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The Influence of Anions on the Distribution Coefficients of Hard Acid–Metals for Anion-exchange Resin in HF–H_3BO_3 Media

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The distribution coefficients, K_d, of eighteen hard acid-metal ions for a strongly basic anion-exchange resin were determined in HF-H_3BO_3 media in the presence of Cl^- or NO_3^-, SO_4^{2-}, and ClO_4^-, and the relation between the adsorbabilities of the coexisting anions and the K_d values of the metal ions was discussed. The fluoride-ion concentration is quite low in HF-H_3BO_3 media because of the complex formation of the fluoride ion with boric acid, and most of the hard acid-metal ions have lower K_d values in HF-H_3BO_3 media than those in a hydrofluoric acid solution. By varying the kinds of coexisting anions and their concentrations in HF-H_3BO_3 media containing less than 0.02 M (1 M=1 mol dm^{-3}) of fluoroborate ions, the K_d values of metal ions can be controlled to allow the anion-exchange separations. As fluoroborate ions, *e.g.*, BF_4^- or BF_3OH^-, are strongly adsorbed on the resin, metal ions which are strongly held on the resin can be eluted by media including fluoroborate ions in higher concentrations. By using HF-H_3BO_3 media and selecting the coexisting anions, an effective mutual separation of titanium-zirconium, titanium-uranium, tin-niobium, and molybdenum-tungsten can be attined.

The highly fluorinated metal complexes in a hydrofluoric acid solution change their forms to poorly fluorinated complexes when boric acid is added to the solution, because the free fluoride-ion concentration is considerably reduced by the formation of such fluoroborate ions as BF_4^- or BF_3OH^-. The free fluoride-ion concentration in HF–H_3BO_3 mixed media is kept constant by the buffer action due to the dissociation of fluoroborate ions, even if the free fluoride ions are consumed by the complex formation with coexisting metal ions. As the fluoroborate ions in the mixed media are strongly adsorbed on the anion-exchange resin, metal-anion comlexes held on the resin can be eluted by the aid of fluoroborate ions in a increased concentration.

In the previous paper,[1] the usefulness of HF–H_3BO_3 media in the anion-exchange separation of hard acid-metals was reported and it was also pointed out that a more effective mutual separation of metals can be attained if nitrate ions coexist in the mixed media.

In the present paper, for the extensive application of the mixed media in the ion-exchange separation, the distribution coefficients of metal ions on the anion-exchange resin are determined in mixed media containing various anions, and the relation between the distribution coefficients and the adsorbabilities of anions on the resin is discussed.

Experimental

Chemicals and Apparatus. The standard solutions of the metal ions were prepared by the procedures described in previous papers.[1,2] The other chemicals and apparatus were the same as those used before.

Ion-exchange Resin. A strongly basic anion-exchange resin, Diaion SA#100, a product of Mitsubishi Chemical Ind. Ltd. (8% DVB, 75—150 µm, Cl^--form), was used. After washing the resin in a column with five times as much as the column volume of 3 M HCl or HNO_3, H_2SO_4, and $HClO_4$ and with a sufficient volume of distilled water, the resin was dried to a constant weight at 70 °C and stored in a vacuum desiccator.

Determination of Distribution Coefficient. Fifty ml of a definite concentration of a hydrofluoric–hydrochloric acid solution or a hydrofluoric–boric–hydrochloric 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 in the Cl^--form. The bottle was then shaken gently for 24 h at room temperature. After the filtration of the resin, the metal-ion concentration in the solution was determined by a suitable method, as has been described previously.[2]

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

K_d = (Amount of metal ion in resin / Amount of metal ion in solution) × (ml of solution / g of resin).

The K_d was also determined in the media containing sulfuric, nitric, or perchloric acid instead of hydrochloric acid by the manner described above.

Column Operation. About 4 g of the dried resin, which had been swelled well with distilled water, was packed in a polyethylene column (8 mmϕ × 180 mm), and was conditioned with about 50 ml of 0.2 M HF. After the addition of a test solution containing 1—250 mg of a metal ion in 0.2 M HF, an eluent of a definite composition was passed through the column. The effluent was then collected with a fraction collector, and the concentration of the metal ion in each fraction was determined by a method described previously.[2] In the mutual-separation experiments, two kinds of metal ions were added together to the column.

Results and Discussion

In the present experiments, the coexisting anions are added as their acid forms in order to prevent the hydrolysis of the hard acid-metals.

In the following discussion, as a criterion for ion-exchange separation, we adopt Ringbom's suggestion for the column-filtration method (*i.e.*, the K_d of an adsorbed ion is larger than 10^2—$10^{2.5}$, method (*i.e.*, the K_d of an adsorbed ion is larger than 10^2—$10^{2.5}$, while that of the emerging ion is less than $10^{0.5}$—10^1).[3]

Distribution Coefficients. The distribution coefficients of the metal ion, K_d, on strongly basic anion-exchange resin were determined in hydrofluoric–boric acid media containing Cl^-, SO_4^{2-}, NO_3^-, or ClO_4^-; they are summarized in Tables 1—4. In the third column of these tables, the K_d values in the absence of boric acid are also tabulated.

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TABLE 1. ANION-EXCHANGE DISTRIBUTION COEFFICIENTS OF METAL IONS IN $HF-H_3BO_3-HCL$ MEDIA

Metal ion	HCl(M)	HF(M)			0.1 M $HF-H_3BO_3$(M)		HF(M)-0.5 M H_3BO_3		
		0.01	0.1	0.5	0.01	0.1	0.01	0.1	0.5
Ta(V)	0.1	4.8×10^3	1.1×10^4	8.9×10^3	2.9×10^3	1.8×10^3	2.9×10^3	2.2×10^3	300
	1	887	911	949	618	352	622	412	235
Nb(V)	0.1	404	577	1.1×10^3	310	97	161	87	7
	1	31	38	29	35	17	149	22	7
Sn(IV)	0.1	501	2.2×10^3	4.2×10^3	1.1×10^3	25	19	15	3
	1	460	433	45	157	800	176	1.7×10^3	577
W(VI)	0.1	83	535	1.1×10^3	83	93	325	170	3
	1	8	22	28	121	243	501	207	20
Mo(VI)	0.1	64	214	376	144	32	151	60	18
	1	36	30	33	45	14	16	19	18
Zr(IV)	0.1	698	2.2×10^3	2.2×10^3	3.5×10^3	76	160	27	3
	1	3	5	12	9	3	9	6	3
Hf(IV)	0.1	1.0×10^3	2.5×10^3	2.4×10^3	3.1×10^3	86	243	33	3
	1	3	9	18	9	3	9	5	3
Ti(IV)	0.1	939	2.2×10^3	2.6×10^3	1.5×10^3	38	10	9	3
	1	15	22	24	16	3	3	3	3
U(VI)	0.1	5	3	10	4	3	3	3	3
	1	6	5	5	3	3	3	3	3

V(V) is slightly adsorbed in HF-HCl. Al(III), V(IV), and Fe(III) are not adsorbed in either HF-HCl or $HF-H_3BO_3-HCl$.

TABLE 2. ANION-EXCHANGE DISTRIBUTION COEFFICIENTS OF METAL IONS IN $HF-H_3BO_3-H_2SO_4$ MEDIA

Metal ion	H_2SO_4(M)	HF(M)			0.1 M $HF-H_3BO_3$(M)		HF(M)-0.5 M H_3BO_3		
		0.01	0.1	0.5	0.01	0.1	0.01	0.1	0.5
Ta(V)	0.05	6.5×10^3	2.0×10^4	1.7×10^3	1.2×10^3	1.0×10^3	1.2×10^3	1.0×10^3	272
	0.5	1.0×10^3	3.7×10^3	4.2×10^3	519	562	867	645	215
Nb(V)	0.05	410	1.1×10^3	754	249	78	306	88	8
	0.5	51	46	41	41	40	109	63	5
Sn(IV)	0.05	451	2.1×10^3	1.7×10^3	788	22	21	13	3
	0.5	8	27	52	53	73	11	30	3
W(VI)	0.05	78	810	946	155	71	889	157	7
	0.5	31	32	46	35	109	445	70	16
Mo(VI)	0.05	315	515	473	142	175	848	280	39
	0.5	46	43	45	15	3	20	6	3
Zr(IV)	0.05	772	1.7×10^3	1.1×10^3	1.0×10^3	82	320	52	3
	0.5	29	51	78	30	18	17	9	3
Hf(IV)	0.05	1.1×10^3	1.5×10^3	1.1×10^3	673	69	152	38	3
	0.5	28	68	85	27	7	14	7	3
Ti(IV)	0.05	833	1.6×10^3	1.3×10^3	867	53	20	13	3
	0.5	30	60	71	58	6	3	3	3
U(VI)	0.05	1.1×10^3	286	205	135	126	2.3×10^3	167	3
	0.5	29	14	11	10	10	44	13	3

V(V) is slightly adsorbed in HF-0.05 M H_2SO_4. Al(III), V(IV), and Fe(III) are not adsorbed in either $HF-H_2SO_4$ or $HF-H_3BO_3-H_2SO_4$.

The concentration of fluoride ions and fluoroborate ions in $HF-H_3BO_3$ media in the presence of 0.1 or 1 M of nitric acid was calculated using the dissociation constants given by Sillen *et al.*[4] and Mesmer *et al.*;[5] they are shown in Fig. 1 as a function of the hydrofluoric acid concentration, C_{HF}.

Qualitatively speaking, the K_{d} values of metals in $HF-H_3BO_3$ media are smaller than those in the absence of boric acid, and decrease with the increase in C_{HF}, though the K_{d} values in HF solutions increase or stay constant. The variation in K_{d} values may be explained as follows: (1) As the addition of boric acid to the hydrofluoric acid solution reduces the free fluoride-ion concentration, C_{F^-} to about one hundredth (Curves b and c in Fig. 1), the fraction of metal-anion complexes to be adsorbed onto the anion-exchange resin in $HF-H_3BO_3$ media becomes smaller than that in the absence of boric acid. (2) In a hydrofluoric acid solution, with the increase in C_{HF}, C_{F^-} and also the fraction of metal-fluoride complexes to be adsorbed onto the resin are increased. On the other hand, in $HF-H_3BO_3$ media, C_{F^-} does not increase when C_{HF} is larger than 0.1 M. (3) The concentration of fluoroborate ions in the mixed media increases with the increase in C_{HF}, and the increased fluoroborate ions which are strongly adsorbed on the resin lower the K_{d} values of the metals.

The influence of coexisting anions on the K_{d} can be interpreted by considering their adsorbabilities on the anion-exchange resin. The following selectivity

Table 3. Anion-exchange distribution coefficients of metal ions in $HF-H_3BO_3-HNO_3$ media

Metal ion	HNO_3 (M)	HF(M)			0.1 M $HF-H_3BO_3$(M)		HF(M)-0.5 M H_3BO_3		
		0.01	0.1	0.5	0.01	0.1	0.01	0.1	0.5
Ta(V)	0.1	638	1.2×10^3	3.4×10^3	963	1.5×10^3	1.5×10^3	1.7×10^3	386
	1	202	178	198	296	252	302	235	172
Nb(V)	0.1	110	130	190	68	18	71	58	3
	1	12	3	3	3	3	29	14	11
Sn(IV)	0.1	350	420	450	322	15	3	3	3
	1	3	3	3	3	3	3	3	3
W(VI)	0.1	140	185	220	28	14	112	56	5
	1	30	3	3	3	3	29	19	3
Mo(VI)	0.1	6	38	57	25	4	33	15	6
	1	5	3	5	3	3	10	8	3
Zr(IV)	0.1	82	283	418	282	6	8	3	3
	1	3	3	3	3	3	3	3	3
Hf(IV)	0.1	90	320	430	245	7	10	3	3
	1	3	3	3	3	3	3	3	3
Ti(IV)	0.1	241	344	411	302	18	3	3	3
	1	4	5	3	3	3	3	3	3

U(VI), Al(III), V(IV), V(V), and Fe(III) are not adsorbed.

Table 4. Anion-exchange distribution coefficients of metal ions in $HF-H_3BO_3-HClO_4$ media

Metal ion	$HClO_4$ (M)	HF(M)			0.1 M $HF-H_3BO_3$(M)		HF(M)-0.5 M H_3BO_3		
		0.01	0.1	0.5	0.01	0.1	0.01	0.1	0.5
Ta(V)	0.1	112	165	252	74	128	182	200	42
	1	38	81	73	26	46	15	18	15
Sn(IV)	0.1	5	3	3	13	12	17	15	10
	1	3	3	3	3	3	3	3	3
W(VI)	0.1	7	3	3	29	21	47	10	20
	1	3	3	3	14	10	23	8	18
Mo(VI)	0.1	3	3	38	25	4	33	15	6
	1	3	3	3	3	3	5	8	10

Nb(V), Zr(IV), Hf(IV), Ti(IV), U(VI), Al(III), V(IV), V(V), and Fe(III) are not adsorbed.

Table 5. Anion-exchange distribution coefficients of tantalum in $HF-H_3BO_3-HNO_3$ media

HF(M)	H_3BO_3(M)	HNO_3(M)	K_d of Ta(V)
2	1	1	25
3	1	1	19
4	2	1	7
6	2	1	3

coefficients of anions for the anion-exchange resin, referred to the Cl^- ion, K_{Cl}^{A}, were calculated from the data presented in a previous paper[1)] according to the method of Wheaton *et al.*:[6)] $K_{Cl}^{BF_4}$ 30, $K_{Cl}^{ClO_4}$ 30, $K_{Cl}^{NO_3}$ 3.3, $K_{Cl}^{(SO_4)_{1/2}}$ 1.4, and K_{Cl}^{F} 0.04. As ClO_4^- and BF_4^- are strongly adsorbed on the resin, in a solution containing more than 0.1 M of $HClO_4$ or 0.5 M HF-0.5 M H_3BO_3, which contains 0.1 M of BF_4^- and 0.05 M of BF_3OH^-, the K_d values of metal ions are extremely small and none of the metal ions presented in Tables 1-4 are adsorbed on the resin except Ta(V). With more concentrated $HF-H_3BO_3$ media, as is indicated in Table 5, Ta(V) comes not to be absorbed on the resin.

In the media where the concentration of $C_{BF_4^-}$ or $C_{BF_3OH^-}$ is less than 0.02 M, the effect of coexisting anions becomes significant. In 0.1 M HF-0.5 M H_3BO_3 media, which contain 0.01 M of BF_4^- and 0.02 M of BF_3OH^-, only Ta(V) is retained on the resin in the presence of 0.1 M $HClO_4$, but in the presence of 0.1 M HNO_3 or 0.1 M HCl instead of $HClO_4$, Nb(V) and W(VI) or Nb(V), W(VI), and Mo(VI) are retained in addition to Ta(V). In the media where $C_{BF_4^-}$ or $C_{BF_3OH^-}$ is further reduced, the adsorbed elements increase in

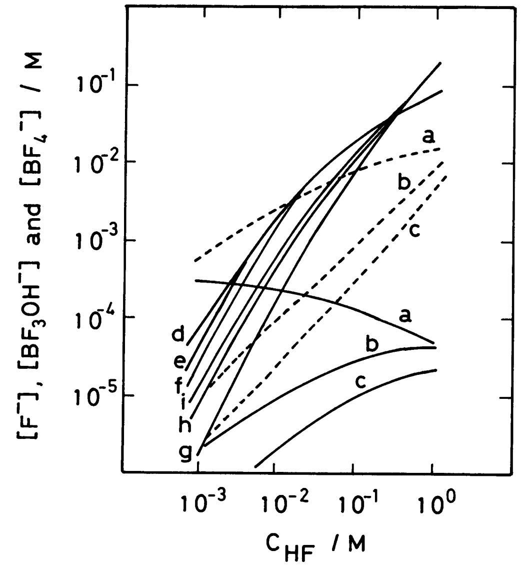

Fig. 1. Concentration of F^-, BF_3OH^-, and BF_4^- in HF and $HF-H_3BO_3$ media containing HNO_3.
——: HF-0.5 M H_3BO_3, ----: HF. a, b, and c $[F^-]$; d, e, and f: $[BF_3OH^-]$; g, h, and i: $[BF_4^-]$ (a, d, and g: without HNO_3; b, e, and h: with 0.1 M HNO_3; c, f, and i: with 1 M HNO_3).

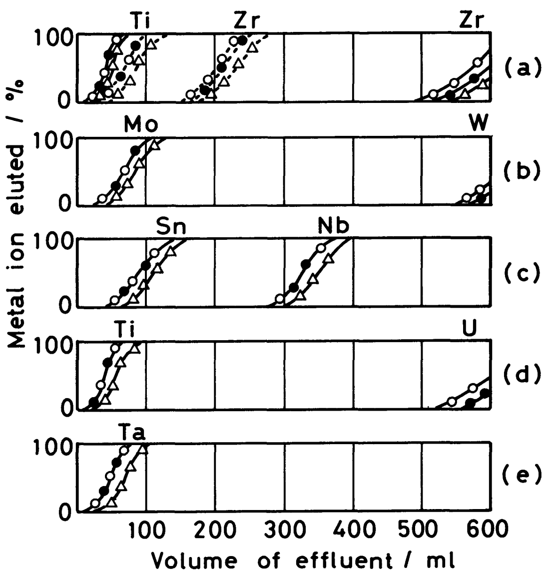

Fig. 2. Column elution behavior of metal ions in $HF-H_3BO_3$ containing various anions.
Column: Diaion SA#100, 4g, 8mmϕ×180mm. Flow rate: 1.0 ml min^{-1}. (a) ——: 0.01 M HF-0.5 M H_3BO_3-0.1 M HCl, ----: 0.1 M HF-0.5 M H_3BO_3-0.05 M H_2SO_4, (b) 0.1 M HF-0.5 M H_3BO_3-1 M HCl, (c) 0.1 M HF-0.5 M H_3BO_3-0.1 M HCl, (d) 0.1 M HF-0.5 M H_3BO_3-0.05 M H_2SO_4, (e) 4 M HF-2 M H_3BO_3-1 M HNO_3. Amount of metal ion; ○: 1 mg, ●: 100 mg, △: 250 mg.

number; *i.e.*, Zr(IV) and Hf(IV), besides Ta(V), Nb(V), W(VI), and Mo(VI), become adsorbed on the resin in 0.01 M HF-0.1 M H_3BO_3-0.1 M HCl media.

Though the discussion above has been carried out from the viewpoint of the adsorbability of a coexisting anion, there are some exceptions which cannot be explained from this point of view. It is thought that the exceptions are due to the complex formation of metal ions with anions other than the fluoride ion and to the adsorption of non-fluorinated metal-oxoacid anions, such as MoO_4^{2-} or WO_4^{2-}, on the resin.

Mutual Separation of Hard Acid-Metals by the Column Method. Referring to the K_d values in Tables 1—4, the mutual separation of hard acid-metals that had been considered to be difficult was attempted by the column method according to the procedure described in the Experimental section. It is clear from Fig. 2 that the several mutual separations described below are possible. The elution curves of metal ions in Fig. 2 are shown in integrated forms.

(a) Ti-Zr: Only one pice of literature concerning the ion-exchange separation of Ti(IV) and Zr(IV) in a solution containing hydrofluoric acid was reported by one (T.A.) of the present authors, who used an anion-exchange resin in $HF-H_3BO_3-HNO_3$ media.[1] As is shown in Fig. 2 (a), an effective separation can also be attained by using HCl or H_2SO_4 instead of HNO_3.

(b) Mo-W: The anion-exchange separation of Mo(VI) and W(VI) in 3 M HF-10 M HCl[7] has been the most recommended method for these ions. The difficulty with this method is that acids of a high concentration are inevitable. In $HF-H_3BO_3$ media, it is possible to separate Mo(VI) from W(VI) in acid mixtures of a lower concentration, *i.e.*, 0.1 M HF-0.5 M H_3BO_3-1 M HCl, as is shown in Fig. 2 (b).

(c) Sn-Nb; Adopting the $HF-H_3BO_3$-HCl media, an effective separation can be attained in a less concentrated acid mixture, as is shown in Fig. 2 (c). The difference *in* K_d between Sn(IV) and Nb(V) is larger than that in the HF-HCl[8] or $HF-HNO_3$[9] media.

(d) Ti-U: In the general method for the anion-exchange separation of Ti(IV) and U(VI), Ti(IV) was adsorbed on the resin, whereas U(VI) was eluted. On the contrary, in the $HF-H_3BO_3-H_2SO_4$ media, U(VI) was adsorbed and Ti(IV) was eluted, as is shown in Fig. 2. Therefore, the media are useful for the separation of Ti(IV) in samples of a uranium matrix.

The media usually used for the elution of Ta(V) from the anion-exchange resin are composed of highly concentrated salts or acids, *e.g.*, 1 M NH_4F-4 M NH_4Cl[7] or 5 M HF-12 M HNO_3.[10] Using 4M HF-2M H_3BO_3-1 M HNO_3, as is shown in Fig. 2 (e), Ta(V) can be eluted from the column.

It is obvious from the above examples that the $HF-H_3BO_3$ media are useful for the effective mutual separation of hard acid-metal ions. In the practical mutual separation of two components, in order to reduce the volume of the effluents it is recommended that, after one metal ion is completely eluted from the column, the other ion should be then eluted by the use of a different composition of the eluent in which the other ion has a low K_d value. Zirconium(IV), W(VI), and U(VI) are quantitatively eluted by 100 ml of 0.1 M HF-0.5 M H_3BO_3-1 M HCl, 150 ml of 0.5 M HF-0.5 M H_3BO_3-1 M HCl, and 120 ml of 0.1 M HF-0.5 M H_3BO_3-0.5 M H_2SO_4 respectively.

In addition, the fluoroboric acids in the effluent can easily be evaporated prior to the subsequent determination. The elution behavior of metal ions are not affected by the amount of metal ions, as is demonstrated in Fig. 2, because the $HF-H_3BO_3$ media have a buffer action relating to C_{F^-}, as has already been mentioned.[1].

Because hydrofluoric acid is indispensable in the dissolution of most hard acid-metals, it should be stressed that the $HF-H_3BO_3$ media will be useful for the consecutive separation of metals in a matrix of hard acid-metals.

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