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Synthesis, Ion-Exchange Properties and Analytical Applications of Tin(IV) Tungstovanadophosphate

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Samples of tin(IV) tungstovanadophosphate have been synthesized under varying conditions and their ion-exchange properties are studied. Among the various samples of tin(IV) tungstovanadophosphate, sample TTVP$_7$R is chosen for detailed study and its ion-exchange properties are compared with sample TTVP$_7$. Both the compounds are synthesized in excess of acid, i.e. at pH less than zero. Sample TTVP$_7$ is synthesized by adding 0.025 mol dm^{-3} sodium metavanadate, 0.025 mol dm^{-3} sodium tungstate and 1.0 mol dm^{-3} phosphoric acid to 0.1 mol dm^{-3} tin(IV) chloride in the volume ratio of 1:1:1:1 at pH=0. Sample TTVP$_7$R was prepared by refluxing the precipitate of sample TTVP$_7$ in the reaction mixture. The chemical and thermal stabilities of this material have been determined. The reproducibility of the material is also checked. Distribution coefficients for numerous metal ions in formic acid-sodium formate buffer systems of different pH were determined. The utility of the material has been demonstrated by achieving a number of binary and ternary separations on its small columns.

Synthetic inorganic ion exchangers have attracted attention because of their versatility in separation science and in many other fields of diverse nature. The inorganic ion-exchange materials which have been synthesized and studied till now are mostly single and double salts of metals. In many instances it has been found that double salts exhibit ion-exchange properties and they are thermally and chemically more stable than single salts. For example tin(IV) vanadotungstate[1] has been found to behave entirely different from tin(IV) tungstate,[2] tin(IV) vanadate,[3] and tin(IV) phosphate.[4] It is our prediction that by incorporating three different types of anions in the matrix, the exchange properties of the material may be improved further. It is with this view in mind we have synthesized tin(IV) tungstovanadophosphate and studied its ion-exchange properties. The following pages summarize our findings in this direction.

Experimental

Reagents. Tin(IV) chloride pentahydrate (Reachim), sodium tungstate (BDH), sodium metavanadate (Riedel Germany), and phosphoric acid (BDH) were used for the synthesis of the material. All other chemicals were of analytical reagent grade.

Apparatus. Spectrophotometric studies were performed using spectrophotometer GS 866D (E. C.). ELICO Model LI-10 pH meter was used for pH measurements and Stanton thermobalance type H$_4$ for TGA. A temperature controlled shaker SICO was used for shaking.

Synthesis. Samples of tin(IV) tungstovanadophosphate were synthesized by mixing aqueous solutions of the appropriate reagents. The solutions used for the synthesis were 0.025 mol dm^{-3} in sodium tungstate, 0.025 mol dm^{-3} in sodium metavanadate, 0.5 mol dm^{-3} in phosphoric acid (1.0 mol dm^{-3} in phosphoric acid for the synthesis of samples TTVP$_7$ and TTVP$_7$R) and 0.1 mol dm^{-3} in tin(IV) chloride. Conditions of synthesis for different samples are indicated in Table 1. The pH for the sample solution in each case was adjusted by adding either concentrated hydrochloric acid or dilute sodium hydroxide solutions. The precipitate so formed was then allowed to settle down for 24 h at room temperature (25±2 °C), washed several times with demineralized water (DMW) to remove excess reagent and finally

Table 1. Conditions of Synthesis and Few Properties of Different Samples of Tin(IV) Tungstovanadophosphate

Sample No.	Concentration/mol dm^{-3}				Mixing volume ratio v/v/v/v	pH	Appearance of precipitate	Appearance of beads after drying at 40 °C	Ion-exchange capacity for K$^+$ /meq (dry g)$^{-1}$
	Tin(IV) chloride	Sodium tungstate	Sodium vanadate	Phosphoric acid					
TTVP$_1$	0.1	0.025	0.025	0.5	1:1:1:1	1	Yellow	Greenish yellow (shining)	1.50
TTVP$_2$	0.1	0.025	0.025	0.5	2:1:1:1	1	Yellow	Greenish yellow (shining)	1.35
TTVP$_3$	0.1	0.025	0.025	0.5	1:2:1:1	1	Yellow	Yellow (shining)	1.14
TTVP$_4$	0.1	0.025	0.025	0.5	1:1:2:1	1	Yellow	Yellow (shining)	1.21
TTVP$_5$	0.1	0.025	0.025	0.5	1:1:1:2	1	Yellow	Yellow (shining)	1.21
TTVP$_6$	0.1	0.025	0.025	P[a)]	1:1:1:1	1	Yellow	Yellow (shining)	1.48
TTVP$_7$	0.1	0.025	0.025	1.0	1:1:1:1	<0	Yellow	Greenish yellow (shining)	2.06
TTVP$_7$R	0.1	0.025	0.025	1.0	1:1:1:1	<0	Yellow	Greenish yellow (shining)	2.15
TTVP$_8$	0.1	0.025	0.025	0.5	1:1:1:1	2.5—3	Yellow	Yellow (shining)	1.30

a) P=0.1 mol dm^{-3} Potassium dihydrogenorthophosphate.

Table 2. Data Showing the Reproducibility of Samples of Tin(IV) Tungstovanadophosphate

Sl. No.	Unrefluxed sample ($TTVP_7$)			Refluxed sample ($TTVP_7R$)		
	Appearance of the precipitate	Appearance of beads after drying at 40 °C	I.E.C. for K^+ meg (dry g)$^{-1}$	Appearance of the precipitate	Appearance of beads after drying at 40 °C	I.E.C. for K^+ meg (dry g)$^{-1}$
1	Yellow	Greenish yellow	2.00	Yellow	Greenish yellow	2.11
2	Yellow	Greenish yellow	1.98	Yellow	Greenish yellow	2.14
3	Yellow	Greenish yellow	2.04	Yellow	Greenish yellow	2.10
4	Yellow	Greenish yellow	1.96	Yellow	Greenish yellow	2.00
5	Yellow	Greenish yellow	2.01	Yellow	Greenish yellow	2.12
6	Yellow	Greenish yellow	1.98	Yellow	Greenish yellow	2.14

Table 3. Ion-Exchange Capacity [meq (dry g^{-1})] of Tin(IV) Tungstovanadophosphate for Various Cations

Cation	Salt used	pH	Hydrated radii[17)]/nm	Sample $TTVP_7R$ meq (dry g)$^{-1}$	Sample $TTVP_7$ meq (dry g)$^{-1}$
Li^+	Lithium chloride	6.8	10.0	1.98	1.81
Na^+	Sodium chloride	6.8	7.9	1.72	1.83
K^+	Potassium chloride	6.8	5.3	2.15	2.06
Rb^+	Rubidium chloride	6.2	—	2.06	1.98
Mg^{2+}	Magnesium chloride	6.5	10.8	2.09	2.04
Ca^{2+}	Calcium chloride	6.5	9.6	2.13	2.08
Sr^{2+}	Strontium chloride	6.2	9.6	2.20	2.10
Ba^{2+}	Barium chloride	6.2	8.8	2.60	2.26

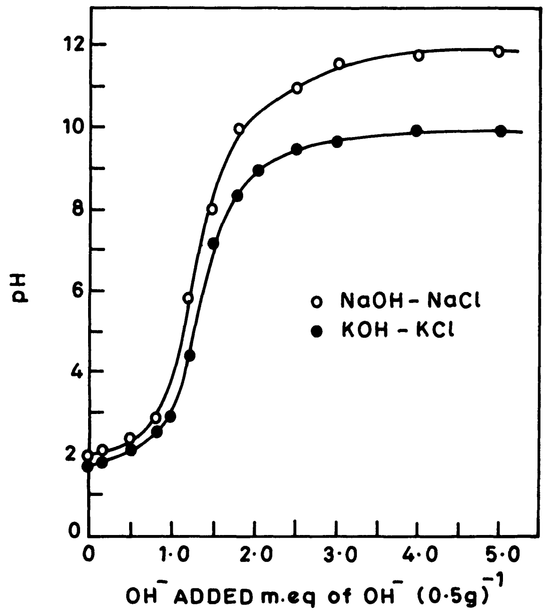

Fig. 1. pH Titration curves of tin(IV) tungstovanadophosphate (Sample $TTVP_7R$).

filtered under suction. It was then dried at 40 °C in an oven. The material was then immersed in DMW where it was broken into fine particles with slight evolution of heat. The material was then converted into hydrogen form by keeping it into 0.1 mol dm^{-3} nitric acid solution for 48 h. Excess of acid was removed by washing with DMW. Sample $TTVP_7R$ was prepared by refluxing the precipitate of sample $TTVP_7$ for 6 h in a mixture of 0.1 mol dm^{-3} sodium tungstate, 0.1 mol dm^{-3} sodium metavanadate and 1.0 mol dm^{-3} phosphoric acid in the volume ratio of 1:1:1. Concentrated hydrochloric acid was also added in sufficient quantity to adjust the pH of the mixture less than zero. The mixture was then allowed to cool. The supernatant liquid removed and the product was washed several times with water and finally filtered, dried, and converted into hydrogen form as described above. To check the reproducibility of the exchanger six sets of samples $TTVP_7$ and $TTVP_7R$ were prepared. Results are given in Table 2.

Ion-Exchange Capacity. The ion-exchange capacity of samples of tin(IV) tungstovanadophosphate was determined by column method.[3)] The hydrogen ion liberation capacity with different mono and bivalent ions is reported in Table 3.

pH Titration. The titrations for samples $TTVP_7R$ and $TTVP_7$ were performed in NaOH-NaCl and KOH-KCl systems using the method.[5)] The pH titration curves are shown in Figs. 1 and 2.

Thermal Treatment. The thermogravimetric analysis of tin(IV) tungstovanadophosphate in hydrogen form was performed at a heating rate of 10 °C min^{-1}. The resulting thermogram is shown in Fig. 3. To examine the effect of heating on the ion-exchange capacity, the material in the hydrogen form was heated at different temperatures (40, 100, 200, 400, 500, 600, and 800 °C) for 1 h in a muffle furnace.

Chemical Stability. The chemical stability of samples $TTVP_7R$ and $TTVP_7$ was studied in a number of solvents (0.1 to 4 mol dm^{-3} of HNO_3, HCl and H_2SO_4, 60% $HClO_4$, 1 mol dm^{-3} oxalic acid, 0.5 mol dm^{-3} aqueous NH_3, and 0.1 mol dm^{-3} NaOH) of analytical interest. One half gram of the ion-exchange material was equilibrated with 50 cm^3 of the solvent at room temperature (25±2 °C) and kept for 24 h with occasional shaking. Tin, tungsten, vanadium, and phosphorus in the solutions were determined spectrophotometrically using standard methods[6–9)] respectively.

Chemical Composition. For the determination of chemical composition of various samples of tin(IV) tungstovanadophosphate, 0.2 g of the material was dissolved in hot concentrated hydrochloric acid. It was then diluted to

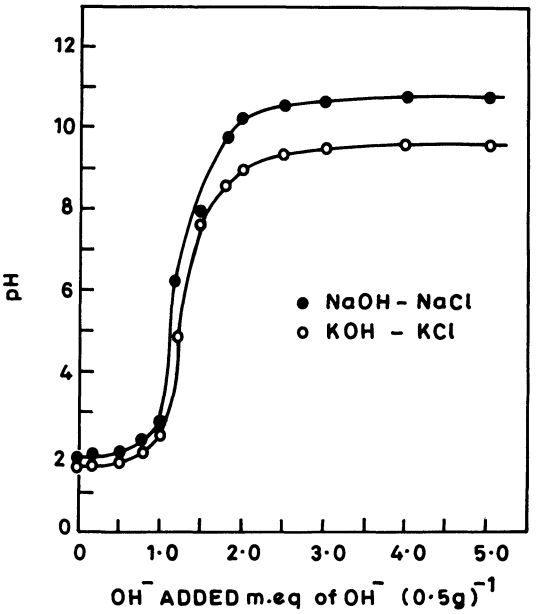

Fig. 2. pH Titration curves of tin(IV) tungstovanadophosphate (Sample $TTVP_7$).

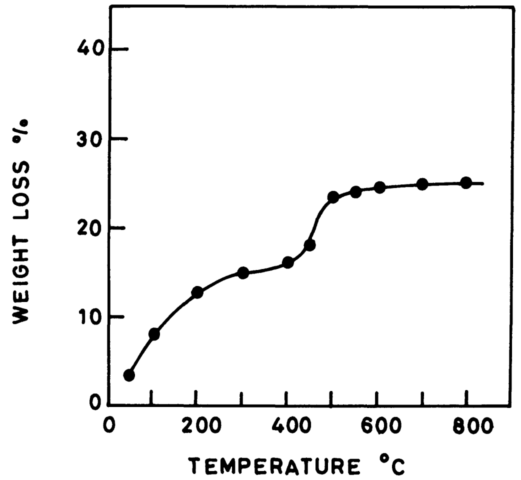

Fig. 3. Thermogram of tin(IV) tungstovanadophosphate($TTVP_7R$) in H^+ form.

100 cm^3 with DMW. Tin was determined spectrophotometrically[6] while tungsten and vanadium were determined by gravimetric[10] and titrimetric[11] methods respectively. Phosphate was determined titrimetrically using the standard method.[12]

Equilibrium Study. Equilibrium times for the adosorption of bivalent, tervalent, and quadrivalent metal ions (Mg^{2+}, Ba^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+}, Fe^{3+}, Pr^{3+}, Zr^{4+}, and Th^{4+}) on tin(IV) tungstovanadophosphate ($TTVP_7R$, 50—100 mesh) in hydrogen form were determined by the earlier described method.[13]

Distribution Coefficient. Distribution coefficients of a number of metal ions in water and formic acid-sodium formate buffer systems of varying pH were determined. One half gram of the exchanger in hydrogen form (50—100 mesh) were added in 25 cm^3 cation solution in a 250 cm^3 Erlenmeyer flask. Concentration of metal ion in the solution was adjusted in such manner that it did not exceed 3% of the total ion-exchange capacity of the exchanger. The flask was then shaken in a shaker incubator at 25±2 °C for 6 h. The amount of cation left in the solution after equilibrium was determined titrimetrically using 0.002 mol dm^{-3} EDTA as titrant. The K_d values were calculated according to the formula.[14] The results are given in Fig. 4.

Quantitative Separations of Metal Ions. Quantitative separations of some important metal ions of analytical utility were achieved on the columns of tin(IV) tungstovanadophosphate. Two grams of the exchanger in hydrogen form (50—100 mesh) was taken into a glass column of i. d. 0.6 cm. DMW was first run and then the mixture of metal ions was poured and allowed to be adsorbed. The metal ions were then eluted separately using suitable eluting reagents and determined by EDTA titrations. The flow rate of the effluent was maintained 1 cm^3 min^{-1} throughout the elution process. Results of separations achieved have been reported in Table 4.

Results and Discussion

Table 1 shows that the ion-exchange capacity of tin(IV) tungstovanadophosphate depends on the conditions of synthesis, that is on the mixing volume ratio of the reactants, the pH at which the precipitation is done and also on the refluxion. The maximum ion-exchange capacity [1.5 meq (dry g)$^{-1}$] is observed in the case of sample $TTVP_1$ prepared by mixing reagents in the volume ratio of 1:1:1:1 at pH 1. However, when the sample is prepared using the same ratio at pH less than zero, the capacity is found to increase significantly from 1.5 to 2.06 meq (dry g)$^{-1}$ (sample $TTVP_7$). It is interesting to observe that on refluxing the same product ($TTVP_7$) in a mixture of sodium metavanadate, sodium tungstate and phosphoric acid, the capacity of the final product ($TTVP_7R$) is further increased to some extent and it becomes chemically more stable. Both the refluxed product ($TTVP_7R$) and the unrefluxed product ($TTVP_7$) show reproducible properties as it is evident from the data given in Table 2.

It is clear from Table 3 that the hydrated radii of alkali metals and alkaline earths have no significant effect on the ion-exchange capacity of tin(IV) tungstovanadophosphate. The refluxed and the unrefluxed product both behave in a similar manner. The highest capacity is observed for Ba^{2+} ion [2.6 meq (dry g)$^{-1}$]. The order of exchange capacity for alkali metals, however, is as follows:

Sample $TTVP_7R$: $K^+ > Rb^+ > Li^+ > Na^+$

Sample $TTVP_7$: $K^+ > Rb^+ > Li^+ > Na^+$

In the case alkaline earths the same order is followed for both the ion-exchange materials

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$$

A comparison of the ion-exchange capacity of different tin(IV) based ion exchangers at 25±2 °C shows that tin(IV) tungstovanadophosphate (TTVP$_7$R) is much superior to other exchangers such as tin(IV) phosphate [(1.44 meq (dry g)$^{-1}$],[4] tin(IV) tungstate [0.58 meq (dry g)$^{-1}$][2] and tin(IV) vanadate [0.85 meq (dry g)$^{-1}$].[3] It is also interesting to note that stannic tungstovanadophosphate has higher ion-exchange capacity and chemical stability as compared to double salts such as tin(IV) vanadophosphate [1.98 meq (dry g)$^{-1}$].[1] The pH titration curves (Figs. 1 and 2) show that tin(IV) tungstovanadophosphate behaves as a monobasic acid. The uptake of ion depends on the pH of the solutions. The adsorption of K$^+$ is greater than

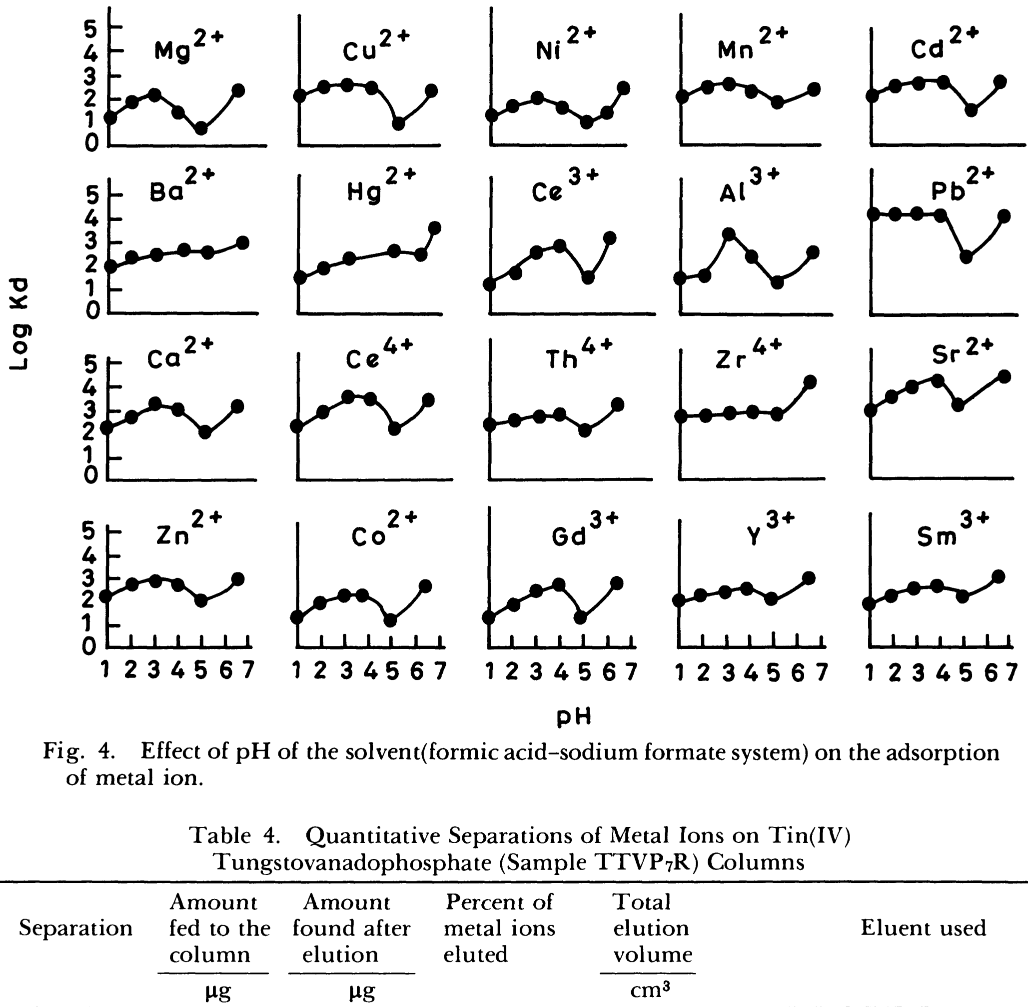

Fig. 4. Effect of pH of the solvent(formic acid–sodium formate system) on the adsorption of metal ion.

Table 4. Quantitative Separations of Metal Ions on Tin(IV) Tungstovanadophosphate (Sample TTVP$_7$R) Columns

Sl. No.	Separation	Amount fed to the column μg	Amount found after elution μg	Percent of metal ions eluted	Total elution volume cm^3	Eluent used
1	Mg^{2+}	264	259.2	98.2	70	0.02 mol dm^{-3} HNO_3
	Ca^{2+}	272	256	94.1	40	0.05 mol dm^{-3} HNO_3
2	Cd^{2+}	1258.9	1213.9	96.4	70	0.02 mol dm^{-3} HNO_3
	Zn^{2+}	627.6	601.4	95.8	50	0.05 mol dm^{-3} HNO_3
3	Cd^{2+}	1258.9	1236.4	98	70	0.02 mol dm^{-3} HNO_3
	Pb^{2+}	2320.5	2237.7	96.4	40	0.05 mol dm^{-3} HNO_3
4	Mn^{2+}	582.4	560.4	96.2	60	Formic acid–sodium formate buffer (pH=5)
	Hg^{2+}	2046	1765.2	86.3	80	0.01 mol dm^{-3} HNO_3
5	Ba^{2+}	1428.3	1291	90.4	80	Formic acid–sodium formate buffer (pH=5)
	Ca^{2+}	272	264	97	40	0.05 mol dm^{-3} HNO_3
6	Hg^{2+}	2046	1805.3	88.2	80	0.01 mol dm^{-3} HNO_3
	Pb^{2+}	2320.5	2237.7	96.4	40	0.05 mol dm^{-3} HNO_3
7	Ce^{4+}	1652	1568	94.9	50	0.02 mol dm^{-3} HNO_3
	Th^{4+}	2505.6	2412.8	96.3	60	0.10 mol dm^{-3} HNO_3
8	Y^{3+}	1386.8	1315.7	94.9	70	0.05 mol dm^{-3} HNO_3
	Th^{4+}	2505.6	2366.4	94.4	60	0.10 mol dm^{-3} HNO_3
	Zr^{4+}	1237.6	1164.8	94.1	50	0.50 mol dm^{-3} HNO_3
9	Gd^{3+}	1130.4	1067.6	94.4	30	0.01 mol dm^{-3} HNO_3
	Y^{3+}	1386.8	1297.9	93.6	70	0.05 mol dm^{-3} HNO_3
	Zr^{4+}	1237.6	1183	95.6	60	0.50 mol dm^{-3} HNO_2

Na^+ in the pH region 2.5—10.

Tin(IV) tungstovanadophosphate has been found to be fairly stable in moderately concentrated nitric acid, hydrochloric acid, sulfuric acid, and perchloric acid. A comparison of the chemical stability data shows that the refluxed sample ($TTVP_7R$) is more stable than the unrefluxed one ($TTVP_7$). Equilibration study demonstrates the equilibrium is reached within 2 h of shaking for most of the metal ions studied except Cu^{2+} and Th^{4+} which take at least 4 h.

Thermogram of tin(IV) tungstovanadophosphate (Fig. 3) shows a continuous loss in weight upto 500 °C. A sharp weight loss upto a temperature of 250 °C may be due to removal of water molecules. It can also be inferred that the decomposition of tin(IV) tungstovanadophosphate starts after 250 °C and continues upto 500 °C. The gradual loss in weight in this temperature region is probably due to the loss of vanadium and phosphorus by volatilization. This conclusion is also supported from the ion-exchange capacity data [I. E. C. at $400\,°C=0.2$ meq (dry g)$^{-1}$ and at $500\,°C=0.1$ meq (dry g)$^{-1}$]. As vanadium and phosphorus contents of the material reduces the capacity becomes smaller and smaller. On increasing the temperature beyond 500 °C, the weight becomes constant due to the formation of stable tin oxide. The exchange capacity, therefore, reduces to a negligible value [0.4 meq (dry g)$^{-1}$].

Some interesting features are observed regarding the adsorption of metal ions on tin(IV) tungstovanadophosphate in sodium formate—formic acid buffer systems. It has been found that the pH of the buffer system affects the adsorption critically. It is apparant from Fig. 4 that the adsorption of metal ions on tin(IV) tungstovanadophosphate in sodium formate—formic acid buffer system vary with the pH. An increase in the pH of buffer system causes higher adsorption of almost all metal ions as expected. In the case of Zr^{4+}, the K_d value remains constant upto pH 5 and then increases sharply as the pH is increased. However, in other buffer systems studied, i. e. sodium citrate–citric acid and sodium acetate–acetic acid, distribution coefficients of metal ions do not vary with the pH of the buffer systems. This is also observed that the K_d values of metal ions are usually much more higher in demineralized water than in sodium formate–formic acid systems. The separation potentiality of tin(IV) tungstovanadophosphate has been demonstrated by achieving some important and difficult separations of metal ions quantitatively on its small columns.

Sphalerite and Calamine contain 0.1 to 0.5% of Cd^{2+}.[15] The binary separation of Cd^{2+}–Zn^{2+} may be utilized for the recovery of Cd^{2+} from these ores. Th^{4+}, Ce^{4+}, and Ca^{2+} may be eluted by different concentration of acid which can be applied for separation of these metal ions in cheralite[16] using tin(IV) tungstovanadophosphate columns.

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