

SYNTHESIS, CHARACTERIZATION AND ADSORPTION BEHAVIOUR OF TX-100 BASED Sn(IV) PHOSPHATE, A NEW HYBRID ION EXCHANGER

Separation of Ni(II) from Hg(II), Pb(II) and Fe(III) on its column

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A new hybrid ion exchanger, Triton X-100 based tin(IV) phosphate (TX-100SnP) has been synthesized and characterized by ion exchange and physico-chemical methods such as ion exchange capacity, elution and concentration behaviour, IR, X-ray, TG/DTA and elemental analysis. Its adsorption behaviour has also been studied for some alkaline earths and heavy metal ions in different acidic media. It has been found generally more selective for metal ions as compared to tin(IV) phosphate prepared earlier. For Pb(II), Hg(II) and Fe(III) its selectivity has been found to be exceptionally good. On this basis, some binary separations have been performed involving these metal ions. Thermal studies show a high thermal stability of the material. It retains 54.54% of its i.e.c. at 200°C and 27.27% at 300°C.

Keywords: characterization, Fe(III), Hg(II), Ni(II), Pb(II), Sn(IV), synthesis, TX-100

Introduction

Hybrid ion exchangers, i.e. the materials obtained by incorporating organic substances into the inorganic ones are of much interest [1] these days. Introduction of organic species into an inorganic material enhances its reproducibility in ion exchange behaviour and its chemical stability to some extent. Various hybrid materials [2–11] have been prepared in these laboratories which have shown promising ion exchange characteristics. Surfactants, when present in the matrix of an ion exchanger may enhance its ion exchange capacity and adsorption of metal ions by way of reducing the interfacial tensions between the material (solid) and the aqueous phase (liquid) [12] from which exchange/adsorption takes place. Therefore, these materials are of great importance in industrial and environmental applications. Following pages summarize our such a study on Sn(IV) phosphate cation exchanger, containing a nonionic surfactant, triton X-100 (TX-100) in its matrix.

Experimental

Tin chloride (SnCl₄·5H₂O) was obtained from CDH (India) while Triton X-100 and phosphoric acid (H₃PO₄) were obtained from Himedia (India) and

Qualigens (India) respectively. All other reagents and chemicals were of AnalaR grade.

X-ray diffraction studies were performed on a Philips Analytical X-ray B. V. diffractometer type PW 170 B.V. and IR studies were carried out on Shimadzu 8201 PC spectrophotometer while elemental studies were performed using a Heraeus Carlo Erba 1108 elemental analyzer. For TG/DTA/DTG, Perkin Elmer Pyris Diamond model was used.

Solutions of tin(IV) chloride, TX-100 and phosphoric acid were prepared in demineralized water (DMW).

TX-100SnP was prepared by adding one volume of 0.3 M tin chloride in two volumes of a (1:1) mixture of 0.6 M H₃PO₄ and 0.0001 M TX-100 solutions, dropwise with constant stirring, provided the highest ion exchange capacity (2.75 meq g⁻¹). The resulting slurry was stayed overnight and then filtered and washed with DMW till pH~4. The material was then dried at room temperature and the dried gel was cracked into small granules by putting in DMW and converted into the H⁺-form by treating with 1 M HNO₃ for 24 h. The material was then washed with DMW to remove excess of acid, dried at room temperature and sieved to 50–70 mesh sized particles.

The ion exchange capacity of the sample was determined by the column process taking 1 g of the material (H⁺-form) in a glass tube of internal diameter

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~1 cm. 250 mL of 1 M NaNO₃ solution was used as eluant, maintaining a very slow flow rate (~0.5 mL min⁻¹). The effluent was titrated against a standard alkali solution to determine the total H⁺-ions released. Table 1 summarizes the i.e.c. of the material for various metal ions.

The extent of elution was found to depend upon the concentration of the eluant. Hence, a fixed volume (250 mL) of the NaNO₃ solution of varying concentrations was passed through the column containing 1 g of the exchanger. The effluent was titrated against a standard alkali solution for the H⁺ ions eluted out. Table 2 shows the variation of i.e.c. of the material with different concentrations of the eluant.

A similar column (as above) containing 1 g exchanger was eluted with 1 M NaNO₃ solution in

Table 1 Ion exchange capacity of TX-100SnP for various metal ions

Metal ion solutions	i.e.c./meq dry g ⁻¹
LiCl	2.90
NaNO ₃	2.75
KCl	2.50
Ca(NO ₃) ₂	3.10
SrCl ₂	3.15
BaCl ₂	3.25
MgCl ₂	2.95

Table 2 Variation of i.e.c. of TX-100SnP with NaNO₃ eluant concentrations

NaNO ₃ /M	i.e.c./meq g ⁻¹
0.2	1.0
0.4	1.75
0.6	1.95
0.8	2.15
1.0	2.75
1.2	2.75

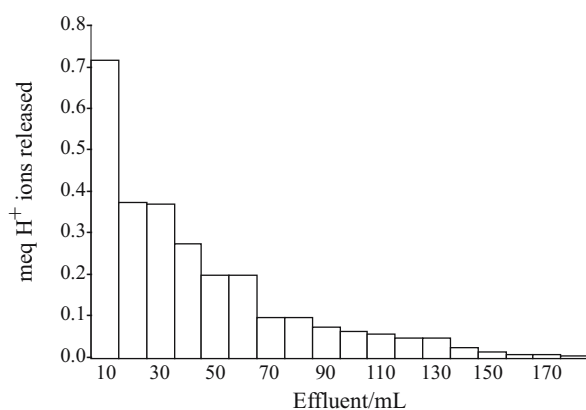


Fig. 1 Histograms showing the elution behaviour of TX-100SnP

Table 3 Thermal stability of TX-100SnP after heating to various temperatures for 1 h

Drying temp./°C	Na ⁺ -ion exchange capacity/meq dry g ⁻¹	Change in colour	Retention of i.e.c./%
45	2.75	Off white	100
100	2.00	Off white	72.73
200	1.50	Off white	54.54
300	0.75	Off white	27.27
400	0.05	White	1.82

different 10 mL fractions with a minimum flow rate as described as above. Figure 1 shows the elution behaviour of the exchanger.

Several 1 g samples of TX-100SnP were heated at various temperatures in a muffle furnace for 1 h each and their i.e.c. was determined by the column process after cooling them to room temperature. The results are reported in Table 3.

200 mg of the exchanger in H⁺-form was added to a mixture containing 18 mL of the acid solution and 2 mL of the metal ion solution. The mixture was kept for 24 h, shaking intermittently to achieve equilibrium. The metal ions in the solution before and after equilibrium were determined by the EDTA titrations and the distribution coefficients (K_d) were calculated by the formula:

$$K_d = \frac{I-F}{F} \frac{V}{M} (\text{mL g}^{-1})$$

where I and F are the initial and final amounts of the metal ions in the solution phase, V the volume (mL) of the solution, and M the amount (g) of the exchanger. The results are reported in Table 4.

For binary separations, 200 mg of the exchanger in H⁺-form was used in a glass tube having an internal diameter of ~0.6 cm. The column was washed thoroughly with DMW and the mixture to be separated was loaded on it. After recycling 2 or 3 times to ensure complete adsorption of the mixture on the column bed, the metal ions were eluted at a flow rate ~2–3 drops min⁻¹, using eluant selected on the basis of K_d values obtained. The metal ions in the effluent were determined quantitatively by EDTA titrations. Table 5 gives the salient features of the separations.

Results and discussion

TX-100, when present in the Sn(IV) phosphate matrix, enhances the ion exchange capacity of Sn(IV) phosphate to a great extent. It was found to be 2.75 meq g⁻¹ as against 1.5 meq g⁻¹ for the SnP pre-

Table 4 K_d values of some metal ions on TX-100SnP in DMW and different acid media

Metal ions	DMW	HCl			HNO ₃			HClO ₄		
		0.01 M	0.1 M	1 M	0.01 M	0.1 M	1 M	0.01 M	0.1 M	1 M
Mg(II)	760.00	760.00	514.29	437.50	975.00	616.67	377.78	975.00	616.67	514.29
Ca(II)	600.00	500.00	425.00	366.67	500.00	425.00	366.67	740.00	500.00	425.00
Sr(II)	528.57	450.00	388.89	340.00	528.57	388.89	297.30	633.33	450.00	388.89
Ba(II)	800.00	800.00	650.00	542.86	650.00	542.86	400.00	800.00	542.86	462.50
Fe(III)	2250.0	1466.7	1025.0	840.00	1466.7	1025.0	571.43	1025.0	840.00	683.33
Mn(II)	666.67	571.14	360.00	283.33	666.67	475.00	318.18	666.67	571.14	360.00
Ni(II)	514.29	437.50	330.00	290.91	616.67	377.78	330.00	514.29	437.50	330.00
Co(II)	720.00	583.33	485.71	412.50	720.00	583.33	485.71	720.00	583.33	412.50
Cu(II)	1400.0	1025.0	650.00	542.86	1400.0	1025.0	462.50	1025.0	542.86	462.50
Cd(II)	1233.3	900.00	700.00	566.67	700.00	471.43	344.44	1233.3	900.00	566.67
Hg(II)	1000.0	780.00	780.00	633.33	1366.7	1000.0	633.33	1366.7	780.00	528.57
Pb(II)	2150.0	1400.0	1025.0	800.00	1400.0	1025.0	542.86	1025.0	800.00	650.00

Table 5 Binary separations of metal ions achieved on TX-100SnP columns

S.N.	Separation achieved		Amount loaded/ μg		Amount found/ μg		Error/%		Eluant/mL
	M ₁	M ₂	M ₁	M ₂	M ₁	M ₂	M ₁	M ₂	
1	Ni(II)–Hg(II)		7043	24071	7207	24071	+0.02	0	Ni: 1M HCl(60) Hg: 1M NH ₄ Cl+1M HCl(50)
2	Ni(II)–Pb(II)		7043	24864	6879	24864	–0.02	0	Ni: 1M HCl(50) Pb(II): 0.1M HClO ₄ (50)
3	Ni(II)–Fe(III)		7043	6701	6879	6416	–0.02	–0.04	Ni: 1M HCl(50) Fe: 1M HClO ₄ (60)

pared earlier. In fact, the i.e.c. of TX-100SnP is higher than almost all the materials of this class prepared so far (Table 6).

The elution behaviour indicates that the exchange is fast and almost all the H⁺ ions are eluted out in the first 180 mL of the effluent from a column of 1 g exchanger (Fig. 1). Similarly, the optimum concentration of the eluant was found to be 1 M (Table 2) for a complete removal of H⁺ ions from the above column. In this respect, the material is similar to the others of this class.

The two-step mass losses (6.58 and 5.22%) up to 150°C (Fig. 4) in the TG/DTA curves show the endo effect at 102°C confirming the removal of external water molecules. Further, the curves show 2.26 and 1.12% losses up to 367°C which may be due to the removal of triton X-100 from the matrix of the exchanger. At this stage, condensation might have also started with the removal of strongly co-ordinated water molecules, showing an endo effect at 317°C, which continued up to 789°C. A 4.53% mass loss up to 500°C may be due to the removal of remaining part of surfactant. Finally, mass losses 1.66 and 1.53% up

Table 6 A comparison in i.e.c. of TX-100SnP with various hybrid materials

S. N.	Name of the materials	i.e.c./ meq g ⁻¹
1	Triton X-100 Sn(IV) phosphate	2.75
2	<i>n</i> -butyl acetate Ce(IV) phosphate [4]	2.25
3	Pectin Ce(IV) phosphate [5]	1.78
4	Pectin Th(IV) phosphate [5]	2.15
5	Acryl amide Ce(IV) phosphate [6]	2.60
6	Acryl amide Th(IV) phosphate [7]	2.00
7	Acryl amide Zr(IV) phosphate [8]	2.26
8	Acryl amide Sn(IV) phosphate [9]	2.10
9	Pyridine Sn(IV) phosphate [10]	2.10
10	Pyridine Zr(IV) phosphate [10]	2.00
11	Cellulose acetate Th(IV) phosphate [11]	1.70

to 789°C represent a kinetic non-stability of the decomposition product. The most important feature of TX-100SnP is its thermal stability zone between 150 and 305°C.

The data of thermal analysis (Table 3) points the decrement in i. e. c. by 27.27% up to 100°C due to the removal of external water molecules. Further decrements in i. e. c. up to 400°C are due to both removal of triton X-100 and removal of strongly co-ordinated water molecules. Thus, the data suggests that decrease of i. e. c. of the material tested, is interrelated with the volatilization of both triton X-100 and co-ordinated water molecules from the matrix of ion exchanger.

However, TX-100SnP is found to be more stable than the others. A comparison with acrylonitrile cerium(IV) phosphate (ANCeP) [13] and acryl amide cerium(IV) phosphate (AACeP) [6] shows that TX-100SnP retains 54.54% of its i.e.c. on heating up to 200°C (Table 3) while ANCeP and AACeP retain only 13.98 and 40.15% respectively, at this temperature.

The IR spectrum of the material (Fig. 2) indicates the presence of phosphate groups [14] by the peaks at 514.6 and 1043.7 cm⁻¹, and metal-oxygen and metal-hydroxide bonding by the peak at 645.0 cm⁻¹. The peak at 1640.3 cm⁻¹ represents the external water molecule [15] in addition to its usual range at 3421.4 cm⁻¹. The bands beyond 3421.4 cm⁻¹ are due to -OH groups. The bands at 1134.1 and 3127.9 cm⁻¹ are due to the presence of alkyl ether and benzene (aromatic C-H str.) part in the material.

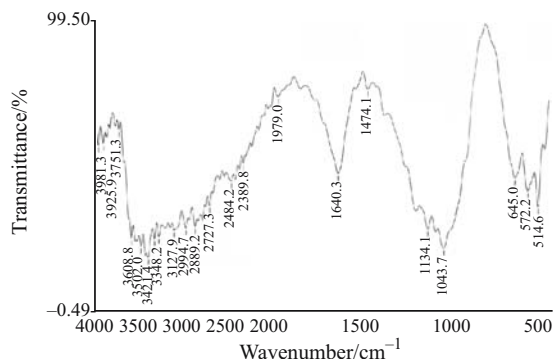


Fig. 2 IR spectrum of TX-100SnP

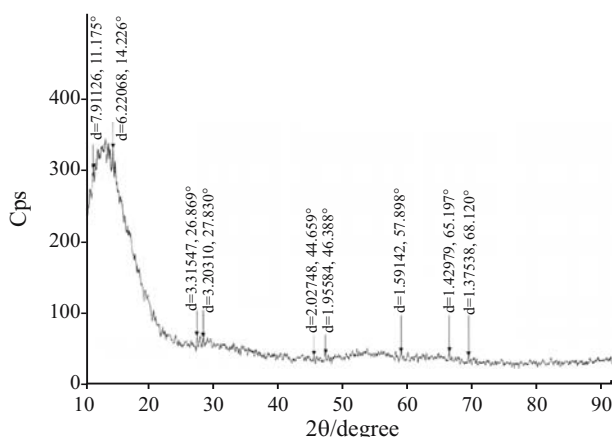


Fig. 3 X-ray diffraction pattern of TX-100SnP

C-H (str.) in CH₃ and/or CH₂ and C-H (def.) in CH₃ and/or CH₂ are represented [16] by the peaks at 2994.7, 2889.2 and 1474.1 cm⁻¹ respectively while the peaks at 3348.2 and 3299.4 cm⁻¹ show the O-H (str.) of intermolecular H-bonded part of the material. Elemental study shows 0.108% carbon and 1.657% hydrogen in the exchanger.

The X-ray diffraction pattern (Fig. 3) shows the amorphous nature of the material.

The adsorption studies reveal the enhanced adsorption of metals on TX-100SnP as compared to that

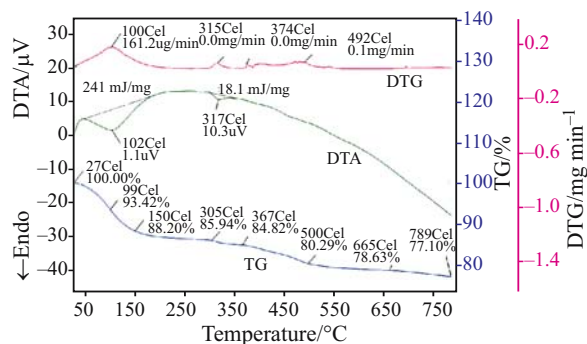


Fig. 4 TG/DTG-DTA curves of TX-100SnP

Table 7 K_d values of some alkaline earths and heavy metal ions on SnP in DMW and different acid media

Metal ions	DMW	HCl			HNO ₃			HClO ₄		
		0.01 M	0.1 M	1 M	0.01 M	0.1 M	1 M	0.01 M	0.1 M	1 M
Mg(II)	162.5	162.5	147.1	133.3	320.0	281.8	200.0	366.7	320.0	200.0
Ca(II)	192.9	215.4	173.3	156.2	192.9	173.3	127.8	272.7	215.4	141.2
Sr(II)	330.0	377.8	258.3	230.8	616.7	616.7	377.8	330.0	290.9	168.7
Ba(II)	900.0	700.0	700.0	471.4	566.7	400.0	207.7	471.4	344.4	207.7
Fe(III)	160.0	143.7	129.4	105.3	160.0	143.7	105.3	225.0	178.6	105.3
Mn(II)	104.4	88.00	80.80	56.70	95.80	88.00	74.10	422.2	327.3	235.7
Ni(II)	41.40	36.70	32.30	28.10	36.70	24.20	17.10	95.20	78.30	64.00
Co(II)	330.0	377.8	258.3	186.7	514.3	330.0	230.8	437.5	377.8	186.7
Cu(II)	666.7	557.1	360.0	206.7	411.1	360.0	253.8	557.1	360.0	253.8

on SnP (Table 7). For TX-100 (nonionic surfactant) [17], metal ions can enter into the polyoxyethylene shell of the surfactant by complex-formation. As a result, the adsorption of metal ions is enhanced. On the basis of these studies, the material is found to be selective for Hg(II), Pb(II) and Fe(III). The potential of this material in environmental pollution control, has been demonstrated by achieving some binary separations, involving the above metals, for example: Ni(II)–Hg(II), Ni(II)–Pb(II) and Ni(II)–Fe(III), as summarized in Table 5. Hg(II) was eluted out using a mixture of NH₄Cl and HCl because it was highly adsorbed and simply 1 M HCl could not elute it out. NH₄⁺ ions, being a bigger ion can easily elute the Hg(II) ions from the exchanger bed.

Conclusions

The addition of surfactant, TX-100 in the matrix of Sn(IV) phosphate enhances the i.e.c. and adsorption of metal ions. Further, TX-100SnP is thermally stable and highly selective for Hg(II), Pb(II) and Fe(III), exploring its importance in the separation of these metal ions from industrial effluents.

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