

## Synthesis, ion exchange properties and analytical application of new hybrid cation exchanger : Acrylonitrile tin(IV)tungstophosphate

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### ABSTRACT

A new hybrid inorganic-organic cation exchanger acrylonitrile tin (iv) tungstophosphate has been synthesized and its analytical application explored. The effect of experimental parameter such as reagent mixing ratio, temperature effect on ion exchange properties of material has been studied. The material behaves as monofunctional acid with ion exchange capacity of 1.91 and 1.94 meq g<sup>-1</sup> was found to be for Na<sup>+</sup> and K<sup>+</sup> respectively. The chemical stability data reveals that the exchanger is quite stable in mineral acid, bases and fairly stable in organic solvent, whereas thermal analysis shows that the material retain 78.65 % I.E.C upto 400° C. The sorption studies reveals that the material is selective for Pb<sup>+2</sup> and Sr<sup>+2</sup> ions.

**Key words:** hybrid ion exchanger ; acrylonitrile tin (iv) tungstophosphate; Pb<sup>+2</sup> & Sr<sup>+2</sup> selective.

### INTRODUCTION

Today ion exchange materials have found extensive application in analytical and industrial chemistry in view of their good elegant characteristics such as insoluble matrix, stiochiometric exchange, good selectivity, specificity and applicability to column operation. Meeting the stringent coolant purity requirement of the nuclear industry is solely attributable to ion exchangers<sup>1</sup>. Molecular combination between organic polymer as supporting materials and inorganic precipitates of polyvalent metal acid salts as ion exchanger has been of great interest<sup>2</sup>. The organic and inorganic composites have attracted great attention in the field of analytical as well as material science because of their unique property to combine the significant features of organic polymers with those of inorganic materials.

Tin(IV) based ion exchanger have received attention because of their excellent ion exchange behaviour. They are expected to have radiation

stability and temperature stability. A large number of inorganic-organic ion exchanger have been synthesized by the incorporation of organic monomer in inorganic matrix with good ion exchange capacity<sup>3-4</sup>.

In the present work we have chosen the synthesis, ion exchange studies and analytical application of inorganic- organic hybrid cation exchanger by the incorporation of organic polymers i.e Acrylonitrile and inorganic ion exchanger Sn(IV)tungstophosphate by sol gel technique.

### EXPERIMENTAL

#### Reagent and chemicals

The main reagents used for the synthesis of hybrid cation exchanger were tin (iv) chloride pentahydrate (SnCl<sub>4</sub>.5H<sub>2</sub>O), acrylonitrile, sodiumtungstate were obtained from CDH (India) while orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) was qualigen (India ) product. All other reagent and chemicals were of analytical grade.

### Instrumentation

A digital pH meter (Elico LI-10, India), an automatic thermal analyzer (V2.2 DuPont 9901), an elemental analyzer (Carlo-Erba 1180), electric shaking machine were used.

### Synthesis of acrylonitrile tin (iv) tungstophosphate cation Exchanger

Inorganic precipitate of tin (iv) tungstophosphate were prepared by adding 0.1 tin chloride solutions to a mixture of 0.5 M orthophosphoric acid and 0.5 M sodium tungstate in different (v/v) ratios with intermittent shaking of the mixture. The pH of the mixture was adjusted at the pH 1 by adding 1M HNO<sub>3</sub> acid. The gel of acrylonitrile prepared in ethanol in different (v/v) ratio were added into the white inorganic precipitate of tin (iv) tungstophosphate and mixed thoroughly with constant stirring. The resultant gel were refluxed for 24 hr at a temperature of (55 ± 5°). After that they were kept for hr at room temperature (25 ± 5°) for digestion. The dried gel was put into the dmw to obtain granules of uniform size suitable for column operation. These granules were converted into H<sup>+</sup> form by placing them in 1 M HNO<sub>3</sub> solution for 24 hr with occasional shaking and intermittently replacing the supernatant liquid with fresh acids. The material thus obtained was then washed with demineralised water to remove the excess acid before drying finally at 55 ± 5° and sieved to obtain particle of size 50-70 mesh.

Hence a number of sample of acrylonitrile tin (iv) tungstophosphate cation exchanger were prepared (table-1) and on the basis of Na<sup>+</sup> exchange capacity various studies were done.

### Ion -exchange capacity

The ion exchange capacity of the materials was determined by the column chromatography process. 1 gm sample in the H<sup>+</sup> form was taken into a glass column having internal diameter (i.d)~ 1 cm and fitted with glass wool support at the bottom. The exchanger was washed with DMW to remove any excess of acid that remained on the particles. 250 ml of 1M solution of different salts was passed through the column maintaining the flow rate at 1 ml/min. The effluent was collected and titrated against a standard 0.1 M NaOH solution for the determination of the total H<sup>+</sup> ions released.

### Chemical composition

To determine the chemical composition of acrylonitrile tin (iv) tungstophosphate, 0.10 gm of exchanger was dissolved in minimum amount of hot concentrated hydrofluoric acid. The material was analyzed for tin (iv) by ICP-MS, tungsten and phosphate gravimetrically and titrimetrically respectively using the standard method (Reilley *et al.*). Carbon, hydrogen and nitrogen contents of the cation-exchanger were determined by elemental analysis. The weight percent composition of the material was : Sn, 21.02; P, 13.35; C, 18.25; H, 4.64; N, 5.10; O, 31.25

### Thermal Stability

1 gm sample of the material were heated at different temperature for 1 hr each in muffle furnace, and their ion exchange capacity for Na<sup>+</sup> were determined by column process after cooling them to room temperature. Table.3 summarizes the result of this study.

### pH titration

pH titration of acrylonitrile tin (iv) tungstophosphate was performed by the method of Topp and Pepper<sup>6</sup>. 500 mg portions of the exchanger in the H<sup>+</sup> form were placed in each of the several 250 mL conical flasks followed by equimolar solution of alkali metal hydroxide and their chlorides in different volume ratio. The final volume being 50 ml to maintain the ionic strength constant. The pH of each solution was measured and plotted against milliequivalent of the OH<sup>-</sup> ions. The capacity corresponding to inflection point was also calculated from the curve [Fig.1].

### Chemical stability

The chemical resistivity of acrylonitrile tin (iv) tungstophosphate in various media (acid and bases) has been assessed. The powdered sorbent was contacted with acid and bases solution for 24 h at ambient temperature. Tin was determined spectrophotometrically and phosphate by titrimetrically using the standard method.

### Distribution (sorption) studies

The exchanger (0.2 gm) in H<sup>+</sup> form was taken in different metal ion solution in 40 ml in required solvent medium in 100 ml Erlenmeyer flasks. The mixture was shaken for 24 h at 25 ± 2°

C in a temperature controlled incubator shaker. The initial metal ion concentration (0.01M) in the solution was so adjusted that it did not exceeds 3% of the total ion exchange capacity of the exchanger. The determination before and after equilibrium were carried out volumetrically using EDTA as the titrant<sup>7</sup>.

The  $K_d$  value, as summarized in table-4 were obtained by the formula

$$K_d = \frac{\text{milliequivalent of metal ions}}{\text{gm of ion exchanger}} \times \frac{\text{milliequivalent of metal ions}}{\text{ml of solution}} \text{ ml/g}$$

$$K_d = \frac{I-F}{F} \times \frac{V}{M} \text{ ml/g}$$

Where I is the initial metal ion concentration, F is final amount metal ion concentration, V is the volume of the solution and M is the mass of the exchanger.

#### Effect of eluent concentration

To find out the optimum concentration of the eluent for complete elution of  $H^+$  ions, a fixed volume i.e 250 mL of  $NaNO_3$  solution of different concentration was passed through the columns containing 1 g of the exchanger in  $H^+$  form with a flow rate of  $0.5 \text{ ml min}^{-1}$ . The effluent were titrated against a standard solution of 0.1 M NaOH to find out the  $H^+$  ions eluted out.

#### Elution Behaviour

For this study, 1 M  $NaNO_3$  solution of optimum concentration was passed for complete elution of  $H^+$  ions through a column containing 1.0 g of the composite cation exchanger ( $H^+$  form) with a flow rate of  $0.5 \text{ mL min}^{-1}$ . The effluent was collected in 15 mL fractions and each fraction was titrated against a standard alkali solution.

#### Quantitative separation of metal ions

Quantitative binary separation of some important metal ions were achieved on acrylonitrile tin (iv) tungstophosphate columns. 1.5 gm of the cation exchanger in  $H^+$  form was packed in a glass column of 0.8 cm internal diameter with a glass wool support at the end. The column was washed thoroughly with demineralised water. The mixture of the metal ions having initial concentration of 0.02

M each was loaded on the column and allowed for 1 h to absorb the metal ions on the exchanger. The mixture was passed gently (maintaining a flow rate of two to three drop per minute). After recycling two or three times to ensure complete absorption of the mixture on column beads, the separation was achieved by passing a suitable solvent at a flow rate of  $0.5 \text{ mL min}^{-1}$  through the column as effluent. The effluents were determined quantitatively by AAS and EDTA titration.

## RESULTS AND DISCUSSION

The sample of acrylonitrile tin (iv) tungstophosphate has been synthesized under varying conditions by sol-gel mixing of inorganic precipitate of tin (iv) tungstophosphate and acrylonitrile. It is evident from table 1 that the mixing ratios of the reactants affect the physical appearance and ion exchange capacity of the material. Sample-3 selected on the basis of better yield, ion exchange capacity, high chemical stability and reproducibility as compared to others. The improvement in these characteristics of organic-inorganic hybrid cation exchanger may be due to binding of organic polymeric material with inorganic moiety. The most interesting characteristics of this hybrid material is its granulometric property, showing good reproducible behaviour as is evident from the fact that these materials obtained from various batches did not show any appreciable deviation in their percentage of yield and ion exchange capacities. The effect of the size and charge of the exchanging ion on the ion exchange capacity was also observed for this hybrid material. Table. 2 shows the ion exchange capacity for alkali and alkaline earth metal ions. The ion exchange capacity of hybrid cation exchanger for alkali and alkaline earth metal ions increases according to decrease in the hydrated ionic radii<sup>8-11</sup>. The ions with smaller hydrated radii easily enter the pores of exchanger, resulting in higher adsorption<sup>5</sup>. Effect of heating at different temperature for 1 h, indicated that on heating at elevated temperature the mass and ion exchange capacity of the dried composite cation exchanger was changed as the temperature increased (Table 3). It was observed that the material possessed high thermal stability about 68 % of the initial mass by heating upto  $500^\circ \text{C}$ . The pH-titration in the presence of acrylonitrile tin (iv)

tungstophosphate was performed for NaCl-NaOH and KCl-KOH system. The pH titration curve show that pH increases when, NaOH and KOH were added 0.5-1.5 m.moles per 0.5 g of composite cation exchanger material and relatively very slow steep increase when these hydroxide were added 1.50-2.50 m mol g<sup>-1</sup> of cation exchanger. This composite cation exchanger may be strong acid cation

exchanger because the pH titration curve usually showed a steep edge at 2.0 m mol g<sup>-1</sup> of cation-exchanger that is, the -H functional groups on the hybrid cation exchanger were depleted and replaced with ,Na<sup>+</sup> and K<sup>+</sup> at this point. The pH titration curve of acrylonitrile tin(IV)tungsto phosphate (Fig.1) showed a gradual rise in the pH at the early stage of titration and steep rise at the point of complete

**Table 1: Condition of preparation and few properties of different sample of acrylonitrile tin (iv) tungstophosphate**

Sample No.	SnCl <sub>4</sub> . 0	H <sub>3</sub> P0 <sub>4</sub> 5H <sub>2</sub> O	Sodium tungstate	Acrylonitrile	Mixing pH	Appearance of bed after drying at 50* C	I.E.C (meqg <sup>-1</sup> )
1	0.1	1	0.1	0.1	1:1:1:1 1	White gelatinous	1.71
2	0.1	1	0.1	0.1	1:2:1:1 1	White gelatinous	1.89
3	0.1	2	0.1	0.1	1:2:2:1 1	White gelatinous	1.92
4	0.1	2	0.1	0.1	1:1:1:2 1	White gelatinous	1.52
5	0.1	2	0.1	0.1	2:1:1:1 1	White gelatinous	1.67

**Table 2: Ion exchange capacity (meq g<sup>-1</sup> dry exchanger) of acrylonitrile tin (iv)tugstophosphate (Sample No.3)**

S. No	Cation	Salt used	pH of the metal solution	Ionic radii (Å)	Hydrated Ionic radii(Å)	I.E.C (meq/g)
1.	Li <sup>+</sup>	LiCl	6.61	0.63	3.21	1.65
2.	Na <sup>+</sup>	NaCl	6.73	0.93	2.69	1.91
3.	K <sup>+</sup>	KCl	6.70	1.33	2.42	1.94
4.	Mg <sup>+2</sup>	Mg(NO <sub>3</sub> ) <sub>2</sub>	6.50	0.80	6.93	1.45
5.	Ca <sup>+2</sup>	Ca(NO <sub>3</sub> ) <sub>2</sub>	6.60	1.14	6.01	1.60
6.	Ba <sup>+2</sup>	Ba(NO <sub>3</sub> ) <sub>2</sub>	6.39	1.40	5.21	1.78

**Table 3: Summarizes the result of the study**

Sample no.	Drying Temp (*C)	Na + ion exchange capacity(meqdry/g)	Change in colour	% Retention
1.	50	1.92	White	100
2.	100	1.90	White	98.96
3.	200	1.81	White	94.27
4.	300	1.63	Grey	84.9
5.	400	1.51	Slight grey	78.65
6.	500	1.32	Grey	68.75
7.	600	1.01	Dark grey	52.6

neutralization of the cation exchanger. Thus the maximum capacity of the strong acidic groups of the hybrid was calculated as 1.92 meq.g<sup>-1</sup>. An optimum concentration of the eluent was found to be 1.0M for the complete removal of H<sup>+</sup> ions from the column. The experiment also established that the minimum volume required for complete elution of H<sup>+</sup> ions, which reflects the column efficiency. It was found that the rate of elution is governed by the concentration of eluent used (Fig.2). The rate of elution is governed by the concentration of the

eluent, which was found as a usual behaviour of these type of ion exchange material. The elution behaviour indicates that the exchange is quite fast and almost all the H<sup>+</sup> ions are eluted out in the first 130 ml of the effluent from a column of 1.0 g exchanger within 4 h as shown in (Fig.3)

In order to explore the potential of this cation exchanger in the separation of metal ions, distribution studies of 12 metal ions were performed in several solvent systems (table 5). The distribution

**Table 4: K<sub>d</sub> value of some metal ion on acrylonitrile tin (iv) tungsto phosphate hybrid cation exchanger column in different solvent systems**

Metal Ions	DMW	0.01M HCl	0.1M HCl	1M HCl	0.01M HNO <sub>3</sub>	0.1M HNO <sub>3</sub>	1M HNO <sub>3</sub>	0.01M HClO <sub>4</sub>	0.1M HClO <sub>4</sub>	1M HClO <sub>4</sub>
K <sup>+</sup>	625	510	689	621	701	823	721	614	601	534.3
Na <sup>+</sup>	1100	401	189	215	389	334	220	1301	705	200
Mg <sup>+2</sup>	1461	601	523	439	811	721	644	832	701	581
Sr <sup>+2</sup>	1720	1325	1222	1222	514	414	414	713	575	575
Mn <sup>+2</sup>	2516	1179	1058	801	1201	693	513	915	821	402
Ba <sup>+2</sup>	2001	1235	1079	1079	1823	1522	1441	1635	1401	1401
Hg <sup>+2</sup>	1485	920	943	615	1480	1415	1465	1260	1120	1092
Cd <sup>+2</sup>	3500	735	814	791	775	694	501	1502	1301	1121
Pb <sup>+2</sup>	1331	1225	1135	893	1517	1501	1322	1287	715	1201
Co <sup>+2</sup>	1190	1224	1150	765	3200	2561	1360	3155	1695	1298
Ni <sup>+2</sup>	3571	344	1389	1154	1735.2	1500	1489	4256	2614	2244
Cr <sup>+3</sup>	5270	2711	1125	790.5	3715	1220	1092.1	4680	2021	980

**Table 5:**

Separation achieved	Amount loaded(μg)	Amount found(μg)	% Recovery	Eluent used	Volume of Eluent(ml)
Pb <sup>+2</sup>	1820	1785	98	1M HNO <sub>3</sub>	70
Sr <sup>+2</sup>	413	408	98.79	1M HNO <sub>3</sub>	60
Pb <sup>+2</sup>	1820	1790	98.35	1M HNO <sub>3</sub>	70
Cd <sup>+2</sup>	1025	995	97.07	1M HNO <sub>3</sub>	50
Zn <sup>+2</sup>	712	705	99.02	1M CH <sub>3</sub> COOH	60
Ba <sup>+2</sup>	1625	1562	96.12	1M HNO <sub>3</sub>	80
Pb <sup>+2</sup>	1112	1091	98.11	1M HNO <sub>3</sub>	50
Cu <sup>+2</sup>	512.6	490	95.59	1M HClO <sub>4</sub>	60
Hg <sup>+2</sup>	732	711	97.13	1M HNO <sub>3</sub>	70
Pb <sup>+2</sup>	925	925	100	1M HNO <sub>3</sub>	60
Ba <sup>+2</sup>	1822	1785	97.97	1M HNO <sub>3</sub>	60
Ca <sup>+2</sup>	713	690	96.77	1M HNO <sub>3</sub>	50

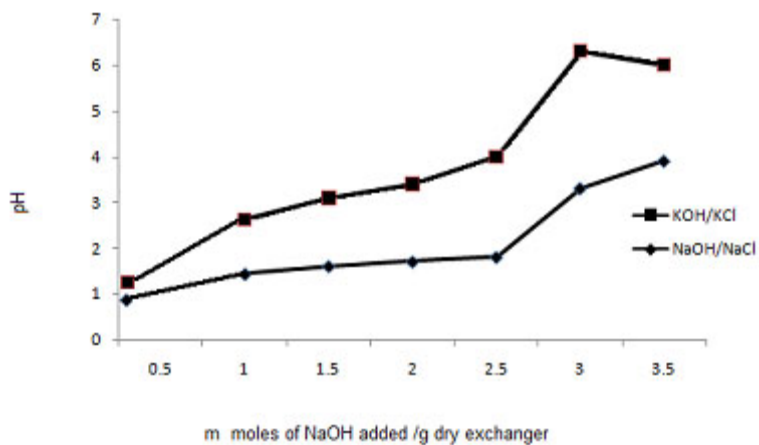


Fig. 1: pH titration curve for Acrylonitrile tin (IV) tungstophosphate

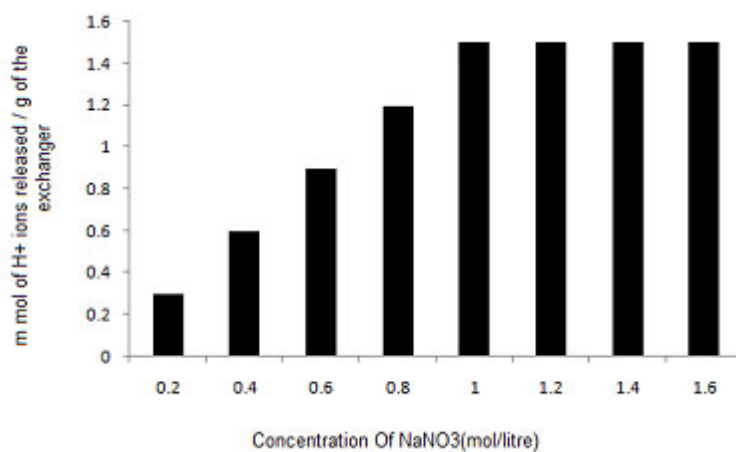


Fig. 2: Effect of eluent concentration on ion-exchange capacity of acrylonitrile tin (IV) tungstophosphate hybridcation exchanger

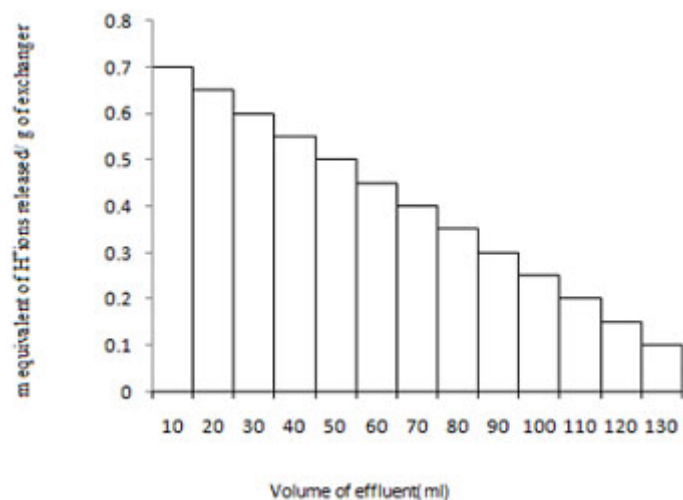


Fig. 3: Elution behaviour of Acrylonitrile tin (IV) tungstophosphate hybridcation exchanger

studies showed that the material was found to possess exceptional high  $K_d$  values for Pb(II) and Sr(II) and hence considered to be highly selective for Pb(II) and Sr(II), which is a major pollutant of water. The separation capacity of the material has been demonstrated by achieving some important binary separation such as Pb(II)-Sr(II), Pb(II)-Cd(II), Pb(II)-Cu(II) etc. Table 5 summarizes the salient features of these separations.

## CONCLUSIONS

Newly synthesized acrylonitrile tin (iv) tungstophosphate was synthesized and its analytical application explored. The ion exchange capacity in meq  $g^{-1}$  for different metal ions are:  $Li^+$ , 1.65;  $Na^+$ , 1.91;  $K^+$ , 1.94;  $Mg^{+2}$ , 1.45 etc. The material is fairly stable in inorganic acids, bases and organic solvents. The promising feature of the material is its selectivity for  $Pb^{+2}$  and  $Sr^{+2}$  ions, most toxic metal ions present in environment.

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