

Synthesis, properties and analytical applications of Titanium (IV) phosphosulphosalicylate - A new hybrid inorganic-organic ion-exchanger

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ABSTRACT

In order to combine the qualities of inorganic and organic ion exchangers, a stable material with good chromatographic properties, a new inorganic-organic ion exchanger Titanium (IV) phosphosulphosalicylate (TiPSS) was synthesized. Sample-1 was chosen for detailed ion exchange studies due to its highest ion exchange capacity, good appearance and chemical stability. Characterization of the resin was done by determining ion exchange capacity, distribution coefficients for various metal ions, chemical analysis, pH titration, FT-IR spectra and TG thermal analysis. The distribution coefficients (Kd) of 10 metal ions were determined in different electrolyte/electrolyte concentration. The significance of the exchanger is revealed by the important separations. Based on the difference in distribution co-efficient (Kd) some analytically important binary (Mg^{2+}/Pb^{2+} , Zn^{2+}/Pb^{2+} , Co^{2+}/Pb^{2+} , Ni^{2+}/Pb^{2+} , Ca^{2+}/Mg^{2+} & Zn^{2+}/Ca^{2+}) and ternary ($Mg^{2+}/Ca^{2+}/Pb^{2+}$, $Zn^{2+}/Ca^{2+}/Pb^{2+}$ & $Co^{2+}/Ca^{2+}/Pb^{2+}$) separations of metal ions have been achieved. Practical utility of the material has been demonstrated by a novel TLC separation technique with the exchanger. It was found to possess high thermal stability and selectivity for lead, thus making it an important exchanger for the environmentalists.

Key words: Titanium(IV) phosphosulphosalicylate, inorganic-organic ion-exchanger.

INTRODUCTION

Synthetic ion-exchangers of single and double salts as well as organic resins are being increasingly used for separation of metal ions. The organic resins have qualities of uniformity, chemical stability, stability to high temperature and radiations^{1,2,3}. Selectivity towards particular metal ion by inorganic ion exchangers⁴⁻⁹ is one of the important factors for their development, and are having extensive applications in separation science specially of heavy metals¹⁰⁻¹⁴. Incorporation of a polymer material into an inorganic ion exchanger provides a class of hybrid ion exchangers with a good ion exchange capacity, high stability, reproducibility, and selectivity for heavy metals¹⁵. Inorganic ion exchangers based on titanium (II) carboxyethylphosphonate¹⁶ was synthesized

exhibited high thermal stability. New thermally stable phase of hybrid inorganic-organic materials were synthesized by anchoring organic moiety, acryl amide tin (IV) phosphate¹⁷, and acryl amide zirconium (IV) phosphate¹⁸ and characterized. The materials are highly selective for Hg (II). Poly (vinyl chloride) supported tetracycline sorbed zirconium (IV) selenomolybdate¹⁹ chelating inorganic exchange membrane was employed for the detection of dysprosium (III) ion. Polyaniline Sn(IV) tungstoarsenate²⁰ a composite materials formed by the combination of inorganic ion exchangers of multivalent metal acid salts and organic conducting polymers (polyaniline, polypyrrole, polythiophene, etc.), providing a new class of organic-inorganic hybrid ion exchangers with better mechanical and granulometric properties, good ion-exchange capacity, higher stability,

reproducibility and selectivity for heavy metals. A three-component inorganic ion exchanger, zirconium(IV) sulfosalicylphosphate²¹ has been synthesized under varying conditions found highly selective to aluminium(III) and magnesium(II) has been utilized for their separation in synthetic mixtures and antacid formulations. A new phase stannic arsenate ion exchanger²² was synthesized and were used in TLC separation of metal ions. The present paper illustrates the synthesis, properties and analytical applications of titanium (IV) phosphosulphosalicylate.

MATERIAL AND METHODS

Reagents

Titanium(IV)chloride(BDH), sodium phosphate(E-merck) and sulphosalicylic acid (Nice Chemicals) were used. All other reagents used were of analytical grade.

Apparatus

Systronic digital P^H meter MKV for pH measurements, FT-IR spectrophotometer, Thermo Nicolet (AVATAR 370 DTGS) for IR studies, Perkin Elmer (Pyris Diamond) for TG/ DTA and magnetic stirrer for shaking.

Synthesis of titanium (IV) phosphosulphosalicylate

Titanium (IV) phosphosulphosalicylate was prepared by adding a mixture of sulphosalicylic acid and sodium phosphate to Titanium(IV)chloride solution. The preparation was done by taking different molar ratios of the reagents. The solution thus obtained was allowed to settle at room temperature for 24 hours, filtered, washed with demineralised water (DMW), dried and finally ground, sieved to 60-100 mesh and was converted to H⁺ form by treatment with 1M HNO₃. The one with the highest ion exchange capacity was selected for further studies.

Characterization of the resin

Characterization of the resin was done by the following methods.

Ion exchange capacity

The ion exchange capacity of the

exchanger sample was determined using column method²³. 1.0 g of the exchanger in H⁺ form was taken in a glass column; the H⁺ ions were eluted by percolating 250 ml of an electrolyte solution (1M NaCl). The flow rate was maintained at 0.5 ml per min. The effluent was collected and titrated with standard NaOH solution.

Chemical analysis

Titanium estimated by literature method^{24,25}. The phosphate determined gravimetrically²⁵. The filtrate was analyzed for sulphosalicylic acid spectrophotometrically using iron(III) nitrate^{26,27}.

pH Titration

pH titrations were performed by the batch process using the method of Topp and Pepper²⁸, using LiOH-LiCl, NaOH-NaCl, KOH-KCl systems. 0.1g of the exchanger in the H⁺ form were placed in different conical flasks and an equimolar solution of alkali metal/alkaline earth metal chloride and their hydroxides in different volume ratios were added, the final volume being 10 ml to maintain the ionic strength constant. The pH of the solutions were recorded after every 24h until equilibrium was attained. At equilibrium, pH was plotted against milliequivalents of OH⁻ ions added.

FTIR spectrum

FT-IR spectrum of the sample was obtained using KBr disc method.

Thermal analysis

Thermogram of sample was recorded at a heating rate of 10°C/min.

Distribution studies

The distribution coefficients of the ion exchanger for various metal ions were determined by batch process. Samples of exchanger (0.1 g), free from surface moisture, were shaken with 0.005 M solutions (20 ml) of the metal ion and kept for 24 h to ensure maximum uptake. The distribution coefficient (ml/g) is determined as $K_d = (I-F)/F \times V/W$, where I and F are initial and final volumes of EDTA used for titrations, V is the volume of metal ion solution used and W is the weight of the ion-exchanger taken.

Column Separations

For separation studies 5g of the exchanger were taken in a glass column (30x1.1cm). The rate of flow in all separations was maintained at 0.5 ml per min. Separations are carried out for the metal ions for which the separation factor greater than five.

exchanger was obtained as white crystalline solid and is found to be stable in water, alcohol, acetic acid, 1M H₂SO₄, 1M HNO₃, and in aqueous solutions of LiCl, NaCl, KCl, MgCl₂ and BaCl₂.

RESULTS AND DISCUSSION

Details of the synthesis and ion exchange capacity of the exchanger Titanium(IV) phospho sulphosalicylate is as given in (Table 1). The exchanger, exhibited higher ion exchange capacity, was used for detailed studies. This

Thermo analytical investigations throw some light on the empirical formula and theoretical exchange capacity of the sample. The sharp loss in weight up to 150 °C can be attributed to the loss of external water molecule. The weight loss in the region 170°C -370°C may be due to the removal of water molecule as a result of condensation of -OH groups and is accompanied by the loss of sulphosalicylic acid by vaporization. Weight loss between 375°C and 450 °C may be due to loss of

Table 1: Preparation and properties of the exchanger titanium (IV) phospho sulphosalicylate

Titanium(IV) Chloride	Sodium phosphate	Sulpho salicylic acid	Mixing Ratio	Colour	pH	Exchange Capacity
0.10M	0.05M	0.05M	2:1:1	white	1.00	1.95
0.10M	0.05M	0.10M	2:1:2	white	1.50	1.23
0.10M	0.10M	0.10M	1:1:1	white	1.00	1.45
0.10M	0.10M	0.05M	2:2:1	white	1.00	0.89
0.05M	0.10M	0.10M	1:2:2	white	1.00	1.01
0.05M	0.05M	0.10M	1:1:2	white	1.10	1.38
0.05M	0.05 M	0.05M	1:1:1	white	1.50	1.80

Table 2: The effect of hydrated ionic radii and temperature on the exchange capacity of titanium (IV) phospho sulphosalicylate

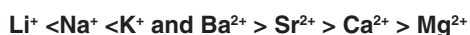
Exchanging Ion	Exchange capacity with hydrated ionic radii		Exchange capacity with temperature	
	Hydrated ioninc radii	Exchange capacity in (Meq/g)	Temperature in °C	Exchange Capacity in (Meq/g)
Li ⁺	3.40	1.52	30	1.95
Na ⁺	2.76	1.95	50	1.72
K ⁺	2.32	2.04	100	1.03
Mg ²⁺	7.00	2.08	150	0.53
Ca ²⁺	6.30	2.12	200	0.28
Sr ²⁺	6.10	2.16	250	0.20
Ba ²⁺	5.90	2.24	-	-

water molecules by the condensation of other types of OH groups and the weight loss between 400°C and 450°C may be due to the loss of phosphate.

IR spectral data^{30,31} of H⁺ form of titanium (IV) phospho sulphosalicylate (dried at 300 C) show peaks at 3360cm⁻¹, 1625cm⁻¹, 1016 cm⁻¹, 742cm⁻¹, 533cm⁻¹. The peaks at 3360 cm⁻¹ corresponds to the vibration of hydroxyl groups and interstitial water. Peaks at 1624cm⁻¹ (due to C=O stretching vibration of carboxylic acid group), 1384cm⁻¹ (characteristic of benzene ring), Other peaks at 1016cm⁻¹, 742cm⁻¹ attributed to may be due to sulphonate and phosphate groups and that at 533 cm⁻¹ can be assigned to a Ti-O stretching vibration.

Based on chemical composition, P^H titration, TGA and IR studies, the following formula²⁹ maybe assigned to the exchanger can be written as TiO₂(C₇H₅O₃SO₃)(P₂O₅)(OH)₅. 6H₂O.

The effect of size and charge of metal ion on the ion exchange capacity of the exchanger for alkali and alkaline earth metals as follows.



The ion exchange capacity increase with the decrease in hydrated ionic radii (Table 2). This trend in the exchange capacity suggests that the exchange of these cation take place in the hydrated form.

The effect of temperature on ion exchange capacity at various temperature (Fig1) was recorded indicates that the ion exchange capacity of the material decreases as the temperature increases. Titanium (IV) phospho sulphosalicylate after drying 300°C, 99% ion exchange capacity was lost decrease in ion exchange capacity on heating is due to loss of external water

The pH titration curve (Fig 2) shows first dissociation in acidic medium and second dissociation in basic medium, which indicates that the exchanger in the acid form behaves as a dibasic acid.

Based on the distribution coefficients (Table 3) of the exchanger for various metal ions, the quantitative separations in their synthetic mixtures were carried out successfully. The details are summarized in (Table 4 & 5). Binary separations achieved were Mg²⁺/Th⁴⁺, Zn²⁺/Th⁴⁺, Co²⁺/Th⁴⁺, Ni²⁺/

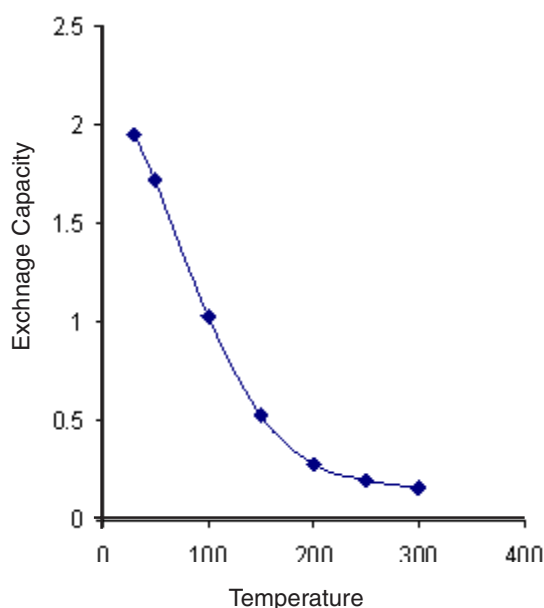


Fig. 1: Effect of temperature on exchange capacity of titanium (IV) phospho sulphosalicylate

Table 3: Distribution coefficients of some metal ions on titanium(IV)phospho sulphosalicylate

Cation	Taken as	Distilled water	K_d Values								1:1mixture of 0.1M HNO ₃ and 0.1M MNH ₄ NO ₃
			HNO ₃				NH ₄ NO ₃				
			1M	0.1M	0.01M	0.001M	1M	0.1M	0.01M	0.001M	
Mg ²⁺	NO ₃ ⁻	00.00	0.00	00.0	0.00	0.00	0.00	0.00	0.00	0.00	00.00
Ca ²⁺	NO ₃ ⁻	00.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	00.00
Ni ²⁺	SO ₄ ²⁻	25.00	0.00	0.00	08.0	12.0	0.00	0.00	05.0	10.0	00.00
Co ²⁺	NO ₃ ⁻	45.00	0.00	05.0	12.0	20.0	0.00	0.00	10.0	16.0	00.00
Zn ²⁺	SO ₄ ²⁻	60.00	0.00	09.0	20.0	35.0	0.00	07.0	16.0	22.0	00.00
Cd ²⁺	NO ₃ ⁻	110.0	12.0	67.4	80.0	90.0	10.0	43.0	63.0	70.0	18.00
Cu ²⁺	SO ₄ ²⁻	160.0	25.0	101	115	145	15.0	74.0	99.0	125	22.00
Hg ²⁺	Cl ⁻	240.0	58.0	123	230	260	50.0	81.5	215	240	47.50
Pb ²⁺	NO ₃ ⁻	370.0	105	253	315	400	100	168	270	295	89.00
Th ⁴⁺	NO ₃ ⁻	1060	320	487	800	910	105	163	690	795	460.0

Table 4: Binary separation of metal ions using titanium (IV) phospho sulphosalicylate column metal ion with eluent

Metal ion with eluent	Amount in (mg)	
	Loaded	Recoverd
Mg ²⁺ (DMW)	9.00	9.00
Th ⁴⁺ (0.1 M HNO ₃ + 0.1 M NH ₄ NO ₃)	6.00	5.46
Zn ²⁺ (0.1M HNO ₃)	3.40	3.40
Th ⁴⁺ (0.1 M HNO ₃ + 0.1 M NH ₄ NO ₃)	6.00	5.76
Co ²⁺ (DMW)	2.00	2.00
Th ⁴⁺ (0.1 M HNO ₃ + 0.1 M NH ₄ NO ₃)	6.00	5.60
Ni ²⁺ (DMW)	6.95	6.94
Th ⁴⁺ (0.1 M HNO ₃ + 0.1 M NH ₄ NO ₃)	6.00	5.67
Cu ²⁺ (DMW)	9.00	8.99
Th ⁴⁺ (0.1 M HNO ₃ + 0.1 M NH ₄ NO ₃)	3.80	3.67
Mg ²⁺ (DMW)	3.40	3.40
Pb ²⁺ (0.1 M HNO ₃)	4.50	4.31
Zn ²⁺ (0.1M HNO ₃)	6.90	6.90
Pb ²⁺ (0.1M HNO ₃)	4.50	4.28
Ca ²⁺ (DMW)	6.90	6.90
Hg ²⁺ (0.1M HNO ₃)	10.50	10.23

* DMW (Demineralised water)

Th⁴⁺, Cu²⁺/Th⁴⁺, Pb²⁺/Mg²⁺ Pb²⁺/Zn²⁺ & Ca²⁺/Hg²⁺ and ternary separations carried out on the exchanger are Th⁴⁺/Zn²⁺/Mg²⁺, Th⁴⁺/Hg²⁺/Mg²⁺ & Th⁴⁺/Cd²⁺/Mg²⁺. The recovery was ranged from 98-100% with a variation of (±)1% for repetitive determinations

Practical utility of the material has been demonstrated. A quantitative separation technique with titanium (IV) phospho sulphosalicylate-Starch TLC layer (2:5) was achieved for Th⁴⁺, Zn²⁺ and Mg²⁺ synthetic mixtures. Three trial runs were demonstrated (Table 6). It was found easy and better method of separation.

Table 5: Ternary separations using titanium (IV) phospho sulphosalicylate column

Metal ion with eluent	Amount in (mg)	
	Loaded	Recoverd
Mg²⁺-Zn²⁺-Th⁴⁺		
Mg ²⁺ (0.1M HNO ₃ + 0.1 M NH ₄ NO ₃)	6.50	6.50
Zn ²⁺ (0.2M HNO ₃)	4.50	4.40
Th ⁴⁺ 0.1 M HNO ₃	3.80	3.45
Mg²⁺-Hg²⁺-Th⁴⁺		
Mg ²⁺ (DMW)	6.90	6.90
Hg ²⁺ (0.2M NH ₄ NO ₃)	4.50	4.42
Th ⁴⁺ (0.1 M HNO ₃)	3.80	3.48
Mg²⁺-Cd²⁺-Th⁴⁺		
Mg ²⁺ (DMW)	8.00	8.00
Cd ²⁺ (0.2M NH ₄ NO ₃)	4.50	4.48
Th ⁴⁺ (0.1 M HNO ₃)	3.80	3.56

*DMW (Demineralised water)

Table 6: Quantitative separation of Th⁴⁺, Zn²⁺ and Mg²⁺ ions on titanium (IV) Phospho sulphosalicylate-starch (2:5) TLC layer

S. No	Separation achieved	Amount loaded (Micro Gm)	Amount recovered (Micro Gm)	Recovery %
1.	Th ⁴⁺	50.00	47.40	94.80
	Zn ²⁺	50.00	48.90	97.80
	Mg ²⁺	50.00	50.00	100.00
2.	Th ⁴⁺	50.00	49.20	98.40
	Zn ²⁺	50.00	49.00	98.00
	Mg ²⁺	50.00	49.80	98.60
3.	Th ⁴⁺	50.00	48.40	96.80
	Zn ²⁺	50.00	48.40	96.80
	Mg ²⁺	50.00	48.40	96.80

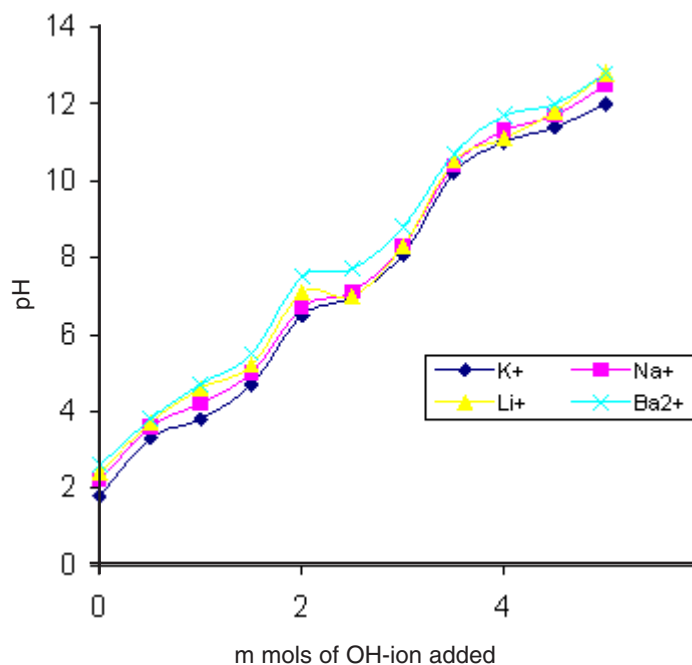


Fig. 2: pH titration curve: Titanium (IV) phospho sulpho salicylate

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