A Comparative Study on the Synthesis and Ion-exchange Behaviour of Tin(IV) Salts of Different Heteropolyanions. Separations of Metal Ions on Tin(IV) Boratomolybdate Columns

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Various samples of tin(IV) boratomolybdate, tin(IV) boratotungstate, tin(IV) boratophosphate, tin(IV) arsenatoborate and tin(IV) boratosulfate has been synthesized by mixing aqueous solutions of appropriate reagents in different volume ratios at pH=1. One of the samples of tin(IV) boratomolybdate has been studied in greater detail for its ion-exchange capacity, thermal and chemical stability, pH-titration and chemical composition. A comparison of few properties of tin(IV) boratomolybdate has been made with other tin(IV) salts of different heteropolyanions. Distribution coefficients of 24 metal ions on tin(IV) boratomolybdate in water, nitric acid, water–dioxane, and nitric acid–dioxane systems have been determined. The effect of temperature on the sorption behaviour of metal ions has also been studied. It has been found that K_d value increases in general with the increase in temperature. The differential selectivity of metal ions on tin(IV) boratomolybdate reveals that tin(IV) boratomolybdate is a useful ion exchanger for the separation of metal ions. As a result ten important separations have been quantitatively achieved on the columns of this ion-exchange material.

The wide spread applications of synthetic inorganic ion-exchangers has now been well established.[1] Recently they have been found useful in portable renal dialysis units. Simple salts of metals as ion-exchanger have been much studied as compared to double salts. Earlier studies[2-4] show that mixed salts usually exhibit higher ion-exchange capacities and better thermal and chemical stability as compared to simple salts. A literature survey shows that a number of tin(IV) salts[5-8] have been studied as ion-exchangers. But no systematic comparison has been made on the ion exchange properties of these materials. In the present paper we therefore describe a comparative study on the synthesis and ion-exchange behaviour of a new series of tin(IV) ion-exchangers based on boron. Tin(IV) boratomolybdate have been chosen for detailed study owing to its high exchange capacity and better chemical stability.

Experimental

Reagents. Tin(IV) chloride pentahydrate (Reachim U.S.S.R.), potassium tetraborate (B. D. H.), ammonium molybdate (B. D. H.) sodium tungstate (B. D. H.); sodium arsenate (B. D. H.); sodium sulfate (E. Merck) and potassium dihydrogenphosphate (E. Merck) were used. Other chemicals were of analytical reagent grade.

Apparatus. The spectrophotometry and pH-measurements were performed using Bausch & Lomb Spectronic 20 Colorimeter, Elico LI-10 pH-meter respectively. A temperature controlled shaker "SICO" was used for shaking.

Synthesis. Samples of tin(IV) boratophosphate, tin(IV) boratosulfate, tin(IV) arsenatoborate, tin(IV) boratotungstate, tin(IV) boratomolybdate were prepared by mixing aqueous solutions of appropriate reagents under the conditions indicated in Table 1a—e. The desired pH was adjusted by adding either dilute hydrochloric acid solution or dilute sodium hydroxide solution. The precipitate so formed was allowed to settle down for 24 h washed several times with demineralized water (DMW) and filtered under suction. It was then dried at 40 °C in an oven. The dried material was then treated with DMW resulting cracking of the substance into smaller particles with slight evolution of heat. To convert the sample in hydrogen ion form, the material was kept for 48 h in 1 mol dm^{-3} nitric acid solutions. It was then washed with DMW to remove excess acid. Tin(IV) boratomolybdate sample (TBM_1) has been chosen for detailed study owing to its higher ion-exchange capacity and higher chemical stability as compared to other materials.

Ion-exchange Capacity. To determine the ion-exchange capacity of the sample, 0.5 g of the ion-exchanger material in hydrogen form was placed in column with glass wool support. The hydrogen ions were eluted with 1 mol dm^{-3} solution of different salt (Table 2). The hydrogen ions released from the exchanger were then determined by titrating the effluent with standard solution of sodium hydroxide. The ion-exchange capacities for Cu(II), Al(III), and Fe(III) were determined as follows.

10 cm^3 solution of the metal ion of known strength was passed through 1 g exchanger in hydrogen form with a flow rate of 1.2 cm^3 min^{-1}. The effluent was passed through the column several times to ensure replacement of maximum hydrogen ion of the exchanger. The column was then

Table 1a. Synthesis and properties of tin(IV) boratophosphate (TBP)

Sample No.	Conditions of synthesis: $SnCl_4 \cdot 5H_2O$ (mol dm^{-3})	$K_2B_4O_7$ (mol dm^{-3})	KH_2PO_4 (mol dm^{-3})	Mixing ratio (v/v/v)	pH	Appearance of precipitate	Appearance of beads after drying at 40 °C	IEC[a] for K^+ (mequiv./dry g)
TBP_1	0.05	0.05	0.05	1:2:1	0—1	White gelatinous	White opaque	0.77
TBP_2	0.05	0.05	0.05	1:1:2	0—1	White gelatinous	White opaque	1.10
TBP_3	0.05	0.05	0.05	2:1:1	0—1	White gelatinous	White opaque	0.73
TP	0.05	—	0.05	1:2	0—1	White gelatinous	White opaque	0.20

Yield order: $TP > TBP_2 > TBP_3 > TBP_1$. a) Ion exchange capacity.

Table 1b. Synthesis and properties of tin(IV) boratosulfate (TBS)

Sample No.	Conditions of synthesis					Appearance of precipitate	Appearance of beads after drying at 40 °C	IEC for K^+ (mequiv./dry g)
	$SnCl_4 \cdot 5H_2O$ (mol dm^{-3})	$K_2B_4O_7$ (mol dm^{-3})	Na_2SO_4 (mol dm^{-3})	Mixing ratio (v/v/v)	pH			
TBS_1	0.05/2	0.05	0.05	1:2:1	0—1	White gelatinous	White opaque	0.55
TBS_2	0.05/2	0.05	0.05	1:1:2	0—1	White gelatinous	White opaque	0.40
TBS_3	0.05/2	0.05	0.05	2:1:1	0—1	White gelatinous	White opaque	0.22
TBS_4	0.05	0.05	0.05	1:2:1	0—1	White gelatinous	White opaque	0.35
TS	0.05	—	0.05	1:1	0—1	White gelatinous	White opaque	0.17

Yield order: $TBS_3 > TBS_1 > TBS_2 > TBS_4 > TS$.

Table 1c. Synthesis and properties of tin(IV) arsenatoborate (ABA)

Sample No.	Conditions of synthesis					Appearance of precipitate	Appearance of beads after drying at 40 °C	IEC for K^+ (mequiv./dry g)
	$SnCl_4 \cdot 5H_2O$ (mol dm^{-3})	$K_2B_4O_7$ (mol dm^{-3})	Na_2AsO_4 (mol dm^{-3})	Mixing ratio (v/v/v)	pH			
TBA_1	0.05	0.05	0.05	1:2:1	0—1	White gelatinous	White opaque	0.96
TBA_2	0.05	0.05	0.05	1:1:2	0—1	White gelatinous	White opaque	0.96
TBA_3	0.05	0.05	0.05	2:1:1	0—1	White gelatinous	White opaque	0.73
TA	0.05	—	0.05	1:1	0—1	White gelatinous	White opaque	0.99

Yield order: $TBA_3 > TBA_2 > TBA_1 > TA$.

Table 1d. Synthesis and properties of tin(IV) boratotungstate (TBT)

Sample No.	Conditions of synthesis					Appearance of precipitate	Appearance of beads after drying at 40 °C	IEC for K^+ (mequiv./dry g)
	$SnCl_4 \cdot 5H_2O$ (mol dm^{-3})	$K_2B_4O_7$ (mol dm^{-3})	Na_2WO_4 (mol dm^{-3})	Mixing ratio (v/v/v)	pH			
TBT_1	0.05	0.05	0.05	1:2:1	0—1	White gelatinous	Dirty white shiny	1.1
TBT_2	0.05	0.05	0.05	1:1:2	0—1	White gelatinous	Yellowish green	1.3
TBT_3	0.05	0.05	0.05	2:1:1	0—1	White gelatinous	White shiny	0.88
TT	0.05	—	0.05	1:2	0—1	White gelatinous	Yellowish green	1.15

Yield order: $TBT_3 > TBT_1 > TT > TBT_2$.

Table 1e. Synthesis and properties of tin(IV) boratomolybdate (TBM)

Sample No.	Conditions of synthesis					Appearance of precipitate	Appearance of beads after drying at 40 °C	IEC for K^+ (mequiv./dry g)
	$SnCl_4 \cdot 5H_2O$ (mol dm^{-3})	$K_2B_4O_7$ (mol dm^{-3})	$(NH_4)_6Mo_7O_{24}$ (mol dm^{-3})	Mixing ratio (v/v/v)	pH			
TBM_1	0.05	0.05	0.05	1:2:1	0—1	Gelatinous yellowish	Yellowish shiny	1.12
TBM_2	0.05	0.05	0.05	1:1:2	0—1	White granular	White fine powder dispersed when immersed in water	—
TBM_3	0.05	0.05	0.05	2:1:1	0—1	Gelatinous yellowish	Yellowish shiny	0.88
TM_1	0.05	—	0.05	1:2	0—1	White granular	White fine powder dispersed when immersed in water	—
TM_2	0.05	—	0.05	1:1	0—1	Gelatinous yellowish	Yellowish	0.68
TB	0.05	0.05	—	1:2	0—1	White gelatinous	White opaque	0.11

Yield order: $TBM_1 = TBM_3 > TM_2 > TB$.

washed with water till the effluent free from metal ions. The whole effluent is titrated with standard EDTA solution. The amount of metal ions adsorbed by the exchanger was calculated. The ion-exchange capacity for different metal ions is reported in Table 2.

Thermal Treatment. To examine the effect of drying temperature on the ion-exchange capacity the materials were heated at different temperatures in Muffle Furnace for 1 h. The ion-exchange capacity for potassium ion at different drying temperatures is given in Table 3.

pH-titration. pH-titrations for sample TBM_1 was performed by the earlier method[9] using sodium chloride–sodium hydroxide system. The pH titration curve is shown in Fig. 1.

Chemical Stability. A 0.5 g of the exchanger material (sample TBM_1) was equilibrated with 50 cm^3 of the solution of analytical interest at room temperature (25±2 °C) and kept for 24 h with occasional shaking. Tin and molybdenum released in the solution were determined spectrophotometrically using hematoxylin[10] and thiocyanate[11] as colouring reagents respectively. The amount of boron released in the solvent was determined titrimetrically[12] using sodium hydroxide as titrant. The results are summarized in Table 4.

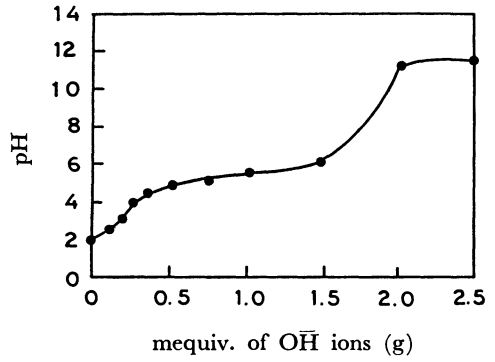

Fig. 1. pH titration curve of tin(IV) boratomolybdate.

Chemical Composition. For the determination of chemical composition of sample TBM_1, 0.2 g of exchanger was dissolved in hot concentrated hydrochloric acid. Then the solution was diluted to 100 cm^3 with water. Tin and molybdenum were determined spectrophotometrically[10,11] while boron is determined titrimetrically.[12] The mole ratio of Sn, B, and Mo is found to 1:1:1.

Distribution Coefficient. The distribution coefficient (K_d) for 24 metal ions in different solution system were determined. 0.5 g of exchanger in hydrogen form (150—200 mesh size) was treated with 50 cm^3 of cation solution in 250 cm^3 Erlenmeyer flask. The mixture was then shaken for 6 h at 25±2 °C in a shaker incubator. The ionic strengths of various metal ion solutions lies between 0.0006 to 0.0057. The amount of cation left in the solution was then determined by titrating against the standard solution of EDTA. The K_d values were calculated according to the formula,

$$K_d = \frac{I-F}{F \times W} \times 50,$$

where F is the volume of EDTA consumed by the solution after equilibrium, I is the volume of EDTA consumed by the original solution (*i.e.* before equilibrium) and W is the weight of ion exchanger in g.

The results of K_d values are summarized in Table 5. The adsorption of metal ions was also studied at different temperatures. The effect of temperature on K_d (values) are described in Table 6 and in Fig. 2.

Quantitative Separations. For separation purpose the column was prepared using 2.0 g of exchanger (150—200

Table 2. Ion exchange capacity (mequiv./dry g) of different tin(IV) based ion exchangers for various cations

Sample No.	Cations	Salt used	pH	Hydrated radii[17) Å	TBP_2	TBS_4	TBT_2	TBM_1
1	Li^+	LiCl	6.8	10.0	0.26	0.18	0.37	0.84
2	Na^+	$NaNO_3$	6.8	7.9	0.42	0.33	0.62	0.90
3	K^+	KCl	6.8	5.3	1.10	0.35	1.30	1.12
4	Mg^{2+}	$Mg(NO_3)_2$	6.2	10.8	0.41	0.42	0.40	0.52
5	Ca^{2+}	$Ca(NO_3)_2$	6.2	9.6	0.54	0.40	0.44	0.77
6	Sr^{2+}	$Sr(NO_3)_2$	6.2	9.6	0.34	0.36	0.21	0.46
7	Ba^{2+}	$Ba(NO_3)_2$	6.2	8.8	0.48	0.35	0.41	0.68
8	Cu^{2+}	$Cu(NO_3)_2$	—	—	0.40	0.91	0.28	0.79
9	Al^{3+}	$Al(NO_3)_3$	—	—	0.23	0.24	0.23	0.29
10	Fe^{3+}	$FeCl_3$	—	—	0.68	0.72	0.68	0.71

Table 3. Effect of drying temperature on the ion exchange capacity (mequiv./dry g for K^+) for tin(IV) based ion exchangers

Sample No.	Temp/°C	TBP_2	TBS_4	TBT_2	TBM_1
1	40	1.10 (white)	0.35 (white)	1.30 (light yellow)	1.12 (yellow)
2	100	0.50 (white)	0.33 (white)	1.20 (light yellow)	0.33 (yellow)
3	200	0.46 (white)	0.32 (white)	0.19 (brown)	0.22 (greenish yellow)
4	300	0.41 (light yellow)	0.31 (white)	0.18 (brownish black)	0.17 (greenish)
5	400	0.36 (light yellow)	0.28 (yellowish)	0.17 (brownish black)	0.13 (grey)
6	500	0.29 (yellowish)	0.22 (yellowish green)	0.14 (brownish black)	0.08 (dark grey)
7	600	0.23 (yellow)	0.14 (light green)	0.13 (brownish black)	0.04 (dark grey)
8	800	0.21 (grey)	0.08 (green)	0.09 (brownish black)	0.00 (greyish white)

Table 4. Chemical stability of sample TBM_1

Sample No.	Solvents	Tin(IV) released (mg/50 cm^3)	Mo released (mg/50 cm^3)	B released (mg/50 cm^2)
1	Water	0.40	0.18	0.22
2	0.1 mol dm^{-3} HNO_3	0.55	—	0.54
3	0.5 mol dm^{-3} HNO_3	0.60	0.60	0.74
4	1 mol dm^{-3} HNO_3	0.70	0.75	0.83
5	0.1 mol dm^{-3} HCl	0.55	—	0.44
6	0.5 mol dm^{-3} HCl	1.45	0.38	0.69
7	1 mol dm^{-3} HCl	1.55	0.63	0.93
8	0.1 mol dm^{-3} $HClO_4$	0.55	—	0.43
9	0.5 mol dm^{-3} $HClO_4$	1.05	0.38	0.65
10	1 mol dm^{-3} $HClO_4$	1.20	0.91	0.91
11	0.1 mol dm^{-3} H_2SO_4	0.80	—	0.67
12	0.5 mol dm^{-3} H_2SO_4	1.45	0.35	0.79
13	1 mol dm^{-3} H_2SO_4	1.70	0.61	1.35
14	0.05 mol dm^{-3} NaOH	3.15	0.75	1.52
15	0.1 mol dm^{-3} NaOH		Completely dissolved	
16	0.05 mol dm^{-3} KOH	2.20	0.64	1.21
17	0.1 mol dm^{-3} KOH		Completely dissolved	
18	0.05 mol dm^{-3} LiOH	1.55	0.60	0.78
19	0.1 mol dm^{-3} LiOH		Completely dissolved	
20	1 mol dm^{-3} KCl	0.0	0.0	0.0
21	1 mol dm^{-3} $NaNO_3$	0.40	0.18	0.42

Table 5. Distribution coefficients (ml/g) of metal ions on tin(IV) boratomolybdate (sample TBM_1) at 25±2 °C

Sample No.	Metal ion	Water	0.01 mol dm^{-3} HNO_3	Dioxane: Water (1:4)	Dioxane: Water (4:1)	Dioxane: 0.01 mol dm^{-3} HNO_3 (1:1)
1	Ni^{2+}	309±5	70±5	800±20	71±5	100±5
2	Fe^{3+}	47±7	29±5	62±5	36±5	24±5
3	Cu^{2+}	497±12	10±2	856±30	335±5	49±5
4	Mn^{2+}	300±5	71±5	380±5	160±5	100±5
5	Co^{2+}	167±5	60±5	182±6	101±5	60±5
6	Vo^{2+}	461±10	79±5	490±5	1375±40	353±5
7	Hg^{2+}	11400±12	70±5	5650±50	383±5	1433±35
8	Zn^{2+}	257±5	55±5	89±5	99±5	62±5
9	Pb^{2+}	24900±240	245±5	733±20	257±5	2400±44
10	Cd^{2+}	28900±300	152±5	318±8	32±5	59±5
11	Ca^{2+}	860±20	153±5	380±5	380±5	4700±136
12	Mg^{2+}	184±5	26±5	145±5	78±5	29±5
13	Ba^{2+}	500±20	58±5	1400±50	650±8	25±5
14	Ce^{4+}	200±5	140±5	100±5	200±5	20±5
15	Al^{3+}	300±5	188±5	136±5	1200±40	136±5
16	Zr^{4+}	1600±25	1550±20	1600±50	410±5	1175±30
17	Th^{4+}	2500±32	165±5	1225±42	1225±45	440±5
18	Sr^{2+}	174±5	33±5	209±5	152±5	32±5
19	Ho^{3+}	265±5	90±5	133±5	71±5	105±5
20	Dy^{3+}	135±5	132±5	115±5	67±5	104±5
21	Nd^{3+}	583±12	162±5	229±8	67±5	104±5
22	Sm^{3+}	560±11	450±10	132±5	210±5	209±5
23	Pr^{3+}	580±15	390±8	156±5	97±5	412±5
24	La^{3+}	695±14	420±10	306±20	76±5	97±5

Table 6. Distribution coefficients (ml/g) of metal ions on tin(IV) boratomolybdate (TBM_1) in 0.005 mol dm^{-3} HNO_3 at different temperatures

Sample No.	Metal ions	22±1 °C	50±1 °C	75±1 °C
1	Ni^{3+}	57±5	157±5	463±12
2	Fe^{3+}	33±5	62±5	100±5
3	Cu^{2+}	49±5	1812±50	9460±180
4	Mn^{2+}	107±5	700±10	2900±84
5	Co^{2+}	125±5	1988±52	10340±156
6	Vo^{+2}	60±5	136±5	136±5
7	Hg^{2+}	10±2	17±5	54±5
8	Zn^{2+}	112±5	507±5	2328±45
9	Pb^{2+}	1900±50	24900±170	49900±200
10	Cd^{2+}	181±5	1080±36	3943±60
11	Ca^{2+}	109±5	1100±22	3100±50
12	Mg^{2+}	75±5	657±10	3686±84
13	Ba^{2+}	300±5	650±12	3650±80
14	Ce^{4+}	150±5	320±6	443±10
15	Al^{3+}	30±5	73±5	420±5
16	Zr^{4+}	53±5	628±5	750±5
17	Th^{4+}	152±5	382±5	430±5
18	Sr^{2+}	109±5	860±20	3100±80
19	Ho^{3+}	80±5	5020±145	25500±163
20	Dy^{3+}	117±5	6420±120	32500±145
21	Nd^{3+}	328±5	8460±60	42200±210
22	La^{3+}	527±5	13700±150	68900±320
23	Sm^{3+}	225±5	12900±135	64900±316
24	Pr^{3+}	553±5	5020±120	25500±225

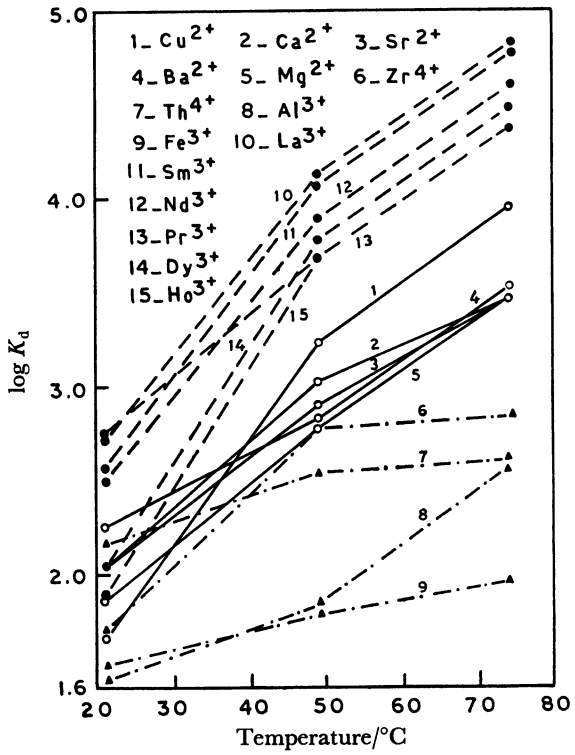

Fig. 2. Plot log K_d *vs.* temperature.

mesh size) in hydrogen form in a glass tube of internal diameter 0.6 cm in each case. A mixture of metal ion solution was applied on the column. The solution was allowed to flowdown very slowly through the column as a result metal ions are adsorbed at the top of exchanger bed forming initial zone. The column was washed with water. The metal ions were then eluted by appropriate eluting reagent. The flow rate of effluent was maintained 1.4 cm^3 min^{-1} throughout the elution process. The effluent was collected in 10 cm^3 fractions and titrated with 0.002 mol dm^{-3} EDTA solution. Ten important separations of metal ions have been quantitatively achieved. The elution curves for each set of separation are shown in Figs. 3(a)—(c).

Results and Discussion

Tables 1a to 1e describe the preprations of samples of tin(IV) salts of different heteropolyanions under identical conditions. Ion exchange capacity of each samples has been compared with single salts prepared under the same conditions. It has been observed that capacity of double salts is higher than the single salts with the exception of tin(IV) boratophosphate and tin(IV) arsenatoborate. An interesting feature is emerged when tin(IV) boratosulfate is compared with tin(IV) sulfate, the latter has a negligible ion-exchange capacity (0.17 mequiv./dry g). Moreover the capacity is significantly increased for sample TBS_1 (0.55 mequiv./dry g). It is important to note that mixing volume ratio of different components affect the ion-exchange capacity of the final product. Also in the case of tin(IV) boratomolybdate the exchange capacity becomes almost two times as high as the exchange capacity of single salts namely tin(IV) molybdate and tin(IV) borate prepared under the same conditions. The order of ion-exchange capacity (for K^+ ions) for tin(IV) salts of different heteropolyanions is as follows:

> Tin(IV) boratotungstate (TBT_2)>Tin(IV) boratomolybdate (TBM_1)>Tin(IV) boratophosphate(TBP_2) >Tin(IV) arsenatoborate (TBA_1, TBA_2)> Tin(IV) boratosulfate (TBS_1).

Results of Table 4 show that tin(IV) boratomolybdate is quite stable in water, hydrochloric acid, perchloric acid, nitric acid, sulfuric acid, and in common salts of moderate concentrations. This material appreciably dissolves in 0.01 mol dm^{-3} solutions of LiOH, NaOH, and KOH on prolonged shaking. The material is apparently stable in various common organic solvents like acetone, dioxane, ethanol, acetaldehyde, formic acid, acetic acid, tartaric acid, and citric acid. Tin(IV) boratomolybdate is relatively more chemically stable than tin(IV) molybdate prepared earlier.[13,14]

Results of Table 2 show that the exchange capacity of all the compounds increases with the decrease in hydrated radii. The ion exchange capacity followed the order $K^+>Na^+>Li^+$ for alkali metals. However, for alkaline earths the exchange capacity remains almost the same as hydrated radii do not vary appreciably.

It is apparent from Table 3 that tin(IV) boratophosphate, tin(IV) boratosulfate, tin(IV) boratomolybdate, and tin(IV) boratotungstate loose ion exchange capacity as the drying temperature of the material is subsequently increased. The thermal stability of these materials can be represented in the order $TBS_4>$

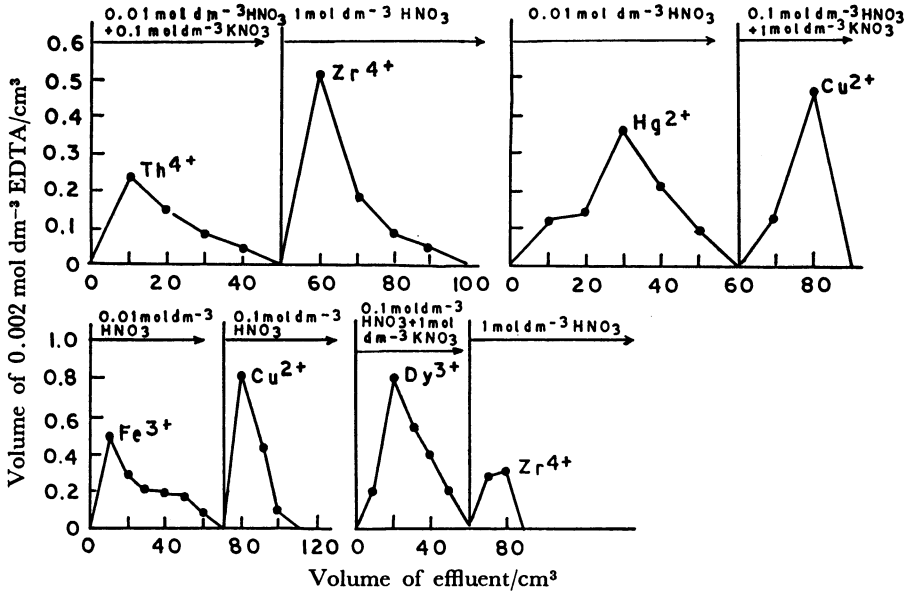

Fig. 3(a). Separation of Th^{4+}-Zr^{4+}, Hg^{2+}-Cu^{2+}, Fe^{3+}-Cu^{2+}, and Dy^{3+}-Zr^{4+}.

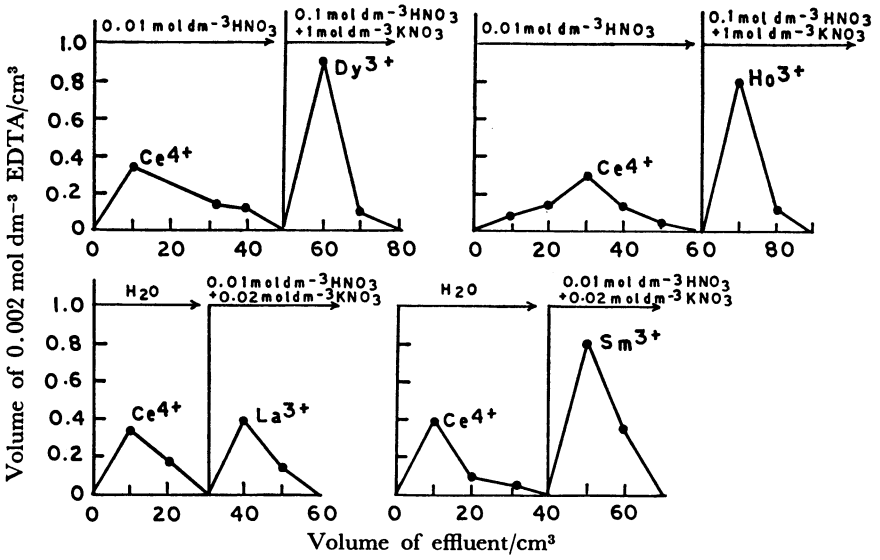

Fig. 3(b). Separation of Ce^{4+}-Dy^{3+}, Ce^{4+}-Ho^{3+}, Ce^{4+}-La^{3+}, and Ce^{4+}-Sm^{3+}.

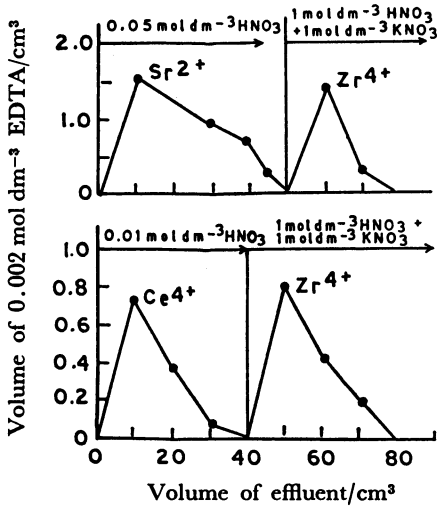

Fig. 3(c). Separation of Sr^{2+}-Zr^{4+} and Ce^{4+}-Zr^{4+}.

$TBP_2 > TBM_1 > TBT_2$. It is observed however, in the case of tin(IV) boratosulfate, the increasing temperature does not affect the capacity significantly. Tin(IV) boratotungstate and tin(IV)boratomolybdate lost their exchange capacity more than 70% when their drying temperature increased to 100 °C. The capacity falls to a negligible value when the drying temperature is raised upto 500 °C (0.08 mequiv./dry g for tin(IV) boratomolybdate and 0.14 mequiv./dry g for tin(IV) boratotungstate). This may be due to conversion of material into their oxides as is also indicated by their colors at these temperatures. Tin(IV) boratotungstate is more thermally stable than tin(IV) tungstate[15] and also tin(IV) boratomolybdate is more stable than tin(IV) molybdate.[13] Tin(IV) boratosulfate and tin(IV) boratophosphate retain their exchange capacity to a greater extent. The capacity of boratosulfate remains almost the same up to 300 °C. Tin(IV) boratophosphate and tin(IV) boratosul-

fate can be conveniently used as ion exchangers even when the drying temperature is raised up to 500 °C. However, when these materials (dried at 40 °C) are heated at 95±5 °C in the presence of water no loss in ion-exchange capacity is observed in all the cases.

pH titration curve (Fig. 1) for NaCl–NaOH system indicates two breaks in the curve showing thereby that tin(IV) boratomolybdate behaves as a bifunctional weak cation exchanger.

It is clear from Table 5 that values of distribution coefficients vary with the composition and nature of solvent system. The K_d values of metal ions are decreasing in general with the increase in dioxane content of the medium. The increased amount of dioxane in dioxane–water system decreases the dielectric constant and thus decreases the K_d value. This is probably due to the fact that the ions of an electrolyte are more ionized in a solvent of relatively high dielectric constant. However, a definite conclusion can only be drawn in the presence of other experimental data. An increase in the K_d value for most metal ions are also observed as one goes from pure dilute acid (0.01 mol dm^{-3}) to a mixture of dioxane+0.01 mol dm^{-3} HNO_3 in 1:1 volume ratio and the increase in the pH of the solvent causes higher adsorption of metal ions as expected.

A study of the adsorption of metal ions on tin(IV) boratomolybdate at different temperatures reveals that extent of adsorption increases with the increase in temperature (Table 6). Thus K_d values are found to be highest in 75±1 °C. From Fig. 2 it can be concluded that the K_d value for quadrivalent and rare earth metal ions increases sharply below 50 °C and then slowly after this temperature.

The sequence of K_d values of some important metal ions in different solvent systems and at different temperatures on tin(IV) boratomolybdate can be shown as follows:

Water	$Th^{4+}>Zr^{4+}>La^{3+}>Nd^{3+}>Pr^{3+}>Sm^{3+}>Ho^{3+}>Ce^{4+}>Dy^{3+}$
0.01 mol dm^{-3} HNO_3	$Zr^{4+}>Sm^{3+}>La^{3+}>Pr^{3+}>Th^{4+}>Nd^{3+}>Ce^{4+}>Dy^{3+}>Ho^{3+}$
Dioxane:Water (1:4)	$Zr^{4+}>Th^{4+}>La^{3+}>Nd^{3+}>Pr^{3+}>Ho^{3+}>Sm^{3+}>Dy^{3+}>Ce^{4+}$
Dioxane:Water (4:1)	$Th^{4+}>Zr^{4+}>Sm^{3+}>Ce^{4+}>Pr^{3+}>Nd^{3+}>La^{3+}>Ho^{3+}>Dy^{3+}$
Dioxane:0.01 mol dm^{-3} HNO_3 (1:1)	$Zr^{4+}>Th^{4+}>Pr^{3+}>Sm^{3+}>Nd^{3+}>Ho^{3+}>Dy^{3+}>La^{3+}>Ce^{4+}$
0.005 mol dm^{-3} HNO_3 (22±1 °C)	$Pr^{3+}>La^{3+}>Nd^{3+}>Sm^{3+}>Th^{4+}>Ce^{4+}>Dy^{3+}>Ho^{3+}>Zr^{4+}$
0.005 mol dm^{-3} HNO_3 (50±1 °C)	$La^{3+}>Sm^{3+}>Nd^{3+}>Dy^{3+}>Ho^{3+}=Pr^{3+}>Zr^{4+}>Th^{4+}>Ce^{4+}$
0.005 mol dm^{-3} HNO_3 (75±1 °C)	$La^{3+}>Sm^{3+}>Nd^{3+}>Dy^{3+}>Ho^{3+}=Pr^{3+}>Zr^{4+}>Ce^{4+}>Th^{4+}$

The sorption studies on tin(IV) boratomolybdate for different metal ions reveal many important separations. As a result ten binary separations of analytical and industrial importance have been achieved successfully on small columns of tin(IV) boratomolybdate (Figs. 3(a)—3(c)). Separation of iron from copper may be utilized in the removal of iron impurities from chalcopyrite ($CuFeS_2$) and Bornite (Cu_5FeS_4) ores.

In the determination of thorium as oxalate good separation from zirconium can not be achieved because of the possible hydration of zirconium.[16] Zirconium also seriously interferes probably in all the spectrophotometric determination of thorium by various coloring reagents such as thoron, dinitrosochromotropic acid, quercetin, SPADN, and Di SNADNS.[16] Therefore columns of tin(IV) boratomolybdate can be conveniently used for separating zirconium impurities prior to the determination of thorium. Tin(IV) boratomolybdate can also be utilized for the recovery of zirconium free thorium from thorianite.

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