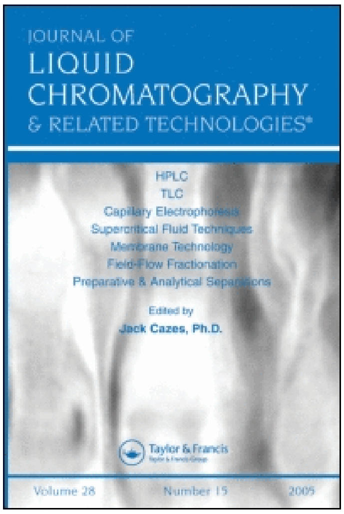

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

A Comparative Study of the Synthesis and Ion Exchange Properties of Iodophosphates of Tin(IV), Zirconium(IV) and Iron(III): Separations of Metal Ions on Tin(IV)-iodophosphate Columns

Syed Ashfaq Nabi[a]; Rifaqat Ali Khan Rao[a]; Weqar Ahmad Siddiqi[a]
[a] Department of Chemistry, Aligarh Muslim University, Aligarh, India

To cite this Article Nabi, Syed Ashfaq , Rao, Rifaqat Ali Khan and Siddiqi, Weqar Ahmad(1983) 'A Comparative Study of the Synthesis and Ion Exchange Properties of Iodophosphates of Tin(IV), Zirconium(IV) and Iron(III): Separations of Metal Ions on Tin(IV)-iodophosphate Columns', Journal of Liquid Chromatography & Related Technologies, 6: 4, 777 — 794

To link to this Article: DOI: 10.1080/01483918308076084

URL: http://dx.doi.org/10.1080/01483918308076084

JOURNAL OF LIQUID CHROMATOGRAPHY, 6(4), 777-794 (1983)

A COMPARATIVE STUDY ON THE SYNTHESIS AND ION EXCHANGE PROPERTIES OF IODOPHOSPHATES OF TIN(IV), ZIRCONIUM(IV) AND IRON(III): SEPARATIONS OF METAL IONS ON TIN(IV)-IODOPHOSPHATE COLUMNS.

Syed Ashfaq Nabi, Rifaqat Ali Khan Rao, Weqar Ahmad Siddiqi

Department of Chemistry,
Aligarh Muslim University,
Aligarh-202001 (India).

ABSTRACT

Iodates and iodophosphates of tin(IV), zirconium(IV) and iron(III) have been synthesized under varying conditions and studied their ion exchange behaviour. Among the various ion exchangers synthesized, tin(IV)-iodophosphate is chosen for detailed study owing to its highest ion exchange capacity and highest chemical stability. The most stable sample is prepared by mixing 0.1M stannic chloride, 0.1M potassium iodate and 0.1M potassium dihydrogen orthophosphate solutions in the volume ratio 1:1:2 respectively at pH 0-1. It is a monofunctional weak cation exchanger. Its ion exchange capacity for K^+ is 1.6 meq/dry g. The thermal and chemical stabilities of this material have been determined and compared with Zr(IV)-phosphoiodate. Effect of heating on the properties of tin(IV)-iodophosphate has been determined. To explore the separation potential of tin(IV)-iodophosphate Kd values of different metal ions have been determined in organic solvents. A number of important separations of metal ions of industrial utility have been successfully achieved on the columns of tin(IV)-iodophosphate.

INTRODUCTION

Various synthetic inorganic ion exchangers which have been developed so far are mostly based on arsenate, phosphate, tungstate, molybdate and selenite of metals (1-6). As far as we are aware iodates of metals have not been studied as ion exchange materials. However, zirconium(IV)-phosphoiodate has been recently reported to show amphoteric behaviour (7). But this material has been mainly studied as an electron exchanger. No systematic studies have been reported on its cation or

0148-3919/83/0604-0777$3.50/0

anion exchange properties. The present work was, therefore, undertaken to synthesize iodates and iodophosphates of different metals and to compare their ion exchange properties in a systematic manner. Among the various ion exchangers which have been synthesized, tin(IV)-iodophosphate was found to possess highest ion exchange capacity and chemical stability and therefore was chosen for detailed studies. The following pages summarize our findings in this direction.

EXPERIMENTAL

Reagents: Tin(IV) chloride pentahydrate (Reachim U.S.S.R.), potassium iodate (E.Merk), potassium dihydrogen-orthophosphate (B.D.H.), zirconium oxychloride (B.D.H.), ferric nitrate (B.D.H.) were used. Other chemicals were of analytical reagent grade.

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

Synthesis: Samples of iron(III)-iodophosphate, iron(III), iodate, zirconium(IV)-iodophosphate, zirconium(IV)-iodate, tin(IV)-iodophosphate and tin(IV)-iodate were prepared by mixing aqueous solutions of appropriate reagents under the conditions indicated in Tables I, II and III.

The desired pH was adjusted by adding either concentrated nitric acid solution or dilute sodium hydroxide solution. The precipitate so formed was allowed to settle down for 24 hrs, 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 into hydrogen form, the material was kept for 48 hrs in 0.1M nitric acid solution. It was then washed with DMW to remove excess acid. Tin(IV)-iodophosphate (sample TIP_5) has been chosen for detailed study owing to its higher ion exchange capacity and higher chemical stability as compared to other materials.

TABLE - I. Synthesis and properties of iodates and iodophosphates of Fe(III).

Sample number	Conditions of synthesis					Appearance of precipitate	Appearance of beads after drying at 40° C	I.E.C. for K^+ meq/dry g
	$Fe(NO_3)_3$ moles/liter	KIO_3 moles/liter	KH_2PO_4 moles/liter	Mixing ratio V/V/V	pH			
FIP_1	0.1	0.1	0.1	1:1:1	1-2	White gelatinous	White opaque	1.03
FIP_2	0.1	0.1	0.1	1:2:1	1-2	"	"	0.82
FIP_3	0.1	0.1	0.1	1:1:2	1-2	"	"	0.91
FIP_4	0.1	0.1	0.1	2:1:1	1-2	Light yellow gelatinous	"	0.69
FI_5	0.1	0.1	-	1:1:0	1-2	Orange gelatinous	Orange opaque	1.17
FP_6	0.1	-	0.1	1:0:1	2-3	- Unstable -		-

I.E.C. = Ion exchange capacity.

TABLE - II. Synthesis and properties of iodates and iodophosphates of Zr(IV).

Sample number	Conditions of synthesis					Appearance of precipitate	Appearance of beads after drying at 40°C	I.E.C. for K^+ meq/dry g
	$ZrOCl_2$ moles/liter	KIO_3 moles/liter	KH_2PO_4 moles/liter	Mixing ratio V/V/V	pH			
ZI_1	0.1	0.1	-	1:1:0	1	White gelatinous	White shining	0.55
ZI_2	0.1	0.1	-	1:1:0	0-1	"	"	0.57
ZIP_3	0.1	0.1	0.1	1:1:1	0-1	"	"	1.01
ZIP_4	0.1	0.1	0.1	1:2:1	0-1	"	"	0.80
ZIP_5	0.1	0.1	0.1	1:1:2	0-1	"	"	1.41
ZIP_6	0.1	0.1	0.1	2:1:1	0-1	"	"	0.48

Yield order: $ZIP_4 > ZI_1 > ZIP_5 > ZIP_3 > ZI_2 > ZIP_6$

TABLE - III. Synthesis and properties of iodates and iodophosphates of Tin(IV).

Sample number	Conditions of synthesis					Appearance of precipitate	Appearance of beads after drying at 40°C	I.E.C. for K^+ meq/dry g
	$SnCl_4\ 5H_2O$ moles/liter	KIO_3 moles/liter	KH_2PO_4 moles/liter	Mixing ratio V/V/V	pH			
TI_1	0.1	0.1	-	1:1:0	0-1	White gelatinous	White shining	0.51
TI_2	0.1	0.1	-	1:1:0	0-1	"	White opaque	0.57
TIP_3	0.1	0.1	0.1	1:1:1	0-1	"	Yellowish white shining	1.50
TIP_4	0.1	0.1	0.1	1:2:1	0-1	"	White shining	1.31
TIP_5	0.1	0.1	0.1	1:1:2	0-1	"	White shining	1.60
TIP_6	0.1	0.1	0.1	2:1:1	0-1	"	"	1.24
TP_7	0.1	-	0.1	1:0:1	0-1	"	"	1.31

Yield order: $TIP_4 > TIP_3 > TIP_5 > TIP_6 > TI_1 > TI_2$

TABLE IV. Ion exchange capacity (meq/dry g) of iodophosphate of different metals for various cations.

Cations	Salts used	pH	FIP_1	ZIP_5	TIP_5
Li^+	$LiCl$	6.8	0.98	0.91	1.35
Na^+	$NaNO_3$	6.8	1.01	1.14	1.21
K^+	KCl	6.8	1.03	1.14	1.60
Rb^+	$RbCl$	6.2	0.89	1.37	1.41
Mg^{2+}	$Mg(NO_3)_2$	6.2	1.98	2.06	2.17
Ba^{2+}	$BaCl_2$	6.2	2.01	2.00	2.60
Sr^{3+}	$Sr(NO_3)_2$	6.2	1.82	2.17	2.43
Ca^{2+}	$Ca(NO_3)_2$	6.2	2.04	2.71	2.71

FIP_1 = Iron(III)-iodophosphate; ZIP_5 = Zirconium(IV)-iodophosphate; TIP_5 = Tin(IV)-iodophosphate.

Ion Exchange Capacity: The ion exchange capacity of different samples (150-200 mesh) of the ion exchange material in hydrogen form was determined by column method as reported earlier (1). The ion exchange capacity of the samples against different metal ions is reported in Table IV.

Thermal treatment: To examine the effect of heating on the properties of tin(IV)-iodophosphate, the material was heated at different temperature in muffle furnace for 1 hr. The results are summarized in Table V. The result compared with other tin(IV) based ion exchangers are given in Table VI.

pH-titration: pH-titrations for sample (TIP_5) were performed by the earlier method (8) using NaCl-NaOH, KCl-KOH, LiCl-LiOH and $BaCl_2$-$Ba(OH)_2$ systems. The pH titration curves are shown in figure 1.

Chemical stability: A 0.5 g of the ion exchange material (sample TIP_5) was equilibrated with 50 ml of the solvent of analytical interest at room temperature (25 ± 2°C) and kept for 24 hrs with occasional shaking. Tin and phosphate released in the solution

TABLE - V: Effect of heating on the properties of tin(IV) iodophosphate (TIP_5).

Temperature °C	Appearance	Amount taken for heating (mg)	Weight loss due to heating (mg)	I.E.C. for K^+ meq/dry g	Composition (m moles)		
					Tin(IV)	I	P
40	White	3500	0.0	1.60	0.150	0.102	0.634
100	White	3500	100	1.44	0.150	0.061	0.472
150	Pink	3500	250	1.33	0.145	0.061	0.382
200	Pink	3500	350	0.99	0.145	0.045	0.227
300	Pink	3500	420	0.72	0.145	0.045	0.110
400	Red	3500	430	0.66	0.145	0.045	0.085
500	Light brown	3500	490	0.44	0.145	0.045	0.075
600	Dark brown	3500	520	0.38	0.143	0.039	0.072
800	Dark brown	3500	540	0.24	0.140	0.035	0.065
950	Dark brown	3500	540	0.24	0.120	0.031	0.059

TABLE - VI. Effect of heating on ion exchange capacity of various tin(IV) based ion exchangers at pH (6.0 - 6.5).

Heating temperature °C	Ion exchange capacity (meq/dry g) for K^+												
	TP	TS	TSP	TTA	TMA	TAP	TVP	TM	TAn	TT	TV	TA	TIP_5
40	1.35	0.75	1.63	1.18	1.20	1.75	1.70	1.00	1.00	0.57	0.85	0.88	1.60
100	1.62	0.75	1.63	-	0.90	1.65	1.30	0.10	0.80	0.13	0.82	-	1.44
150	-	-	-	1.24	-	-	-	-	-	-	-	-	1.33
200	0.82	0.75	1.00	-	0.60	0.90	1.10	0.07	0.56	0.10	0.80	0.88	0.99
300	0.23	0.75	0.88	0.51	0.61	-	0.50	0.07	-	0.10	-	0.84	0.72
400	0.02	0.75	0.70	-	0.35	0.20	-	0.04	-	0.10	0.36	-	0.66
500	-	0.75	0.64	0.31	-	-	-	-	0.50	0.10	-	0.72	0.44
600	-	0.20	0.38	-	0.28	0.10	-	-	-	0.10	-	0.70	0.38
700	-	-	-	-	0.04	-	-	-	-	0.10	0.10	0.53	-
800	-	-	0.20	0.04	-	0.00	-	-	-	0.10	-	0.04	0.24

TP = tin(IV)-phosphate (15), TS = tin(IV)-selenite (6), TSP = tin(IV)-selenophosphate (14),
TTA = tin(IV)-tungstoarsenate (14), TMA = tin(IV)-molybdoarsenate (14), TAP = tin(IV)-arsenophosphate (14), TVP = tin(IV)-vanadophosphate (14), TM = tin(IV)-molybdate (5),
TAn = tin(IV)-antimonate (16), TT = Tin(V)-tungstate (17), TV = tin(IV)-vanadate (18),
TA = tin(IV)-arsenate (19), TIP_5 = tin(IV)-iodophosphate.

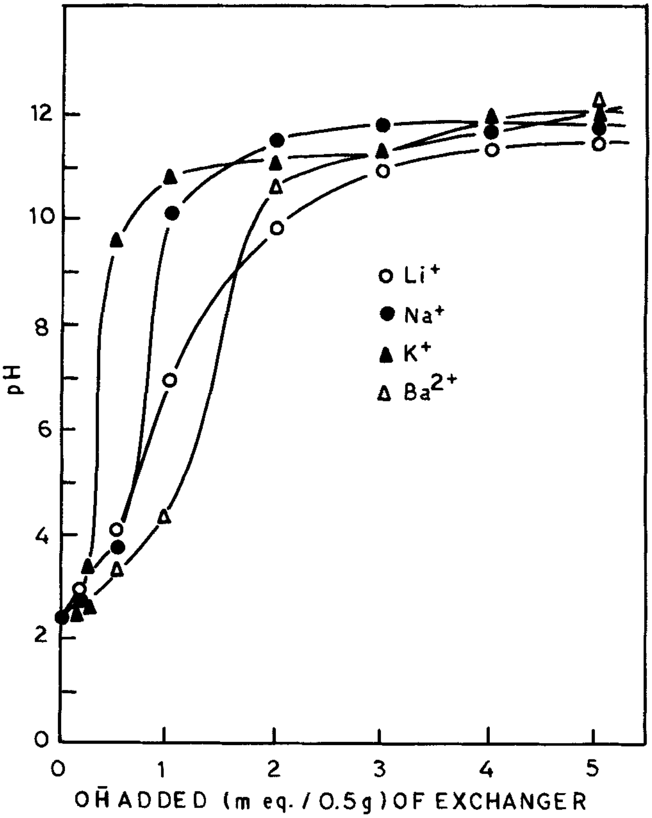

FIG. 1 pH Titration Curves of Tin(IV)-Iodophosphate

were determined spectrophotometrically using hematoxylin and ammonium molybdate as colouring reagents respectively (9,10). The amount of iodate released in the solvent was determined idometrically with standard sodium thiosulphate solution (11). The results are summarized in Table VII.

<u>Chemical Composition</u>: For the determination of chemical composition of sample TIP_5, 0.2 g of exchanger was dissolved in hot concentrated hydrochloric acid. Then the solution was diluted to 100 ml with water (DMW). Iodate and tin contents were determined titrimetrically by using sodium thiosulphate and potassium

TABLE VII. Chemical stability of tin(IV)-iodophosphate sample (TIP_5) in different solvents.

Solvent	Tin(IV) released mq/50 ml	IO_3^- released mq/50 ml	PO_4^{3-} released mq/50 ml
4M HCl	3.50	3.21	5.10
0.1M HNO_3	0.00	0.00	0.00
0.5M HNO_3	0.00	0.00	0.00
4M HNO_3	0.40	4.28	1.60
4M H_2SO_4	3.90	6.06	1.20
2M H_2SO_4	0.50	5.38	0.13
0.1M NaOH	10.00	7.34	7.50
1.0M NaOH		dissolved completely	
1.0M NH_4OH	0.00	7.80	1.12
4M Acetic acid	0.00	0.55	0.17
1M Acetic acid	0.00	0.42	0.10
1M NH_4NO_8	0.00	0.43	0.20
IM Formic acid	0.00	4.60	1.60
1M Oxalic acid	1.20	0.00	0.00
2M Oxalic acid	1.20	0.00	0.60
1M Tartaric acid	0.00	0.00	0.00
1M Sodium acetate	0.00	0.67	0.51
1M Citric acid	0.00	0.46	0.00
1M $NaNO_3$	0.00	0.49	0.26
DMW	0.00	0.49	0.00
0.5M DMSO	0.00	0.00	0.00
2M DMSO	0.07	0.33	0.10
4M DMSO	0.12	0.43	0.16

dichromate respectively, as titrants (11,12). Phosphate was determined titrimetrically after precipitation as phosphomolybdate (13).

<u>Equilibration study</u>: Equilibrium times for the adsorption of bivalent, trivalent and tetravalent metal ions were determined

TABLE VIII. Effect of time on the adsorption of metal ions on tin(IV)-iodophosphate (150-200 mesh) at 25 ± 2°C (pH 5.5-6.5).

Metal ions	Amount of metal ion added m moles	Amount of metal ions absorbed (m moles)			
		After 2 hrs	After 4 hrs	After 6 hrs	After 8 hrs
Mg^{2+}	$11x10^{-3}$	$10.72x10^{-3}$	$10.75x10^{-3}$	$10.77x10^{-3}$	$10.77x10^{-3}$
Al^{3+}	$9.2x10^{-3}$	$9.00x10^{-3}$	$9.05x10^{-3}$	$9.10x10^{-3}$	$9.10x10^{-3}$
Zr^{4+}	$13.6x10^{-3}$	$13.33x10^{-3}$	$13.34x10^{-3}$	$13.34x10^{-3}$	$13.34x10^{-3}$

by treating 0.5 g of exchanger in H^+ form (150-200 mesh) with metal ions solutions in separate flasks. The mixtures were shaken in a shaker incubator for different times. The results are reported in Table VIII.

Distribution Coefficient: 0.5 g of exchanger in hydrogen form (150-200 mesh) was treated with 50 ml of cation solutions in 250 ml Earlenmeyer flask. The mixture was then shaken for 6 hrs at 25 ± 2°C in a shaker incubator. The amount of cation in solution was so adjusted as not to exceed 3% of the total ion exchange capacity of the exchanger (23). The amount of cation left in the solution was then determined by titrating against the standard solution of EDTA (0.002M). The Kd values were calculated by the earlier method (14). The results of Kd values are summarized in Table IX.

Quantitative Separations of metal ions: 2.0 g of exchange in hydrogen form (150-200 mesh) was taken into the glass column of internal diameter 5 mm. The appropriate solvent was first run through the column and then the mixture of metal ions was poured and allowed to be adsorbed. The metal ions were then eluted with suitable eluting reagent. The flow rate was maintained 1 ml/minute during elution process. The metal ions after elution were determined by EDTA titration.

TABLE - IX. Kd values (ml g^{-1}) of metal ions (ionic strength 0.02-0.056) on tin(IV)-iodophosphate (sample TIP$_5$) in different solvent systems at 25 ± 2 °C.

Metal ions	Salts used	2M DMSO (pH=6.5)	2M Formic acid (pH=1.7)	2M DMSO+ 2M Formic acid (1:1) (pH=1.87)	2M DMSO+ 2M Formic acid (2:1) (pH=1.97)
Mg^{2+}	Nitrate	29±1	10±1	22±1	22±1
Zn^{2+}	Chloride	175±3	84±1	38±1	52±1
Pb^{2+}	Chloride	25900±13000	25900±13000	25900±13000	25900±13000
Hg^{2+}	Chloride	13±1	28±1	10±1	86±2
Cd^{2+}	Chloride	165±3	52±1	165±3	165±3
Ba^{2+}	Chloride	940±40	160±3	247±5	197±4
Mn^{2+}	Nitrate	49±1	2±1	40±1	40±1
Co^{2+}	Nitrate	52±1	38±1	47±1	49±1
Tb^{3+}	Chloride	2700±2500	2700±2500	2700±2500	2700±2500
Gd^{3+}	Chloride	3500±600	3500±600	3500±600	3500±600
Pr^{3+}	Chloride	15400±7750	15400±7750	15400±7750	15400±7750
Cu^{2+}	Nitrate	1667±110	33±1	52±1	112±2
Ni^{2+}	Nitrate	100±2	4±1	35±1	16±1
Fe^{3+}	Chloride	1160±49	19±1	97±2	118±2
Ce^{3+}	Sulphate	107±2	139±2	122±2	343±7
Al^{3+}	Chloride	28±1	13±1	15±1	318±7
VO_2^{2+}	Sulphate	247±5	13±1	24±1	420±10
Sr^{2+}	Nitrate	303±7	58±1	62±1	90±2
Ca^{2+}	Chloride	372±7	47±1	32±1	90±2
Th^{4+}	Nitrate	184±4	148±2	155±3	155±3
Sm^{3+}	Chloride	25400±12750	25400±12750	25400±12750	25400±12750
Zr^{4+}	Oxy-chloride	1600±53	580±11	666±13	716±13
Ce^{4+}	Ammonium sulphate	555±10	211±4	269±5	254±5

TABLE - X. Quantitative separations of metal ions on tin(IV)-iodophosphate (Sample TIP_5) columns.

Sl. No.	Separations	Amount found to the column (µg)	Amount found after elution (µg)	Percent of metal ions eluted	Total elution volume (ml)	Eluent used
1.	Hg^{2+}	1440.00	1364.00	94.7	80	0.5M DMSO
	Co^{2+}	377.60	360.00	95.3	50	0.05M HNO_3
2.	Mg^{2+}	129.60	124.80	95.3	50	0.01M HNO_3
	Cu^{2+}	327.60	315.00	96.2	60	0.1M HNO_3
3.	Mn^{2+}	253.00	242.00	95.7	60	0.01M HNO_3
	Cu^{2+}	327.60	322.60	98.3	60	0.1M HNO_3
4.	Co^{2+}	377.60	368.00	97.5	60	0.05M HNO_3
	Cu^{2+}	327.60	312.00	95.2	60	0.1M HNO_3
5.	Ni^{2+}	340.46	317.00	93.2	60	0.01M HNO_3
	Cu^{2+}	327.60	315.00	96.2	60	0.1M HNO_3
6.	Ni^{2+}	340.46	305.00	90.0	60	0.01M HNO_3
	Fe^{3+}	358.40	342.00	95.4	80	0.1M HNO_3
7.	Hg^{2+}	1440.00	1364.00	94.7	80	0.5M DMSO
	Fe^{3+}	358.40	345.00	96.3	80	0.1M HNO_3
8.	Hg^{2+}	1440.00	1404.00	97.5	80	0.5M DMSO
	Mn^{2+}	353.00	231.00	91.3	60	0.01M HNO_3
9.	Hg^{2+}	1440.00	1377.00	95.6	80	0.5M DMSO
	Cu^{2+}	327.60	318.00	97.6	60	0.1M HNO_3
10.	Co^{2+}	377.60	464.00	96.4	50	0.05M HNO_3
	Fe^{3+}	358.50	335.00	93.5	80	0.1M HNO_3

RESULTS AND DISCUSSION

It is apparent from Tables II and III that the ion exchange capacity of double salts i.e., for iodophosphate are in general higher than that of single salts i.e. iodates of metals.

It has been observed that the ion exchange capacity for Fe(III)-iodophosphate samples (Table I) do not change by changing the mixing ratio of the reagents, except in case of sample FIP_4. Fe(III)-iodate (sample (FI_5) when prepared under identical conditions show highest ion-exchange capacity (1.17 meq/dry g) but of little practical importance as it is not appreciably stable in various solvents.

Zirconium(IV)-iodophosphate samples were prepared under identical conditions at pH 1. Sample ZIP_5 which is prepared in the presence of excess of phosphate shows highest ion exchange capacity (1.14 meq/dry g). However, zirconium(IV)-iodate when prepared under similar conditions shows small exchange capacity (0.55 meq/dry g).

Similar is the case with tin(IV)-iodophosphate which shows much higher ion exchange capacity (1.6 meq/dry g) as compared to tin(IV)-iodate (0.57 meq/dry g) prepared under the same conditions. The precipitation of the material was done at low pH values so as to avoid the possibility of formation of metal hydroxide. The chemical composition (Table V), I.R. Spectrum and ion exchange capacity data of sample TIP_5 (Table III) also indicate that the material formed is not the mixed salts of tin(IV)-iodate (0.57 meq/dry g) and tin(IV)-phosphate (1.31 meq/dry g) but a single compound tin(IV)-iodophosphate (1.6 meq/dry g).

It is clear from table III that by increasing the phosphate contents of the reactants in the mixture the ion exchange capacity of the material is increased. Tin(IV)-iodophosphate (sample TIP_5) has been chosen for further studies owing to its highest ion exchange capacity and highest chemical stability as compared to Zr(IV)-iodophosphate and Fe(III)-iodophosphate.

It can be inferred from table IV that the ion exchange capacity of most of the ion exchange materials increases with the decrease in hydrated radii of the ion. However, for alkaline earths the exchange capacity remains almost the same as the hydrated radii do not vary appreciably.

It is interesting to note from figure 1 that the uptake of metal ions is affected by pH of the electrolyte solution. pH titration curves show the following uptake order for alkali metals at different pH values:

(i) 3.5 to 4.5 $Na^+ > Li^+ > K^+$
(ii) 5.2 $Li^+ = Na^+ > K^+$
(iii) 5.3 to 11.0 $Li^+ > Na^+ > K^+$

pH titration curves show that tin(IV)-iodophosphate appears to behave as a weak cation exchanger.

It is apparent from table V that the composition and ion exchange capacity of tin(IV)-iodophosphate varies as the heating temperature is increased. The ion exchange capacity falls sharply from 1.6 to 0.99 (meq/dry g) when the sample is subjected to heating at 200°C. This decrease in capacity may be referred to the loss of iodate and phosphate contents of the sample, which is also evident from the chemical composition of the sample. A further loss in phosphate content of the sample together with the elimination of water molecules by condensation, decreases the capacity as the heating temperature is increased. The capacity, however, becomes unaffected (0.24 meq/dry g) when the temperature is raised above 800°C. The ion exchange capacity data (table VI) shows that almost all the exchangers are affected by heating. A comparison of the ion exchange capacities of various ion exchangers at 600°C heating temperature shows the sequence:

tin(IV)-arsenate > tin(IV)-iodophosphate = tin(IV)-selenophosphate > (tin(IV)-molybdoarsenate > tin(IV)-selenite > tin(IV)-arsenophosphate = tin(IV)-tungstate. However, at 800°C and higher heating temperature, tin(IV)-iodophosphate appears to be most thermally stable with respect to ion exchange capacity as it retains considerable ion exchange capacity i.e., 0.24 meq/dry g.

The material is found to be fairly stable in lower concentrations of mineral acids such as HCl, H_2SO_4 and HNO_3. The sample is quite stable in organic acids like formic acid, acetic acid, tartaric acid and citric acid of all concentrations.

The I.R. spectrum of tin(IV)-iodophosphate (sample TIP_5) in hydrogen form shows five absorption peaks. The broad peak in the region 3600-3000 cm^{-1} may be due to interstitial water molecules and -OH groups (20). A sharp peak in the region 2450-2300 cm^{-1} probably indicates the presence of P-H linkage (21). Another sharp peak at 1650 cm^{-1} may be due to the interstitial water molecules (20). Another broad peak in the region 1300-900 cm^{-1} may be attributed to PO_4^{3-} and IO_3^- (20). A small and sharp peak at 500 cm^{-1} is also seen in the spectrum that may be due to the presence of HPO_4^{2-} group in the sample (20).

The equilibrium studies for bivalent, trivalent and tetravalent metal ions (Table VIII) show that the equilibrium is attained in six hours.

To explore the separation potential of tin(IV)-iodophosphate, distribution coefficients of several metal ions have been determined in important solvents. It is clear from the Table IX that the distribution coefficients vary with the composition and nature of the solvent systems. It has been observed that in most of the cases the Kd values are higher in aqueous DMSO medium than in aqueous formic acid. This behaviour of tin(IV)-iodophosphate is different from that of Dowex-50 resin which shows the reverse trend (22). Kd values of metal ions are increasing in general with the increase in dimethyl sulphoxide (DMSO) content of the solvent system. It is found that the adsorption of Pb^{2+}, Gd^{3+} and Sm^{3+} is very high in all solvents whereas Mg^{2+}, Hg^{2+}, Mn^{2+} and Al^{3+} are least adsorbed.

It appears from the data on Kd values (Table IX) a number of important separations are possible. Some of the more important separations of industrial and analytical utility which have been successfully achieved on the columns of tin(IV)-iodophosphate are listed in Table X.

The separations of copper-nickel and copper-cobalt can be utilized in the determination of cobalt in steels and copper-nickel base alloys where copper usually interferes. Therefore, copper can be removed conveniently prior to the determination of these metals. In nickel plating solution, copper is an objectionable impurity and should be removed as it may darken the plate. The separation of Fe^{3+}-Ni^{2+} can be utilized in the determination of Fe^{3+} and other metal ions in natural alloys e.g. awaruite, josephinite and minerals of nickel namely, pentalandite, polydynite and olivine. It has been found that Pb^{2+} is strongly adsorbed on the column of tin(IV)-iodophosphate and could not be eluted by the common solvents (different concentrations of DMSO, formic acid, formic acid + DMSO and dilute nitric acid). Pb^{2+} has been successfully removed quantitatively from a synthetic mixture of Hg^{2+}, Co^{2+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+} and Fe^{3+}. Therefore, this separation is of practical importance where Pb^{2+} is present as impurity and necessary to be eliminated e.g. in the analysis of brass and bronze.

Acknowledgement

The authors thank Prof. W.Rahman, Head, Department of Chemistry for providing research facilities. C.S.I.R. (New Delhi) is also gratefully acknowledged for providing financial assistance to W.A.S. and R.A.K.R.

REFERENCES

1. M.Qureshi and S.A.Nabi, J.Inorg.Nucl.Chem., <u>32</u>, 2059 (1969).
2. A.Dyer and J.S.Gill, J.Inorg.Nucl.Chem., <u>40</u>, 97 (1978).
3. M.Qureshi and S.A.Nabi, J.Chem.Soc., (A), 139 (1971).
4. M.Qureshi, K.Husain and J.P.Gupta, J.Chem.Soc.,(A), 29 (1971).
5. M.Qureshi and J.P.Rawat, J.Inorg.Nucl.Chem., <u>30</u>, 305 (1968).
6. M.Qureshi and S.A.Nabi, Talanta, <u>19</u>, 1033 (1972).
7. J.P.Rawat and M.Iqbal, Annalidichimica, <u>69</u>, 241 (1979).
8. N.E.Topp and K.W.Pepper, J.Chem.Soc., 323 (1949).
9. F.D.Snell and C.T.Snell, Colorimetric methods of analysis Vol. (IIA), p. 135 (1959), D.Van Nostrand Company Inc. Princeton, New Jersey.
10. N.H.Furman, Standard methods of chemical analysis 6th Edn.

Vol. I, p. 819 (1962), D.Van Nostrand Inc. Princeton, New Jersey.

11. I.M.Kolthoff, R.Belcher, Volumetric Analysis, Interscience, New York, (1957), Vol. 3, p. 235.

12. Ref. 11, p. 320-322.

13. Ref. 10, p. 814.

14. S.A.Nabi, A.R.Siddiqui, R.A.K.Rao, J.Liq.Chromatogr., 4(7), 1225 (1981).

15. Y.Inoue, Bull.Chem.Soc., Japan, 36, 1318 (1963).

16. M.Qureshi, J.P.Gupta and V.Sharma, Anal.Chem., 45, 1903 (1973).

17. M.Qureshi, K.G.Varshney, J.Inorg.Nucl.Chem., 30, 3081 (1968).

18. M.Qureshi, S.A.Nabi, N.Zehra, Can.J.Chem., 55, 1667 (1977).

19. M.Qureshi, R.Kumar and H.S.Rathore, J.Chem.Soc. (A), 272 (1970).

20. Mansel Davies, Infrared spectroscopy and molecular structure, p. 318 (1963), Elsevier Publishing Company, Amsterdam.

21. L.J.Bellainy, The infrared spectra of complex molecules, p. 311 (1950), John Wiley and Sons, Inc. New York.

22. M.Qureshi and K.Husain, Anal.Chem.Acta, 57, 387 (1971).

23. H.Hamaguchi, R.Kuroda, K.Aoki, R.Sugisita and N.Onuma, Talanta, 10, 153 (1963).