
	10^{-1}	4.0×10^3	1.5×10^3	1.2×10^3	1.0×10^3	790	102	955	790	315
W(VI)	10^{-2}	$>5\times10^3$	5×10^3	765	97	232	4.3×10^3	2.4×10^3	232	13
	10^{-1}	115	110	28	14	56	182	112	56	5
Nb(V)	10^{-2}	5×10^3	5.0×10^3	531	90	95	321	383	95	6
	10^{-1}	102	91	68	18	58	79	71	58	3
Hf(IV)	10^{-2}	4.2×10^3	2.2×10^3	1.4×10^3	181	152	1.0×10^3	1.6×10^3	152	19
	10^{-1}	360	320	245	7	<3	<3	10	<3	3
Zr(IV)	10^{-2}	$>5\times10^3$	$>5\times10^3$	5.0×10^3	162	140	306	1.3×10^3	140	4
	10^{-1}	375	346	282	6	<3	<3	8	<3	<3
Mo(VI)	10^{-2}	1.2×10^3	906	209	33	44	995	613	44	11
	10^{-1}	75	56	25	4	15	48	33	15	6
Ti(IV)	10^{-2}	$>5\times10^3$	$>5\times10^3$	3.8×10^3	70	15	18	150	15	3
	10^{-1}	405	355	302	18	<3	<3	<3	<3	<3
Sn(IV)	10^{-2}	$>5\times10^3$	$>5\times10^3$	5.0×10^3	57	15	39	141	15	14
	10^{-1}	420	390	322	15	<3	<3	<3	<3	<3
V(V)	10^{-2}	92	76	15	11	<3	4	3	<3	<3
	10^{-1}	4	<3	<3	<3	<3	<3	<3	<3	<3
U(VI)	10^{-2}	72	49	5	<3	<3	20	15	<3	<3
	10^{-1}	<3	<3	<3	<3	<3	<3	<3	<3	<3
V(IV)	10^{-2}	12	6	13	15	<3	6	10	<3	<3
	10^{-1}	<3	<3	<3	<3	<3	<3	<3	<3	<3
Al(III)	10^{-2}	30	20	12	10	7	8	5	7	3
	10^{-1}	<3	<3	<3	<3	<3	<3	<3	<3	<3
Cr(III)	10^{-2}	31	28	14	<3	5	3	14	5	<3
	10^{-1}	<3	<3	<3	<3	<3	<3	<3	<3	<3
Fe(III), Cu(II), Cd(II), Ni(II), Mn(II), Co(II)				<3				<3		

At constant $C_{H_3BO_3}$ (column 4 in Table 1), the K_d of Hf(IV) or Sn(IV) is at a maximum when C_{HF} is at around 10^{-2} M, but the K_d of W(VI) and Mo(VI) are large even when C_{HF} is at 10^{-3} M and decrease monotonously with the increase of C_{HF}. This is similar to the results for Ti(IV), Zr(IV), Nb(V), and Ta(V) (Fig. 1). The large K_d values of W(VI) and Mo(VI) at low C_{HF} may be due to the fact that these metals exist as such anions as WO_4^{2-} and $Mo_7O_{24}^{6-}$ even in the absence of complexing agents.

The K_d of V(V), V(IV), U(VI), Al(III), Cr(III), and Fe(III) are small at most of C_{HF} and $C_{H_3BO_3}$.

According to the Ringbom's criterion for ion exchange separation by column filtration (*i.e.* K_d of an adsorbed ion is larger than 10^2 to $10^{2.5}$ and that of the emerging ion is less than $10^{0.5}$ to 10^1),[20] the following results are expected from the K_d values in Fig. 1 and Table 1 for the column separation of hard acid-metals; (a) In 0.1 M HF–10^{-2} M HNO_3, hard acid-metals such as Ta(V), W(VI), Nb(V), Hf(IV), Zr(IV), Mo(VI), Ti(IV), Sn(IV), V(V), and U(VI) are retained in the column and V(IV) and Fe(III) are eluted from the column. Al(III) and Cr(III) are retained loosely or eluted slowly. (b) In 0.1 M HF–0.5 M H_3BO_3–10^{-2} M HNO_3, among the metals retained in the column in (a), V(V) and U(VI) are eluted and Ti(IV) and Sn(IV) are eluted slowly. Mo(VI) is retained loosely. (c) In 0.1 M HF–0.5 M H_3BO_3–0.1 M HNO_3, among the metals retained in (b), Hf(IV) and Zr(IV) are eluted and Mo(VI) is eluted slowly. W(VI) and Nb(V) are retained loosely. (d) In 0.5 M HF–0.5 M H_3BO_3–0.1 M HNO_3, among the metals retained in (c), W(VI) and Nb(V) are eluted. Ta(V) cannot be eluted by the media mentioned above.

Although the media mentioned in (a) to (d) are chosen as an example, other possibilities for separation are obtained by selecting C_{HF}, $C_{H_3BO_3}$, and C_{HNO_3} properly.

Effect of Concentrations of HCl, H_2SO_4, HNO_3, and $HClO_4$ on K_d of Metals in HF–H_3BO_3 Media. The effects of various acids and their concentrations on the K_d of Ti(IV), Zr(IV), Nb(V), and Ta(V) in 10^{-2} M HF–0.5 M H_3BO_3 are presented in Fig. 3. In this experiment the anion exchange resin used had been converted to the respective anion form, as in the coexisting acids (*e.g.* when coexisting acid is $HClO_4$, the resin was converted to the ClO_4^--form).

Although the K_d values of all metals examined decrease with increasing the acid concentration regardless of the kind of acids, the degree of the effect of coexisting acids on K_d depends on the kind of acids; the effect is most serious with $HClO_4$.

The effect of concentration of sulfuric acid on K_d is gentle compared with those of other acids.

The K_d values of Nb(V) and Ta(V) are decreased

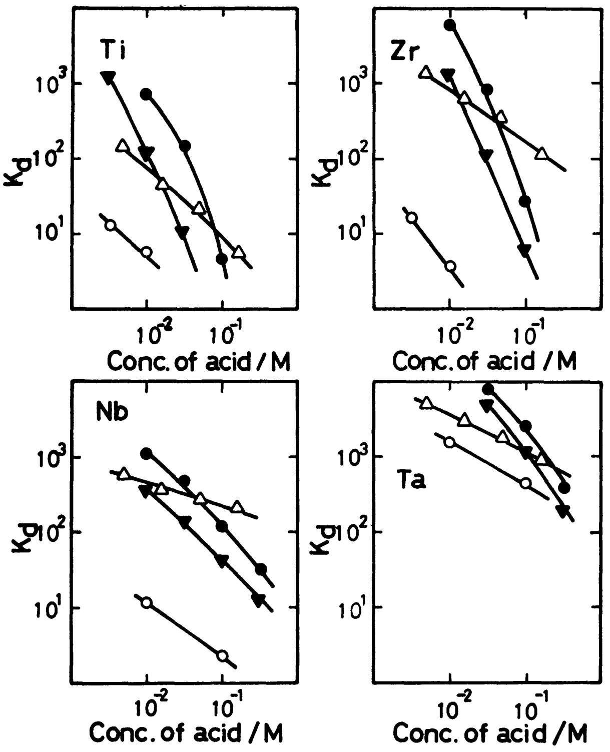

Fig. 3. Effect of concentration of coexisting acids on K_d of Ti(IV), Zr(IV), Nb(V), and Ta(V) in 10^{-2} M HF–0.5 M H_3BO_3.

●: HCl, △: H_2SO_4, ▼: HNO_3, ○: $HClO_4$.

more gently with the increase of acid concentration than those of Ti(IV) and Zr(IV).

Elution Behavior. In order to determine the practical conditions for the separation of Ti(IV), Zr(IV), Nb(V), and Ta(V), the elution behavior in HF–H_3BO_3 media was investigated after adsorption of these metals in a column (4 g of the dried resin, 8 mmϕ × 180 mm) in 0.2 M HF prior to the elution experiment. The flow rate of elution was adjusted to be 1.0 to 1.5 ml min^{-1}. The elution curves are shown in integrated form in Fig. 4.

As expected from the K_d values obtained by the batch method (Fig. 1 and Table 1), the mutual separation of these metals is possible by the column method as follows.

Ti(IV) is eluted when 100 ml of 10^{-2} M HF–0.5 M H_3BO_3–3 × 10^{-2} M HNO_3 or 0.1 M HF–0.5 M H_3BO_3–10^{-2} M HNO_3 is passed through the column, while Zr(IV), Nb(V), and Ta(V) are retained in the column even with 400 ml of these eluents (Fig. 4, (a)). Ti(IV) and Zr(IV) are eluted with 100 ml of 10^{-2} M HF–0.5 M H_3BO_3–0.1 M HNO_3 or 0.1 M HF–0.5 M H_3BO_3–0.1 M HNO_3, and Nb(V) is eluted with 300 ml of these eluents (Fig. 4, (b)). Ti(IV), Zr(IV), and Nb(V) are eluted with 100 ml of 0.5 M HF–0.5 M H_3BO_3–0.1 M HNO_3, while Ta(V) is not eluted with 300 ml of the eluent (Fig. 4, (c)). Ta(V) is eluted with 100 ml of 1 M HF–0.5 M H_3BO_3–5 M HNO_3 (Fig. 4, (d)-4), since the K_d value for Ta(V) in the medium is about 10.

The successive separation of Ti(IV), Zr(IV), Nb(V), and Ta(V) can be achieved when the media mentioned in (a) to (c) in Fig. 4 are properly combined as (d) in Fig. 4, as long as the amount of each metal is less than 1 mg.

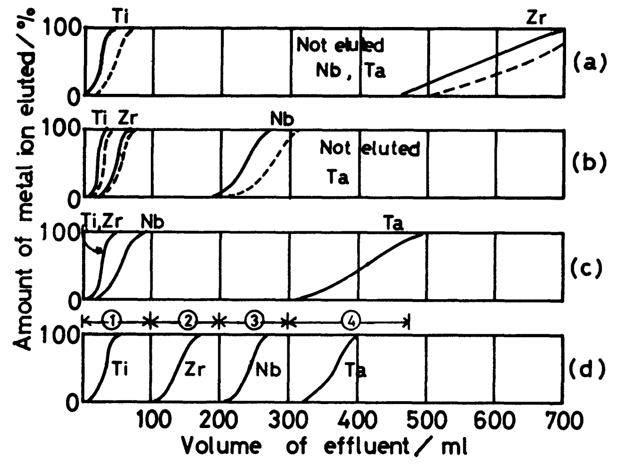

Fig. 4. Column elution behavior of Ti(IV), Zr(IV), Nb(V), and Ta(V) in HF–H_3BO_3 media containing HNO_3.

Diaion SA ♯ 100: 4 g, flow rate: 1.0 ml/min. Concentration of HF–H_3BO_3–HNO_3 (M); (a) 0.1–0.5–10^{-2} (——), 10^{-2}–0.5–3 × 10^{-2} (------), (b) 0.1–0.5–0.1 (——), 10^{-2}–0.5–0.1 (------), (c) 0.5–0.5–0.1, (d) ①: 0.1–0.5–10^{-2}, ②: 0.1–0.5–0.1, ③: 0 5–0 5–0.1, ④: 1–0.5–5.

Effect of Amount of Metal Ions on K_d and Elution Behavior of Metals. In HF–H_3BO_3 media, the free fluoride ion concentration is extremely low, as mentioned in the previous paper.[3] Therefore, the K_d values might be affected by the amount of metal ions owing to the deficiency of fluoride ions caused by the complex formation of large amount of metals with fluoride and/or the surplus of fluoride ions which are released from the large amount of metal fluoride complexes. This would occur especially when metals are adsorbed to the column in rather concentrated hydrofluoric acid in the beginning of the elution procedure.

The effect of the amount of Zr(IV) on K_d of Zr(IV) investigated by the batch method is summarized in Table 2. In this experiment, 2 g of the dried resin was used in order to keep the loading less than 0.1 and the solution of Zr(IV) was made free from fluoride ion. The C_{HF} was chosen so that the K_d of Zr(IV) is around 10^2 at 1 mg level of Zr(IV), *i.e.* 10^{-3} M C_{HF} in the absence of H_3BO_3 and 0.1 M C_{HF} in the presence of 0.5 M H_3BO_3.

The K_d obtained by equilibrating the media containing Zr(IV) with the resin (Method I in Table 2) is decreased by the increase of the amount of Zr(IV) from 0.25 to 50 mg, when 10^{-3} M HF–10^{-2} M HNO_3 is used as the medium. But the K_d is not changed with the amount of Zr(IV) up to 20 mg, when 0.1 M HF–0.5 M H_3BO_3–10^{-2} M HNO_3 is used as the medium.

The K_d obtained by equilibrating zirconium-free media with the resin on which Zr(IV) had been adsorbed in 0.2 M HF (Method II in Table 2) is extremely large compared with that by Method I and is more than 5 × 10^3 regardless of the amount of Zr(IV) when 10^{-3} M HF–10^{-2} M HNO_3 is used as the medium. On the other

Table 2. Effect of the amount of metal ions on distribution coefficients by batch method

Ion	Amount		K_d	
	mg	mmol	Method I[a]	Method II[b]
			(10^{-3} M HF–10^{-2} M HNO_3)	
Zr(IV)	0.25	2.7×10^{-3}	1.0×10^{3}	$>5\times10^{3}$
	1.0	1.1×10^{-2}	90	$>5\times10^{3}$
	10.0	0.11	6	$>5\times10^{3}$
	50.0	0.53	3	$>5\times10^{3}$
			(0.1 M HF–0.5 M H_3BO_3–10^{-2} M HNO_3)	
Zr(IV)	0.25	2.7×10^{-3}	145	165
	1.0	1.1×10^{-2}	142	160
	10.0	0.11	132	168
	20.0	0.21	126	162
	50.0	0.53	42	155
			(0.1 M HF–0.5 M H_3BO_3–0.1 M HNO_3)	
Nb(V)	1.0	1.1×10^{-2}	65	68
	10.0	0.11	66	82
	20.0	0.22	70	75

a) Determined by equilibrating the medium containing a metal ion with the resin. b) Determined by equilibrating the metal-free medium with the resin on which a metal ion had been adsorbed in 0.2 M HF.

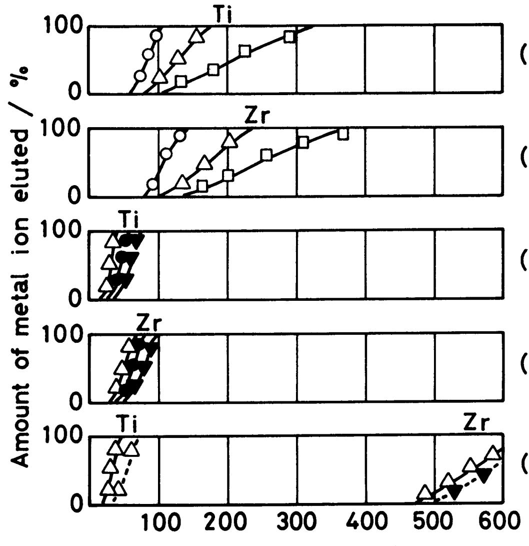

Fig. 5. Effect of amount of metal ions on elution behaviors of Ti(IV) and Zr(IV).
(a) and (b): 10^{-3} M HF–0.1 M HNO_3, (c) and (e): 0.1 M HF–0 5 M H_3BO_3–10^{-2} M HNO_3, (d): 0 1 M HF–0 5 M H_3BO_3–0.1 M HNO_3. Amount of metal ions; ○: 0.25 mg, △: 1 mg, □: 5 mg, ●: 10 mg, ▼: 50 mg.

hand, when 0.1 M HF–0.5 M H_3BO_3–10^{-2} M HNO_3 is used as the medium, the K_d by Method II is identical with that by Method I and is not affected by the amount of Zr(IV) up to 50 mg.

The reason why the K_d value in HF–H_3BO_3–HNO_3 media does not change may be attributed to the F^--buffer action of this media, as mentioned in the previous paper.[3]

The large K_d obtained by Method II in 10^{-3} M HF–10^{-2} M HNO_3 cannot be explained clearly, but it may be due to the irreversible adsorption of Zr(IV)–fluoride complexes and/or the change of C_{HF} caused by the partial dissociation of highly fluorinated zirconium complexes on the resin.

The K_d of Nb(V) in 0.1 M HF–0.5 M H_3BO_3–0.1 M HNO_3 is the same regardless of the equilibrating method used and the amount of Nb(V), up to 20 mg.

The effect of the amount of Zr(IV) or Ti(IV) on their column elution behavior is shown in Fig. 5. These metals had been adsorbed to the column in 0.2 M HF prior to this elution experiment. Though the elution of Ti(IV) or Zr(IV) was extremely retarded by the increase of metal ions in 10^{-3} M HF–0.1 M HNO_3 (Figs. 5(a) and (b)), the elution was hardly affected by increasing the amount of the metal ions up to 50 mg, when 0.1 M HF–0.5 M H_3BO_3–10^{-2} M HNO_3 or 0.1 M HF–0.5 M H_3BO_3–0.1 M HNO_3 was used as the eluent (Figs. 5(c) and (d)). Less than 50 mg of coexisting Zr(IV) hardly affected the elution behavior of 1 mg of Ti(IV) in 0.1 M HF–0.5 M H_3BO_3–10^{-2} M HNO_3 (Fig. 5(e)).

Discussion

The K_d values of metals for the anion exchange resin in solutions involving complexing agents are generally expressed by the equation presented by Helfferich.[21] The equation can be modified into Eq. 1, by considering the adsorption of a metal ion M^{n+} to A^{a-}-form anion exchange resin in a solution containing fluoride ions as a complexing agent:

$$K_d=\sum_{j=0}^{N}[x_j(K_A^{MF_j})^{1/a}([A^{a-}]_r/[A^{a-}])^{j-n/a}], \quad (1)$$

$$x_j=[F^-]^j\beta_j/(1+[F^-]\beta_1+\cdots+[F^-]^N\beta_N). \quad (2)$$

Here j is the number of fluoride ions complexed with the metal ion M^{n+}, N is the maximum coordination number of fluoride ion for M^{n+}, x_j is the molar fraction of MF_j to the total metal species in the solution, $K_A^{MF_j}$ is the selectivity coefficient of MF_j to A^{a-}, $[A^{a-}]_r$ and $[A^{a-}]$ are the concentration of anion A^{a-} in resin and solution and β_j is the cumulative stability constant of MF_j.

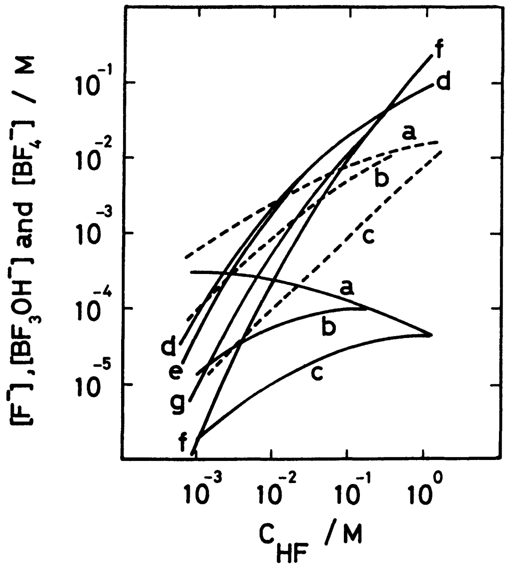

Fig. 6. Concentration of F^-, BF_3OH^-, and BF_4^- in HF and HF–H_3BO_3 media containing HNO_3.
——: HF-0.5 M H_3BO_3, ------: HF. a, b, and c: $[F^-]$ (a: without HNO_3, b: with 10^{-2} M HNO_3, c: with 0.1 M HNO_3), d and e: $[BF_3OH^-]$ (d: without HNO_3, e: with 0.1 M HNO_3), f and g: $[BF_4^-]$ (f: without HNO_3, g: with 0.1 M HNO_3).

As is evident from Eq. 1, the K_d value is a function of x_j, which is controlled by $[F^-]$ in the solution (Eq. 2), of $(K_A^{MF_j})^{1/a}$ which indicates the relative adsorbability of MF_j to A^{a-} (and hence, the value depends on the kind of anion), and of $([A^{a-}]_r/[A^{a-}])^{j-n/a}$, which depends on the valency and the concentration of anion A^{a-}.

Concentrations of free fluoride ion and other anions which exist in hydrofluoric acid and HF–H_3BO_3 media containing HNO_3 are calculated by the procedure described in the previous paper.[3] These are illustrated in Fig. 6; the dissociation constants of hydrofluoric acid and fluoroboric acids were used.

Figur 6 and the dependency of K_d on C_{HF} shown in Fig. 1 can be explained as follows: In solutions containing less than 10^{-2} M HF and 10^{-2} M HNO_3 with and without 0.5 M H_3BO_3, the resin stays as NO_3^-–form because the concentration of anions in solution other than nitrate is low and, hence, the second and third terms in Eq. 1 can be considered as constant at a definite C_{HNO_3}. Therefore, the increase of K_d with increasing C_{HF} up to 10^{-2} M may be ascribed to the change of x_j term, that is, to the increase of anionic metal fluoride complexes.

As an example, the species of Zr(IV) fluoride complexes and their fractions x_j in HF–H_3BO_3 media are calculated using the stability constants of Zr(IV) fluoride complexes.[22] The free fluoride ion concentration in the media of 0.5 M H_3BO_3–10^{-2} M HNO_3 containing 10^{-3} or 10^{-2} M HF is $10^{-5.0}$ or $10^{-4.3}$ M, respectively (see Fig. 6). The molar fraction of major species of Zr(IV) in solutions containing $10^{-5.0}$ M or $10^{-4.3}$ M of free fluoride ion are 35% of ZrF_4, 15% of ZrF_5^-, and 2% of ZrF_6^{2-} or 30% of ZrF_4, 55% of ZrF_5^-, and 15% of ZrF_6^{2-}, respectively. Consequently, the increase of the K_d of Zr(IV) with increasing C_{HF} is mainly due to the increase of the fraction of ZrF_5^- (and ZrF_6^{2-}).

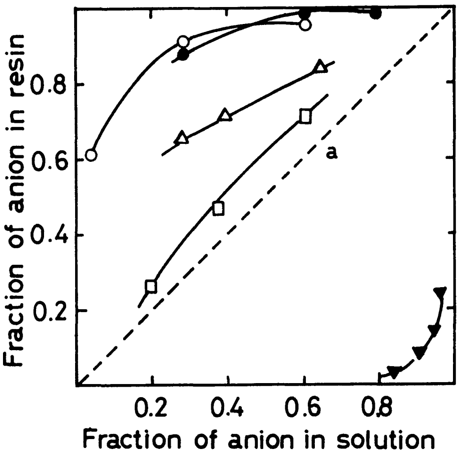

Fig. 7. Exchange of anions with Cl^- in the resin.
Diaion SA # 100: 1.0 g. Amount of acids: 0.5 to 20 mmol in 20 ml of solution. ○: BF_4^-, ●: ClO_4^-, △: NO_3^-, □: SO_4^{2-}, ▼: F^-.

The decrease of K_d with the increase of C_{HF} in HF–H_3BO_3 media containing more than 10^{-2} M HF (see Fig. 1) cannot be explained by the change of x_j because the free fluoride ion concentration slightly increases with the increase of C_{HF} (Fig. 6), but may be attributed to the change of the second and third terms in Eq. 1. Because the concentration of BF_4^- and BF_3OH^- increases remarkably with increasing C_{HF} in the solutions which are more than 10^{-2} M HF and 0.5 M H_3BO_3 (Fig. 6), it is suspected that BF_4^- and BF_3OH^- are adsorbed rather strongly on the resin, reducing the relative adsorbabilities of the metal fluoride complexes.

The adsorbability of BF_4^- was investigated and compared with the adsorbabilities of ClO_4^-, NO_3^-, SO_4^{2-}, and F^- according to Wheaton *et al.*[23] After equilibrating 1.0 g of Cl^--form dry anion exchange resin with 20 ml of various concentrations of HBF_4, $HClO_4$, HNO_3, H_2SO_4, or HF for 24 h at room temperature, the amount of chloride ion desorbed from the resin was determined by the Volhard method.[24] Assuming the amount of chloride desorbed is equivalent to the anions adsorbed, the molar fractions of the anion examined both in resin and solution are calculated (Fig. 7). In Fig. 7, the curve of an anion which lies above line (a) suggests the stronger adsorbability of the anion than that of chloride ion.[23] It is seen from Fig. 7 that the adsorbability of BF_4^- is very strong and is comparable to that of ClO_4^-. The order of adsorbabilities of anions is as follows:

$$BF_4^- \simeq ClO_4^- > NO_3^- > SO_4^{2-} > Cl^- > F^-. \qquad (3)$$

Although the adsorbability of BF_3OH^- cannot be determined experimentally because of the difficulty of the preparation of BF_3OH^- free from BF_4^-,[25] it is considered that BF_3OH^- has the similar adsorbability to that of BF_4^- since the structure and the ionic charge of BF_3OH^- resemble those of BF_4^-.[25]

According to the considerations mentioned above, the decrease of K_d with the increase of C_{HF} in HF–H_3BO_3 media containing more than 10^{-2} M HF (Fig. 1) may be attributed to the increase of BF_4^- and BF_3OH^- which are strongly adsorbed on the resin. And the decrease of K_d with the increase of $C_{H_3BO_3}$ in $HF-H_3BO_3$ media containing more than 10^{-2} M H_3BO_3 (column 3 in Table 1) may also be attributed to the increase of BF_4^- and BF_3OH^-.

The effects of coexisting acids and their concentrations on K_d (Fig. 3) may also be due to the difference in the adsorbabilities of the anions included in the coexisting acids. The different adsorbability given by various kinds of anions changes the second term in Eq. 1, $(K_A^{MF_j})^{1/a}$, and the concentrations of anions affect the third term in Eq. 1, $([A^{a-}]_r/[A^{a-}])^{j-n/a}$.

Based on the above discussions, the separation of Ti(IV), Zr(IV), Nb(V), and Ta(V) in $HF-H_3BO_3$ media shown in Fig. 4(d) is interpreted as follows: Metals in 0.2 M HF are adsorbed on the resin as fully fluorinated complexes. When the eluent, 0.1 M HF–0.5 M H_3BO_3–10^{-2} M HNO_3, is introduced to the column, metal complexes tend to be transformed to partially fluorinated complexes and the K_d values of these metals are reduced, because the concentration of free fluoride is extremely low in the medium. With this eluent Ti(IV), whose K_d is the smallest among these metals in this medium, is eluted from the column. With the increase of C_{HNO_3} in the eluent, the amount of NO_3^- adsorbed on the resin is increased, and Zr(IV) is eluted. When C_{HF} is increased from 0.1 M to 0.5 M, BF_4^- or BF_3OH^-, whose adsorbabilities are stronger than that of NO_3^-, is increased and Nb(V) is eluted. Since the adsorbability of Ta(V) fluoride complexes is extremely strong, a medium containing strong adsorptive anions in rather high concentration such as 1 M HF–0.5 M H_3BO_3–5 M HNO_3 is required to elute Ta(V).

Generally, in the separation of hard acid-metals by anion exchange, mixtures of HF (more than 0.1 M) and fairly concentrated HCl[4–7] or HNO_3[10] are used as eluents. Using these media, however, a separation such as that of Ti(IV) from Zr(IV) is difficult, because the adsorbabilities of fully fluorinated complexes of these metals resemble each other. Although for the elution of Ta(V) a solution of salt in high concentration such as 1 M NH_4F–4 M NH_4Cl[4,7] or a mixture of concentrated acids such as 5 M HF–12 M HNO_3[10] are employed in the works of HF–HCl or $HF-HNO_3$ media, it is difficult to remove the large amount of salts from the effluent and the concentrated acids decompose the resin. Using $HF-H_3BO_3$ media proposed in the present paper, these disadvantages are eliminated.

In conclusion, there is a buffer action relating to fluoride ion based on the dissociation of fluoroboric acids in $HF-H_3BO_3$ media, as discussed in the previous paper.[3] Therefore, despite the low fluoride ion concentration in $HF-H_3BO_3$ media, the separation can be attained without any effect of the amount of metal ions (up to 50 mg) as illustrated in Table 2 and Fig. 5.

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