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Synthesis, Characterization and Analytical Applications of Tin(IV) Tungstoborate

M.P. SUJITH and C. JANARDANAN*
Department of Chemistry, Sree Narayana Postgraduate College and Research Centre, Kannur-670 007, India

A new inorganic ion exchanger of the class of multivalent metal acid salt, tin(IV) tungstoborate has been synthesized by varying the conditions and characterized based on ion exchange capacity determinations, distribution coefficients for various metal ions, pH titration curves, temperature and electrolyte impact on ion exchange capacity, FTIR spectroscopy, TGA-DTA and XRD studies. The distribution study shows that the exchanger is having selectivity for Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Ca^{2+}, Mg^{2+}, Al^{3+} and negligible selectivity for Th^{4+}. It is stable in organic solvents like ethanol, acetone, ether and in dilute mineral acids. Binary separations of Pb^{2+}-Th^{4+}, Cu^{2+}-Th^{4+}, Cd^{2+}-Th^{4+}, Co^{2+}-Th^{4+}, Ni^{2+}-Th^{+}, Ca^{2+}-Th^{4+} mixtures were carried out using the exchanger column. Separations of binary mixtures using tin(IV) tungstoborate column found to be 98-100 %.

Key Words: Tin(IV) tungstoborate, Inorganic ion exchanger, Distribution coefficient, Binary separations.

INTRODUCTION

Tin(IV) based ion exchangers have been studied previously by Varshney *et al.*[1-3] and reported to have excellent ion exchange properties and radiation stability. Mishra[4] reported the analysis of magnesium and aluminium in antacid formulations using stannic antimonate columns. Resistance to ionizing radiations and stability in good number of solvents and electrolyte conditions makes inorganic ion exchanger attractive compared to organic ion exchange resins[5-7]. Among the inorganic ion exchangers tin(IV) tungstate was synthesized by Qureshi *et al.*[8] with tin-tungsten ratio 2:1. Uma *et al.*[9] produced a new phase of tin(IV) tungstate with greater ion exchange capacity and higher (thermal/chemical) stability. The new phase of amorphous tin(IV) tungstate synthesized through modified sol-gel method reported good results in separating Co^{2+} from Zn^{2+}, Cu^{2+} and Th^{4+} present in binary mixtures.

The first and foremost merit of ion exchangers is the separating capability based on separation factor K_{dA}/K_{dB}(K_{dA} and K_{dB} are distribution coefficients of metal ions A and B). Synthesis of ion exchangers with separating capability for radioactive compounds have greater importance and efforts are on to make the specific selectivity for certain metal ions[10-13]. Mode of preparation has significant effect on the size, shape and cavities inside an exchanger[14]. The present work deals with the tin(IV) tungstoborate, which has negligible ion exchange property towards Th^{4+}. This property is applied to separate thorium from various binary mixtures.

EXPERIMENTAL

Stannic chloride, sodium tungstate, ammonium borate all of analytically pure grade were used for the preparation of the ion exchanger. Ion free double distilled water was used throughout the experiments.

Stannic chloride, sodium tungstate and ammonium borate were taken in distinct molarities and various possibilities of mole ratios were tried for the preparation of the exchanger (Table-1). Out of these maximum ion exchange capacity was shown by the combination of 0.1 M stannic chloride solution with a mixture of 0.2 M ammonium borate and 0.1 M sodium tungstate in the volume ratio 1:1:1. The mixture of borate and tungstate solution was added slowly and continuously to the solution of tin(IV) with continuous stirring. The pH of the gel adjusted at 1, kept at room temperature for 24 h, filtered washed with demineralized water several times to remove excess reagent and dried at room temperature. This is converted to H^+ form by treating it with 1 M HNO_3 as usual, washed with demineralized water till free of acid and again dried at room temperature. Tin(IV) was estimated using cupferron method, tungsten gravimetrically as barium tungstate and boron determined spectrophotometrically using ferroin[15].

TABLE-1
DIFFERENT PREPARATIONS OF THE ION EXCHANGER AND THEIR ION EXCHANGE CAPACITY

Sn^{4+} solution	Tungstate solution	Borate solution	Volume ratio	Eluent	Ion exchange capacity (meq/dry g)
0.1 M	0.10 M	0.10 M	1:1:1	NaCl	0.81
0.1 M	0.20 M	0.10 M	1:1:1	NaCl	0.62
0.1 M	0.10 M	0.20 M	1:1:1	NaCl	1.01
0.2 M	0.10 M	0.10 M	1:1:1	NaCl	0.71
0.1 M	0.05 M	0.20 M	1:1:1	NaCl	0.64
0.1 M	0.20 M	0.05 M	1:1:1	NaCl	0.62

Infra red spectral studies were carried out on Magna-560 (Nicolet, USA) FTIR spectrometer and TGA-DTA studies on TG/DTA32 Sicko (Japan) apparatus. X-ray diffraction studies ($2\theta = 10\text{-}80^{\circ}$) was performed on X-ray diffractometer PW 1830 generator with CuKα radiation. pH meter model mkVI from Systronics Ltd. was used for pH measurements.

Ion exchange capacity determination: The ion exchange capacity of the sample was determined by column operation[16]. The exchanger (1.0 g) in the H^+ form was placed on the column with glass wool support. Sodium chloride 1.0 M was used as the eluent and 250 mL of the eluate from the column was titrated with standard NaOH solution. From the titre value the exchange capacity in (meq/dry g) was evaluated using the formula av/w, where a is molarity, v is the volume of alkali used during the titration and w is the mass of the sample. Further the effect of temperature on ion exchange capacity was also studied by heating the sample at different temperatures for 1 h in an air oven.

pH Titration studies: The pH titrations were performed by batch process using the method of Topp and Pepper[17]. 500 mg portions of the exchanger in H^+ form were placed in each of the several 250 mL conical flasks followed by equimolar solutions of metal chlorides and their hydroxides in different volume ratios, the final volume being 50 mL to maintain constant ionic strength. The pH of various solutions were recorded after attaining equilibrium and plotted against milli equivalents of OH^- ions added.

Distribution studies: Using batch process[18] distribution studies were carried out. For this 100 mg of the exchanger in H^+ form was made to equilibrate with 20 mL of 0.005 M metal ion solutions and the exchange of the metal ion was determined by titration method using EDTA. The titrations were carried out before and after sorption. The evaluations were made using the expression

$$K_d = \frac{I - F}{F} \times \frac{V}{W}$$

where I is the initial amount of metal ion in solution phase, F is the final amount of metal ion in solution phase, V is the volume of metal ion solution and W is the mass of the ion exchanger.

Binary separations: The separations of metal ions of analytical utility were achieved on the column of tin(IV) tungstoborate. For binary separations, 5 g of the exchanger in H^+ form were taken in a glass wool column (30 × 1.1 cm). The column was first washed with about 20 mL demineralized water, then mixture of metal ions were introduced in to the column and allowed to be absorbed. The separations were achieved by passing suitable eluent through the column and metal ions in the effluents were determined quantitatively by EDTA titrations. The rates of flow in all separations were 3-4 drops/min.

RESULTS AND DISCUSSION

Tin(IV) tungstoborate obtained was yellowish white amorphous substance. The exchanger was found to be stable in 1.0 M mineral acids and 1.0 M metal chlorides. From the chemical composition studies the Sn:W:B ratio was obtained as 1:1:2. The exchanger showed maximum exchange capacity 1.01 meq/dry g. The effect of size and charge on ion exchange capacity was studied for alkali metals and the order found was Li^+ (0.81 meq/dry g) < Na^+ (1.01 meq/dry g) < K^+ (1.21 meq/dry g). The exchanger is found to have stability up to 100°C (ion exchange capacity 0.41 meq/g) and above that temperature the exchange capacity decreases sharply.

FTIR spectra of the exchanger exhibits broad bands in the region between 3513 and 3229 cm^{-1} which is attributed to asymmetric and symmetric hydroxo –OH and aquo –OH stretching. A sharp medium band at 1625 cm^{-1} is attributed to H–O–H bending. The peaks 1403, 963 and 875 cm^{-1} corresponds to metal oxides of boron,tungsten and tin, respectively. Absence of any characteristic peak in the X-ray diffractogram confirms the non-crystalline nature of tin(IV) tungstoborate.

The thermoanalytical investigations can be used to calculate the mixed oxide formula of the exchanger using Alberti's method[19]. The weight loss up to 111.5ºC is 15.29 %. Hence the number of water molecules incorporated in the exchanger, as H–OH is 5. Therefore, the formula assigned to the exchanger is $SnO_2{\cdot}WO_3{\cdot}B_2O_3{\cdot}5H_2O$. Thus the hydroxyl groups attached to the metal ions may be responsible for ion exchange behaviour of the material.

The pH titration curves at equilibrium conditions (Fig. 1) for NaCl/NaOH and KCl/KOH exchange reveal that the material behaves as bifunctional.

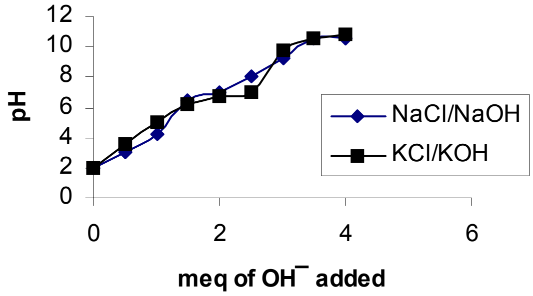

Fig. 1. pH Titration curve

The distribution coefficients for the metal ions (Table-2) show the sequence $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Ca^{2+} > Mg^{2+} > Al^{3+} > Th^{4+}$. The negligible sorption of Th^{4+} may be due to the specific nature of the exchanger.

TABLE-2
K_d (mL/g) VALUES OF DIFFERENT CATIONS IN DMW

Ions	K_d	Ions	K_d
Pb^{2+}	294.43	Ca^{2+}	65.20
Zn^{2+}	80.04	Mg^{2+}	55.13
Ni^{2+}	71.36	Cu^{2+}	116.11
Co^{2+}	70.33	Al^{3+}	52.27
Cd^{2+}	94.49	Th^{4+}	Negligible sorption

DMS = Demineralized water.

The effects of electrolyte (HNO_3 or NH_4NO_3) concentration on the distribution coefficients of some metal ions used for binary separations were also studied. The values of distribution coefficients of metal ions were found to decrease with increase in electrolyte concentration (Table-3). These studies are useful for separating the metal ions using exchanger column and electrolytes as eluents.

TABLE-3
EFFECT OF ELECTROLYTE CONCENTRATION ON
K_d VALUES (mL/g) K_d VALUES

Metal ions	0.001 M NH_4NO_3	0.01 M NH_4NO_3	0.1 M NH_4NO_3	0.001 M HNO_3	0.01 M HNO_3	0.1 M HNO_3
Pb^{2+}	292.23	233.35	206.27	250.58	188.13	92.54
Cu^{2+}	112.45	103.86	72.29	106.24	74.17	31.96
Ca^{2+}	65.85	46.74	26.32	57.59	8.06	NS*
Ni^{2+}	68.12	50.78	32.83	64.43	9.26	NS*
Cd^{2+}	90.12	72.26	44.48	82.34	52.17	17.28
Co^{2+}	64.33	40.95	18.86	58.17	8.73	NS*

NS* = Negligible sorption

The important binary separations carried out on the column of the exchanger are Th^{4+}-Pb^{2+}, Th^{4+}-Cd^{2+}, Th^{4+}-Co^{2+}, Th^{4+}-Ni^{2+}, Th^{4+}-Cu^{2+} and Th^{4+}-Ca^{2+} (Table-4). Eluents used were 0.001 M NH_4NO_3 and 0.1 M HNO_3.

TABLE-4
SEPARATION OF BINARY MIXTURE ON THE EXCHANGER

Mixture with eluents	Metal ion (mg)		Error (%)
	Loaded	Recovered	
Th^{4+}(0.001 M NH_4NO_3)	5.00	5.00	0.00
Pb^{2+} (0.1 M HNO_3)	0.86	0.85	-1.16
Th^{4+}(0.001 M NH_4NO_3)	5.00	5.00	0.00
Cd^{2+}(0.1 M HNO_3)	5.00	4.98	-0.40
Th^{4+}(0.001 M NH_4NO_3)	5.00	5.00	0.00
Co^{2+}(0.1 M HNO_3)	4.00	3.92	-2.00

Mixture with eluents	Metal ion (mg)		Error (%)
	Loaded	Recovered	
Th^{4+}(0.001 M NH_4NO_3)	5.00	5.00	0.00
Ni^{2+}(0.1 M HNO_3)	1.30	1.30	0.00
Th^{4+}(0.001 M NH_4NO_3)	5.00	5.00	0.00
Cu^{2+}(0.1 M HNO_3)	1.30	1.27	-2.31
Th^{4+}(0.001 M NH_4NO_3)	5.00	5.00	0.00
Ca^{2+}(0.1 M HNO_3)	4.00	3.95	-1.25

Conclusion

Tin(IV) tungstoborate behaves as a cation exchanger on the basis of different studies carried out. It can successfully be utilized for the quantitative separation of thorium from other metal ions of analytical importance. The ion exchanger has also been tested for the quantitative separations of lead from other metal ions, which are of importance for environmentalists.

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