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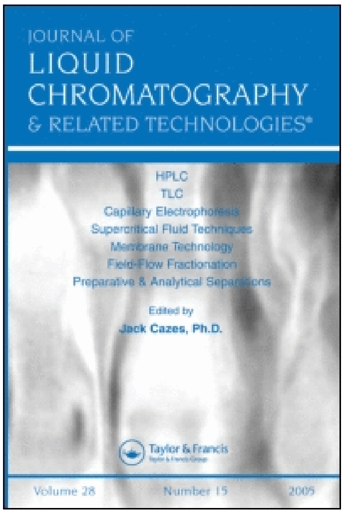

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Sorption Studies in DMSO-NITRIC Acid and DMSO-Acetic Acid Systems and Separation of Metal Ions on TIN(IV)-Iodophosphate

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SORPTION STUDIES IN DMSO-NITRIC ACID AND DMSO-ACETIC ACID SYSTEMS AND SEPARATION OF METAL IONS ON TIN(IV)-IODOPHOSPHATE

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ABSTRACT

Some new samples of tin(IV)-iodophosphate have been synthesized and their ion exchange properties have been studied. Adsorption behaviour of different metal ions on tin(IV)-iodophosphate (TIP_5), in H^+ form, in different solvent systems have been examined. Kd values of few metal ions, in 4M DMSO medium, have also been determined on the same ion-exchanger in NH_4^+ form. Effect of particle size of tin(IV)-iodophosphate (TIP_5), in H^+ form, on the Kd values of metal ions has been studied. Separations of a number of metal ions have been achieved on tin(IV)-iodophosphate (TIP_5) columns.

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INTRODUCTION

Studies on synthetic inorganic ion exchangers have attracted much attention in recent years owing to their high thermal stability and selectivity towards metal ions. In our earlier paper (1) we have reported the synthesis and ion exchange properties of iodates and iodophosphates of tin(IV), Zr(IV) and iron(III). Tin(IV)-iodophosphate has been found to show better properties than other iodophosphates and therefore has been chosen for further studies. The adsorption of metal ions on ion exchange materials has been found to depend largely on the nature of solvents used. The ion exchange behaviour of metal ions in aqueous mineral acids of different concentrations has been studied extensively (2). Solvents other than mineral acids have also been found useful as eluents. DMSO as a solvent offers excellent separation possibilities for the separation of metal ions in thin layer and column chromatography (3). The present paper deals with the adsorption behaviour of metal ions in DMSO-acetic acid and DMSO-nitric acid mixtures in a systematic manner.

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EXPERIMENTAL

Reagents: Tin(IV) chloride penterhydrate (Reaction U.S.S.R.), potassium iodate (E.Merk), potassium dihydrogen-ortho phosphate (B.D.H.), were used. Other chemicals were of analytical reagent grade.

Apparatus: The spectrophotometry and pH measurements were performed by using Bauch and Lomb spectronic 20 spectrophotometer Elico LI-10 pH meter respectively. Perkin Elmer 137 spectrophotometer was used for I.R.study. An electric temperature controlled shaker (SICO) was used for shaking.

Synthesis: Tin(IV)-iodophosphate was synthesized by mixing 0.1M solution of tin(IV) chloride to a solution which is 0.1M in potassium iodate and 0.1M in potassium dihydrogen phosphate in a mixing ratio of 1:2:1 at pH = 1. The precipitate was then allowed to settle down for 24 hours with mother liquor. It was then filtered off, washed several times with distilled water and dried at 40°C. The dried material was immersed in water which broke down into fine particles with cracking. The material was then converted into H^+ form as usual (4). Synthesis of tin(IV)-iodophosphate was also done in highly acidic medium and the effect of refluxion on the ion exchange capacity of the product was studied. The results are shown in table 1.

<u>IR spectra</u>: IR spectra, of tin(IV)-iodophosphate dried at various temperatures, were recorded using KBr disc method (Figs. 1 and 2).

<u>Thermogravimetric analysis</u>: The thermogravimetric analysis of tin(IV)-iodophosphate was performed using 5.0 mg of the sample in H^+ form with a heating rate of 10°C, min^{-1} (Fig. 3).

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TABLE - 1

SYNTHESIS AND PROPERTIES OF SOME NEW SAMPLES TIN(IV)-IODOPHOSPHATE

Sample number	Conditions of synthesis					Appearance of precipitate	Appearance of beads after drying at 40°C	I.E.C. for K^+ meq/dry g
	$SnCl_4 \cdot 5H_2O$ moles/liter	KIO_3 moles/liter	KH_2PO_4 moles/liter	Mixing V/V/V	pH			
TIP_5R	0.1	0.1	0.1	1:1:2	0-1	White gelatinous	White opaque	1.60
TIP_6	0.1	0.1	0.1	1:1:2	0-<0	-do-	White shining	1.80
TIP_6R	0.1	0.1	0.1	1:1:2	0-<0	-do-	Dirty white shining	1.84

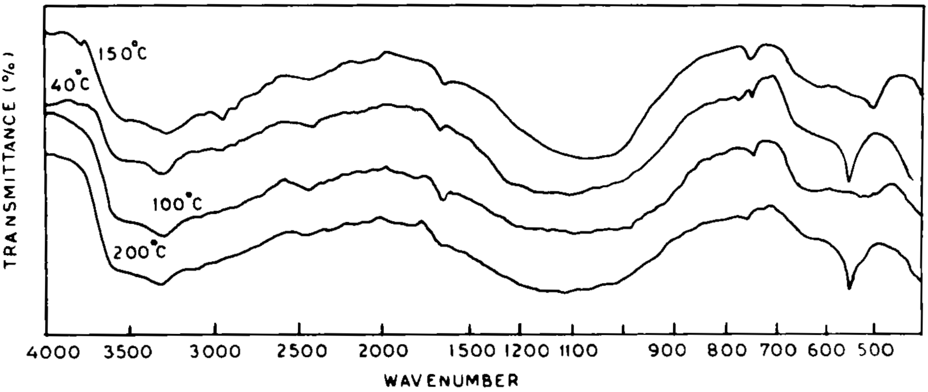

FIGURE 1. IR Spectra of Tin(IV)-Iodophosphate (Sample Tip_5) Dried at Various Temperatures.

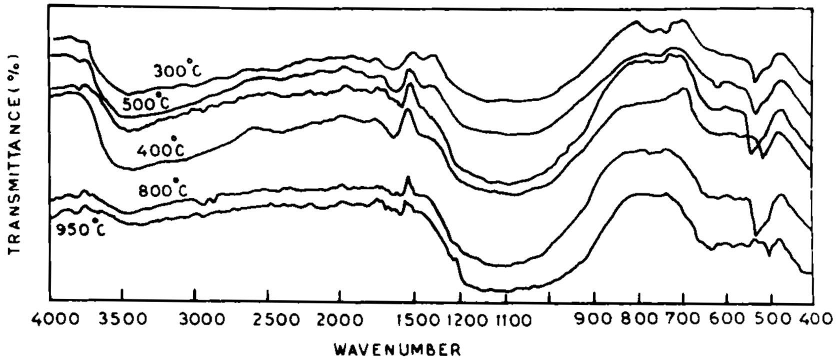

FIGURE 2. IR Spectra of Tin(IV)-Iodophosphate Sample (Tip_5) Dried at Various Temperature.

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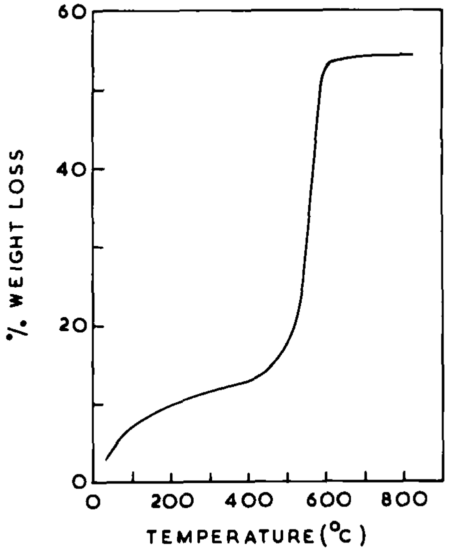

FIGURE 3. Thermogram of Tin (IV)-Iodophosphate in H^+ Form (Sample Tip_5).

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TABLE - 2

Kd VALUES (ml g^{-1}) OF DIFFERENT METAL IONS (IONIC STRENGTH 0.02-0.06) ON TIN(IV)-IODOPHOSPHATE (MESH SIZE 50-100) AT 25 ± 2°C

Metal ions	4M DMSO		DMW (pH 6.5)
	NH_4^+ form of the exchanger	H^+ form of the exchanger	NH_4^+ form of the exchanger
Pb^{2+}	13950 ± 7000	13950 ± 7000	13950 ± 7000
Ba^{2+}	210 ± 12	470 ± 47	470 ± 47
Cu^{2+}	197 ± 11	240 ± 14	337 ± 24
Ca^{2+}	18 ± 1	86 ± 5	63 ± 3
Ce^{3+}	630 ± 117	630 ± 117	1310 ± 389
Al^{3+}	203 ± 8	330 ± 18	330 ± 18
Fe^{3+}	417 ± 29	650 ± 64	650 ± 64
Th^{4+}	359 ± 29	1030 ± 180	490 ± 21
Zr^{4+}	921 ± 52	1650 ± 155	1650 ± 155
Ce^{4+}	417 ± 29	540 ± 23	343 ± 25

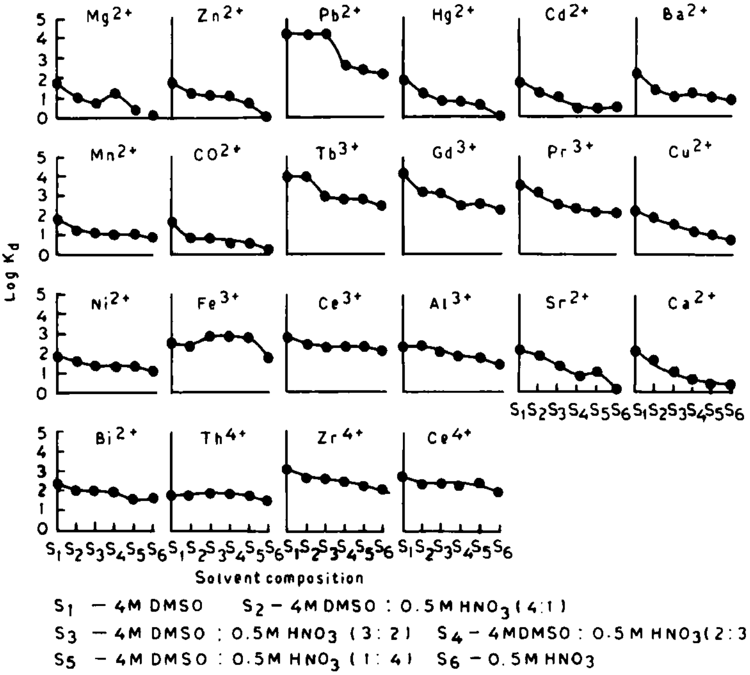

FIGURE 4. Plot of Log K_d vs Solvent Composition.

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Distribution coefficients: Distribution coefficients of several metal ions in various organic and mixed solvents were determined using earlier method (5). The effect of particle size on the Kd value of metal ions was also studied. The results are shown in figures 4, 5 and 6. The adsorption of metal ions in NH_4^+ form of the exchanger is reported in table 2.

Quantitative separations: Quantitative separations of metal ions on tin(IV) iodophosphate were achieved using 2.0 g of the exchanger in H^+ form (50-100 mesh) in a glass column of 0.6 cm id. The ion exchange column was run with 4M DMSO or 1M acetic acid before the application

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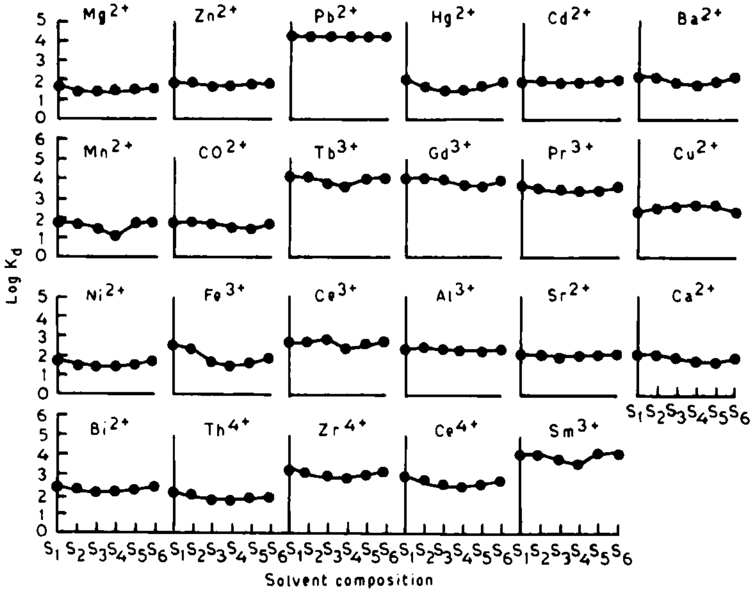
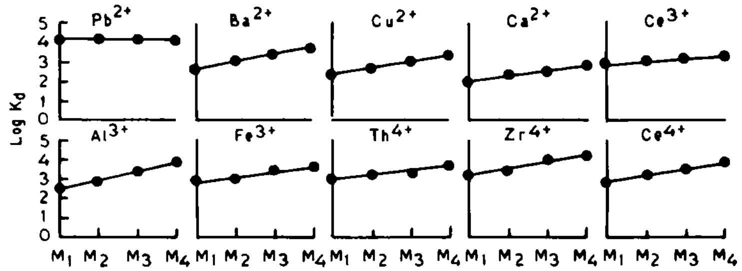


S_1 – 4M DMSO S_2 – 4M DMSO : 1 M Acetic acid (4 : 1)

S_3 – 4M DMSO : 1M Acetic acid (3 : 2) S_4 – 4 M DMSO : 1 M Acetic acid (2 : 3)

S_5 – 4M DMSO : 1M Acetic acid (4 : 1) S_6 – 1 M Acetic acid

FIGURE 5. Plots of Log K_d vs Solvent Composition.



M_1 = 50 – 100 mesh, M_2 = 100 – 150 mesh, M_3 = 150 – 200 mesh

M_4 = 200 – 250 mesh

FIGURE 6. Effect of Particle Size of Tin(IV)-Iodophosphate (H^+ Form) on the K_d-Values of Metal Ions in 4M DMSO.

of the metal solutions. The mixture of metal ions was then poured into the column and allowed to be adsorbed. The metal ions adsorbed were then eluted with an appropriate eluting agent. The rate of elution was maintained 1 ml min^{-1} throughout the elution process. The metal ions were collected in 20 ml fraction and then determined titrimetrically using 0.002M EDTA solution. The results are reported in table 3. Elution curves for few binary separations are shown in figure 7.

RESULTS AND DISCUSSION

It has been observed that the ion exchange capacity of tin(IV)-iodophosphate is increased when the precipitation of the material is carried out in highly acidic medium. However, the ion exchange capacity is not significantly altered when the product is subjected to refluxion for 6 hours.

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TABLE - 3

QUANTITATIVE SEPARATIONS OF METAL IONS ACHIEVED ON THE COLUMNS OF TIN(IV)-IODOPHOSPHATE

Sl. No.	Separations	Column developed in 4M DMSO				
		Amount fed to the column (µg)	Amount found after elution (µg)	Percent of metal ions eluted	Total elution volume (ml)	Eluent used
1.	Gd^{3+}	1130	1005	88.9	70	E_1
	Th^{4+}	2506	2320	92.6	80	E_4
2.	Hg^{2+}	2045	2005	98.0	70	4M DMSO
	Pb^{2+}	1822	1780	97.7	40	E_3
3.	Cd^{2+}	928	880	94.8	40	E_1
	Pb^{2+}	1822	1739	95.4	70	E_3

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(Table 3 continued)

Sl. No.	Separations	Column developed in 4M DMSO				
		Amount fed to the column (μg)	Amount found after elution (μg)	Percent of metal ions eluted	Total elution volume (ml)	Eluent used
4.	Mg^{2+}	264	259	98.1	60	E_1
	Pb^{2+}	1822	1780	97.7	70	E_3
5.	Zn^{2+}	550	524	95.2	80	E_1
	Pb^{2+}	1822	1780	97.7	60	E_3
6.	Mn^{2+}	572	550	96.2	80	E_1
	Pb^{2+}	1822	1780	97.7	60	E_3
7.	Ba^{2+}	1430	1375	96.2	100	E_1
	Pb^{2+}	1822	1739	95.4	70	E_3
8.	Sr^{2+}	963	928	96.4	80	E_1
	Pb^{2+}	1822	1739	95.4	70	E_3
9.	Gd^{3+}	1130	1068	94.5	70	E_1
	Zr^{4+}	1056	1019	96.5	90	1M HNO_3
10.	Sm^{3+}	1535	1475	96.1	80	E_1
	Ce^{4+}	1652	1596	96.6	90	E_4
11.	Pr^{3+}	987	931	94.3	60	E_2
	Th^{4+}	2506	2413	96.2	60	E_4
12.	Pr^{3+}	987	902	91.4	60	E_2
	Zr^{4+}	1056	1001	94.8	80	1M HNO_3
13.	Pr^{3+}	987	931	94.3	60	E_2
	Ce^{4+}	1652	1568	94.9	70	E_4
14.	Gd^{3+}	1130	1036	91.7	70	E_1
	Ce^{4+}	1652	1624	98.3	80	E_4

E_1 = 2:8 solution of 0.5M HNO_3+4M DMSO; E_2 = 4:6 solution of 0.5M HNO_3+4M DMSO; E_3 = 6:4 solution of 0.5M HNO_3+4M DMSO; E_4 = 8:2 solution of 0.5M HNO_3+4M DMSO

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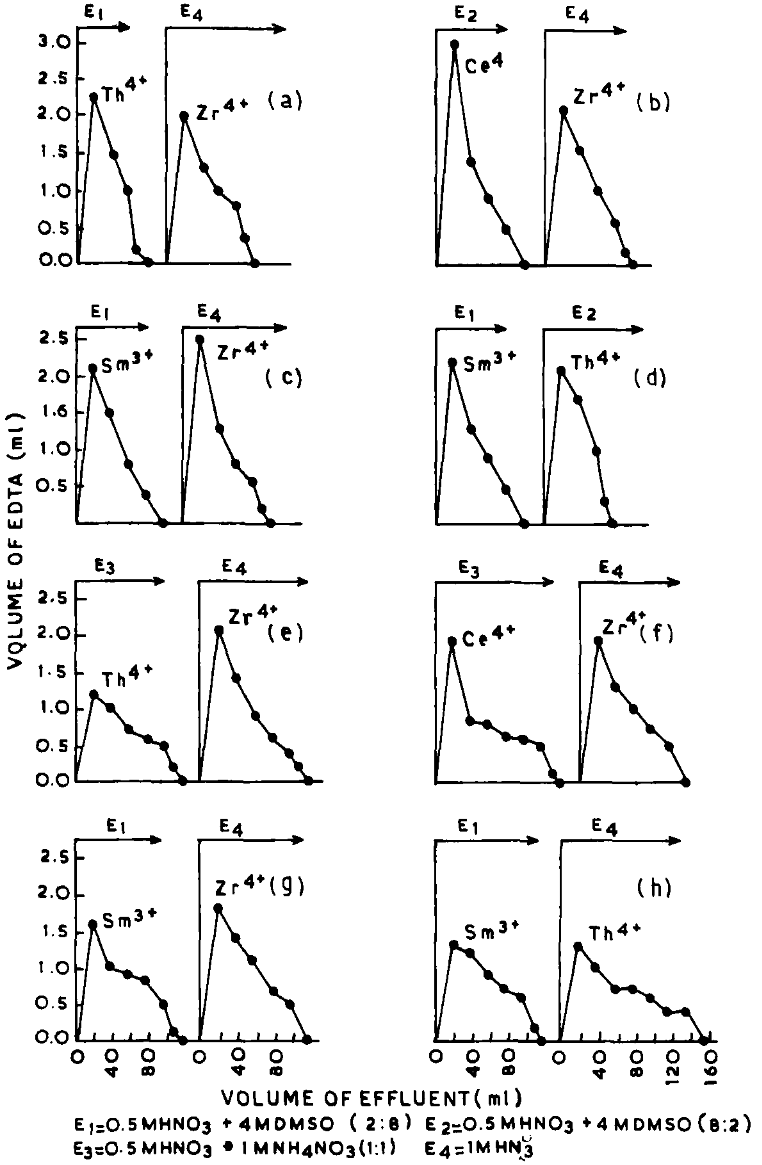

FIGURE 7. Effect of Adsorption Media and Eluent on the Separation of Th^{4+} -Zr^{4+} Ce^{4+} -Zr^{4+}, Sm^{3+} -Zr^{4+} and Sm^{3+} -Zr^{4+}

a, b, c, and d Curves in 4M DMSO Medium

e, f, g, and h Curves in 1M Acetic Acid Medium

The thermogram of tin(IV)-iodophosphate (Fig. 3) shows continuous loss in weight upto 500°C. The weight loss upto 150°C may be due to the removal of external water molecules along with some loss of iodate as iodine. A continuous loss in weight in the region 150-400°C may be attributed to the loss of water molecules owing to the condensation of -OH groups along with the loss of phosphorous and iodine from the sample. The ion exchange capacity in this temperature range decreases sharply from 1.30 to 0.66 meq/dry g (1). The ion exchange capacity of stannic phosphate (6) almost vanishes completely when the material is heated at 400°C. This is probably due to the conversion of phosphate into pyrophosphate. It can, therefore, be inferred that the retention of ion exchange capacity in the case of tin(IV)-iodophosphate even after drying at 400°C is because of the presence of iodate group only. However the material experiences a drastic loss in weight in the region between 500-600°C which is indicated by the steep portion of the thermogram. The formation of some stable species possibly accounts for the constant weight of the sample beyond 600°C. The dark brown colour of the material is also unaffected and the capacity becomes almost constant (1). Tin(IV)-iodophosphate is more thermally resistant than stannic phosphate as the latter loses ion exchange capacity almost completely at 400°C.

The IR spectra of tin(IV) iodophosphate (in H^+ form) dried at various temperatures are shown in figures 1 and 2. The IR spectrum of the sample at 40°C shows fine peaks in the regions 2600-3600 cm^{-1}; 1600-1700 cm^{-1}; 900-1300 cm^{-1}; 730-780 cm^{-1} and 470-660 cm^{-1}. The broad peak in the region 2600-3600 cm^{-1} may be due to the presence of -OH groups and water molecules (7). The second sharp peak in the region 1600-1700 cm^{-1} with a maximum at 1650 cm^{-1} shows the presence of intenstial water (7). Another broad peak in the region 900-1300 cm^{-1} may be attributed to HPO_4^{-2} group (7). A small peak in the region 730-780 cm^{-1} is observed which may be attributed to iodate group (8). Another sharp peak at 500 cm^{-1} may be due to HPO_4^{2-} group (7). The

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IR spectra show no change upto 600°C. However above this temperature the peak due to -OH group in the region 3600-2600 cm^{-1} disappears. The other peaks due to phosphate and iodate groups still persist upto 950°C which is also confirmed from the chemical composition of the samples dried at various temperatures (1).

The distribution studies (Figs. 4 and 5) show that Kd values of Pb^{2+} and rare earth metals are exceptionally very high in 4M DMSO medium while Mg^{2+}, Hg^{2+}, Cd^{2+}, Mn^{2+} and Co^{2+} are found to be adsorbed to a very little extent in this medium. It is interesting to note that the Kd values of metal ions in general decrease with the increase in nitric acid concentration in DMSO nitric acid mixture.

Interesting results have been obtained when adsorption behaviour of these metal ions is observed in DMSO-acetic acid mixtures. The adsorption behaviour of tin(IV)-iodophosphate for metal ions in 1M acetic acid is almost similar to that 4M DMSO medium. Kd values of Pb^{2+} and rare earth metals in the two solvents are very high as compared to other metal ions. When the concentration of acitic acid is increased in the mixture, the adsorption of almost all the metal ions decreases to a certain extent (6:4 and 4:6 :: DMSO:acetic acid mixture) and after which the adsorption again increases (Fig. 5). However Cd^{2+}, Pr^{3+}, Al^{3+} and Sr^{2+} behave in a different manner as their uptake is not affected by change in the composition of DMSO-acetic acid mixture.

A comparison of adsorption behaviour of metal ions (Table 2) on NH_4^+ form and H^+ form of the exchanger shows that Kd values are significantly higher in the later case. This may be due to the fact that H^+ ions are easily exchanged by a metal ion as compared to NH_4^+ ions. It can also be inferred from table 2 that Kd values of metal ions are usually higher in water than in dimethyl sulphoxide medium.

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It is interesting to note from figure 6 that the adsorption of metal ions in general is affected by particle size of the exchanger. The Kd values are found to increase linearly with the decrease in the particle size of the exchanger except in the case of Pb^{2+} which shows exceptionally high Kd value.

The differential selectivity of some metal ions on tin(IV)-iodophosphate has been utilized for the separations of a number of metal ions. Figures 7-a,b,c,d and e,f,g,h demonstrate the enhanced efficiency of separation by the use of DMSO-nitric acid as eluent. The elution curves for Th^{4+} and Ce^{4+} show that their elution with nitric acid - ammonium nitrate is difficult and more time consuming as compared to elution by DMSO - nitric acid mixture. Figures 7-a,b,c,d and e,f,g,h compare the efficiency of separation, of the exchanger columns, when these were conditioned in solutions of 4M DMSO and 1M acetic acid respectively. It shows that the columns developed with DMSO were more useful as compared to the column developed with acetic acid.

Separation of Th^{4+} from rare earths can be utilized for the separation and determination of Th^{4+} content in minerals like Thucholite, Monazite and Fergusonite (9). Tin(IV)-iodophosphate can also be utilized for the separation and determination of Zr^{4+} in zirconium containing ores like polymignite, zirkelite and minerals like Cerite, Auerlite, Chalcolamprite and Loranskite (10). The possible separation of Pb^{2+} from a number of metal ions makes the exchanger a potentially useful adsorbent for affective separation of analytical importance. Composition of lead containing alloys, such as Steam Boiler Plug, Wood's alloys, Statuary Bronze, British Navy Bronze and Japanese Bronze (8), can be determined conveniently utilizing columns of this ion exchange material. Similarly Pb^{2+} and Cd^{2+} can be determined in the lead containing cadmium alloys. These

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separations on tin(IV)-iodophosphate also suggest that water pollutant metals such as Pb^{2+}, Cd^{2+}, Hg^{2+} can be conveniently removed from water and can be recovered separately.

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