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Synthesis and Ion Exchange Properties of Tin(IV) Silicotungstate

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A new thermally stable inorganic ion exchanger tin(IV) silicotungstate has been synthesized and characterized based on ion exchange capacity determinations, distribution coefficients for various metal ions, temperature and electrolyte impact on ion exchanger capacity, FTIR spectroscopy, TGA and ICP studies. The quantitative separations of Hg^{2+}-Pb^{2+}, Cd^{2+}-Pb^{2+}, Mg^{2+}-Pb^{2+}, Hg^{2+}-Cu^{2+}, Hg^{2+}-Ni^{2+} and Hg^{2+}-Zn^{2+} have been achieved on tin(IV) silicotungstate columns. Separations of binary mixtures using tin(IV) silicotungstate columns found to be 98-100 %.

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

INTRODUCTION

The insoluble salts of heteropolyacids with polyvalent metals especially tin(IV) are preferred to other ion exchangers as they exhibit selective ion exchange behaviour. Qureshi *et al.* have studied vanadophosphate[1], vanadotungstate[2], tungstoarsenate[3,4], molybdoarsenate[5], molybdosilicate[6] and phosphotungstate[7] of tin(IV). Tin(IV) phospoborate[8] and tin(IV) tungstoborate[9] were also reported with excellent ion exchange properties. Misra *et al.*[10] studied and compared the thermal stability of stannic tungstate and stannic tungstate silicate. This study summarizes the present findings on the synthesis and ion exchange behaviour of tin(IV) silicotungstate.

EXPERIMENTAL

Hydrated stannic chloride (BDH), sodium tungstate (BDH) and sodium silicate (SQ lab reagent) were used. All other chemicals used were of analar grade. The absorbance measurements for estimation of tin and tungsten were done in an inductively coupled plasma spectrophotometer, while pH measurements were performed using a global digital pH meter model DPH-500. IR and TGA studies were done using a Perkin-Elmer model 21 spectrometer and Perkin-Elmer TGA 7.

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Synthesis: Tin(IV) silicotungstate was synthesized by mixing 0.1 M stannic chloride solution, 0.1 M sodium silicate and 0.1 M sodium tungstate solutions in 2:1:1, 1:1:2 and 1:2:1 ratios. The pH was adjusted to 1 by adding dilute HCl. The precipitate was filtered off after 24 h and washed several times with deionized water. The air dried particles were then converted into H^+ form by dipping in 1 M HCl. The dull white beads obtained were filtered, washed, dried and sieved to 80-100 mesh size and stored over NH_4Cl in a desiccator.

Chemical composition: The composition of the exchanger was determined by dissolving 100 mg of the sample in dilute H_2SO_4 and determining tin(IV) volumetrically[11], silicon as SiO_2 by HF method and tungsten gravimetrically[12]. Tin and tungsten were directly measured in inductively coupled plasma spectrophotometer[13]. IR and TGA studies were also made to give the composition of the exchanger. The ratio of Sn:Si:W in tin(IV) silicotungstate is 2:1:2 with a variation of ± 0.01 % for repetitive determinations.

Determination of capacity: The ion exchange capacity of various samples of tin(IV) silicotungstate in hydrogen form was determined by column operation by eluting with 1.0 M NaCl solution. The hydrogen ions eluted from the column were determined titrimetrically with standard NaOH. One gram of the exchanger was used in each case to determine the capacity. The exchanger could be regenerated twice without any appreciable loss of ion exchange capacity. The sample 2 had comparatively higher capacity (IEC = 1.13) and hence it is used for further studies (Table-1). 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.

TABLE-1
CONDITIONS OF PREPARATION AND PROPERTIES OF TIN(IV) SILICOTUNGSTATE

Sample	Molarity of reagents			Mixing ratio	Ion exchange capacity (meq/g)
	Sn^{4+}	SiO_3^{2-}	WO_4^{2-}		
1	0.1	0.1	0.1	2:1:1	0.67
2	0.1	0.1	0.1	1:1:2	1.13
3	0.1	0.1	0.1	1:2:1	0.50

Distribution coefficients: The distribution coefficients (K_d) for 10 metal ions were found out by batch process[14]. The exchanger (100 mg) was equilibrated with 20 mL of 0.005 M metal ion solution for 6 h. Each solution was then analyzed for metal ion by complexometric titration. The K_d values were calculated using the equation $K_d = \left(\frac{I-F}{F}\right) \bullet \frac{V}{m}$ where I and F are the initial and final volumes of EDTA respectively, V is the volume of metal ion solution and m is the mass of the exchanger taken. The K_d values are given in Table-3. Separations of metal ions were carried out on a tin(IV) silicotungstate (60-100 BSS mesh) column (30 cm × 1.1 cm).

TABLE-2
EFFECT OF SIZE AND CHARGE OF THE EXCHANGING ION ON THE EXCHANGE CAPACITY

Exchanging ion	Hydrated ionic radii Å	Ion exchange capacity (meq/g)
Li^+	3.40	1.42
Na^+	2.76	1.13
K^+	2.32	1.64
Mg^{2+}	7.00	2.27
Sr^{2+}	6.10	1.92
Ba^{2+}	5.90	2.08

TABLE-3
DISTRIBUTION COEFFICIENTS OF SOME METAL IONS ON TIN(IV) SILICOTUNGSTATE

Cation	Taken as	Kd (mL/g)	Cation	Taken as	Kd (mL/g)
Cd^{2+}	Chloride	36.36	Co^{2+}	Sulphate	19.05
Pb^{2+}	Nitrate	271.43	Cu^{2+}	Sulphate	86.57
Zn^{2+}	Sulphate	81.12	Hg^{2+}	Chloride	12.56
Ni^{2+}	Sulphate	70.83	Bi^{3+}	Nitrate	21.42
Mg^{2+}	Sulphate	45.68	Th^{4+}	Nitrate	5.03

Binary separations: The separations of metal ions of analytical utility were achieved on the column of stannic(IV) silicotungstate. For binary separations 5 g of exchanger in the H^+ form were taken in a glass wool column (30 cm × 1.1 cm). The column was first washed with about 20 mL demineralized water, then mixture of metal ions were introduced into the column and allowed to be absorbed. The separation 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

The exchanger (sample 2, Table-1) was obtained as dull white amorphous mass. It is soluble in H_2O, ethanol, acetic acid and 1.0 M solutions of Li_2SO_4, NaCl, KCl, $MgSO_4$, $Sr(NO_3)_2$ and $BaCl_2$. Further it is fairly stable in 2.0 M solutions of HCl, HNO_3 and H_2SO_4. The exchanger can be regenerated thrice without any appreciable loss in ion exchange capacity.

The thermoanalytical investigations show that when heated to 110 °C the mass loss is 6.04 %. The empirical formula and the theoretical ion exchange capacity can be calculated using the method of Alberti *et al.*[15] 1800 n/(824 + 18 n) = 6.04 and n = 2. The empirical formula can be written as $2SnO_2.SiO_2.2WO_3.3H_2O$. Cation exchange capacity calculated per one proton formula weight is 1000 /860 = 1.2 which is in good agreement with the experimental result.

IR spectrum shows broad maximum at 3450 cm^{-1} due to OH stretching reveals the presence of water of hydration[16]. Lattice water is usually adsorbed at 3600-

3200 cm^{-1}. The H-OH bending vibrations at 1620 and 1686 cm^{-1} confirms the presence of water of crystallization. The peaks at 1327 and 1292 cm^{-1} show the Si-O-Si linkage in the compound.

The effect of size and charge of the ingoing hydrated ion on the capacity of the exchanger is shown in Table-2 for alkali and alkaline earth metal ions. The sequence shown by tin(IV) silicotungstate was $Li^+ > Na^+ < K^+$ and $Ba^{2+} > Sr^{2+} < Mg^{2+}$. Usually ion exchange capacities are in the order of hydrated ionic radii. In this case the sequence is not followed. This may be due to the decisive role of the solubility products of the corresponding silicates of the metal ion in the adsorption process[17,18].

The maximum ion exchange capacity for tin(IV) silicotungstate (1.1369) decreased on drying the compound at higher temperatures and retains some ion exchange capacity even on treating to 200 ºC (0.49 meq/g).

The distribution studies with 10 metal ions reveals that tin(IV) silicotungstate shows high affinity for Pb^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} and least affinity for Hg^{2+}, Th^{2+} and Co^{2+}. It may be assumed that the ion exchange reaction and the ion sieve properties of the exchanger are responsible for the high uptake of these elements.

Binary separations of analytical importance have been achieved on tin(IV) silicotungstate columns (Table-4).

TABLE-4
BINARY SEPARATIONS

Mixtures with eluents	Amount loaded (mg)	Amount recovered (mg)	Error (%)
Hg^{2+} [0.01M HNO_3 + 0.01 M NH_4NO_3]	4.82	4.64	96.26
Pb^{2+} [1.0M HNO_3 + 1.0 M NH_4NO_3]	4.89	4.60	94.06
Cd^{2+} [0.1M HNO_3]	2.75	2.60	94.54
Pb^{2+} [1.0M HNO_3 + 1.0 M NH_4NO_3]	5.17	4.98	96.32
Mg^{2+} [0.1M HNO_3 + 0.1 M NH_4NO_3]	0.59	0.55	93.22
Pb^{2+} [1.0M HNO_3 + 1.0 M NH_4NO_3]	4.89	4.60	94.06
Hg^{2+} [0.1M HNO_3 + 0.1 M NH_4NO_3]	4.82	4.55	94.39
Cu^{2+} [0.5M HNO_3 + 0.5 M NH_4NO_3]	1.44	1.20	83.33
Hg^{2+} [0.01M HNO_3 + 0.01M NH_4NO_3]	4.82	4.55	94.39
Ni^{2+} [0.5M HNO_3 + 0.5 M NH_4NO_3]	1.35	1.30	96.29
Hg^{2+} [0.01M HNO_3 + 0.01M NH_4NO_3]	4.55	4.27	93.84
Zn^{2+} [0.5M HNO_3 + 0.5 M NH_4NO_3]	1.66	1.60	96.38

The metal ions were eluted in the order indicated, using the eluents given in parantheses. The recovery ranged from 96 to 100 % with a variation of 2 % for repetitive determinations.

Conclusion

The studies on the ion exchange properties of tin(IV) silicotungstate have shown that the compound is suitable for binary separations such as Pb^{2+}- Hg^{2+}, Pb^{2+}- Cd^{2+}, Pb^{2+}- Mg^{2+}, Cu^{2+}- Hg^{2+}, Ni^{2+}-Hg^{2+} and Zn^{2+}-Hg^{2+}. Most of the separations are environmentally important.

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