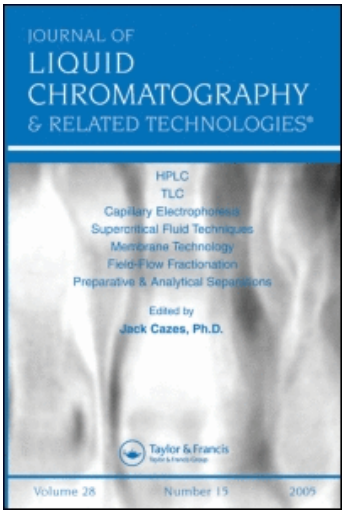

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SILICA BASED DOUBLE SALTS AS CATION-EXCHANGERS. II. SYNTHESIS AND ANALYTICAL APPLICATIONS OF Sn(IV) PHOSPHOSILICATE

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Abstract: This paper deals with the synthesis of Sn(IV) phosphosilicate as a new, reproducible and stable inorganic ion-exchanger. The composition, ion-exchange capacity for different metals, pH titrations, chemical stability, distribution and IR studies have also been performed on a sample of this material. On the basis of distribution studies, a number of binary separations of analytical importance have been achieved. The limits of separations have also been determined by taking various ratios of the two components.

INTRODUCTION

Inorganic ion exchangers based on silica are of particular interest because of their extra stability and reproducible behaviour. Silicates of Zr(IV), Ti(IV) and Sn(IV) are reported[1-3] in the literature which show good ion exchange capacity and are useful for metal separations. Double salts based on silica have also received attention because of their enhanced ion exchange properties. Phosphosilicates of zirconium[4] and titanium[5] have established well their superiority over other materials of this type. In these laboratories we have synthesized earlier Sn(IV) arsenosilicate[6] and cerium(IV) phosphosilicate[7] both of which have shown reproducible behaviour and appreciable chemical and thermal stability. In order to widen the scope of these materials the synthesis of new such salts is of interest. The present study, therefore, summarizes our efforts to synthesize a new ion exchange material which shows good ion exchange properties and is useful for some important metal separations.

EXPERIMENTAL

Reagents: Stannic chloride used in these studies was a Polish product (P.P.H. Polskie Odczniki Chemiezne Gliwice) while sodium silicate powder was a Reidel (Germany) product. All other reagents and

chemicals were of AnalaR grade procured from either BDH (Poole) or E.Merck (Darmstadt).

Apparatus: An ELICO model LI-10 pH-meter was used for pH-measurements. IR studies were made on a Perkin-Elmer 621 Grating Infrared Spectrophotometer, while the mechanical shaker was a temperature controlled SICO (India) unit.

Preparation of ion-exchange material: A stock solution of sodium silicate (0.75 M) was prepared in demineralised water (DMW). A fixed volume of this solution (50-150 ml) was diluted to 500 ml with DMW followed by the 50 ml of HCl and 500 ml of 0.1M stannic chloride solution stirring continuously. It was made basic (pH$\sim$8) by adding ammonia dropwise and the gel obtained was left for 6 hrs. to settle down. It was filtered, washed with DMW and dispersed in a 1000 ml mixture of phosphoric and nitric acids containing 0.5 moles each of these acids maintaining the temperature at$\sim$70 °C. The resultant gel was stirred vigorously for 2 hours, filtered, washed and dried at this temperature in an air oven. The dried material was cracked into small and white shining granules by immersing in cold DMW. They were converted into the H^+ form as usual with 1M HNO_3. Several batches of the same material were prepared to check its reproducibility the details of which are shown in table - 1. Sample S-4 was selected for further studies on the basis of its ion exchange capacity.

Composition: 500 mg of the exchanger were boiled with 20 ml of 8M HCl and the undissolved SiO_2[8] was filtered out which was estimated gravimetrically. The filtrate was treated with H_2S to precipitate Sn(IV) which was dissolved in HCl and estimated volumetrically[9] with

TABLE - 1: Preparation of Sn(IV) phosphosilicate by mixing different amounts of $SnCl_4$ and sodium silicate.

Sample No.	Volume of 0.1M $SnCl_4$	Volume of sodium silicate solution (0.75M)	Ion-exchange capacity meq/dry g.
S-1	500	50	1.20
S-2	500	75	1.26
S-3	500	100	1.34
S-4	500	125	1.60
S-5	500	150	1.60

$K_2Cr_2O_7$ after reduction with lead powder. The filtrate thus obtained was analysed for the phosphate content by the ammonium molybdophosphate method[10] and the composition was found to be 2:2:3 for Si:Sn:P.

Ion exchange capacity (i.e.c): Since the ion-exchanger is a cation exchanger its i.e.c. was determined by taking different metal solutions as eluant for a column containing 500 mg of the material in H^+ form. The flow rate was maintained at $\sim$0.5 ml $minute^{-1}$ and the eluted H^+ ions were titrated against a standard alkali solution. Na(I), K(I) and Ba(II) gave the maximum i.e.c. (1.60 meq/dry g.) while other metal ions showed a slight variation as reported below: Li(I)-1.21, Rb(I)-1.27, Mg(II)-1.03, Ca(II)-1.32, Sr(II)-1.46.

Chemical and thermal stability: For chemical stability the material was treated with different acids and bases by placing 250 mg of it in 25 ml of the respective solution for 24 hours with intermittent shaking. Supernatant liquid was analysed spectrophotometrically for the tin[11], silicon[12] and phosphorus[13] content. This study shows that the material is partially unstable in 4M HCl while it is fairly stable in 4M HNO_3. In alkalies it is hydrolysed to form stannic hydroxide and soluble phosphate and silicate.

For thermal stability the loss in i.e.c. of the material was observed after heating it at different temperatures for 1 hour each. The K^+ i.e.c. after this treatment are summarized below:
1.60 (100°C), 1.20 (200°C), 1.00 (300°C), 0.65 (500°C), 0.45 (700°C), 0.20 (800°C).
An experiment was also set to obtain the i.e.c. at the 100°C working temperature. The column containing the ion-exchanger was surrounded by a steam jacket and the H^+ ions were eluted with a hot solution of 1M KNO_3. It gave the same i.e.c. as obtained at room temperature.

pH-titrations: They were performed by the batch method of Topp and Pepper[14]. 500 mg of the material were taken in each of the several conical flasks followed by a NaOH-NaCl mixture (50 ml) having a known $\bar{O}H$ ion concentration. The pH was recorded after the equilibrium was attained and was plotted against the milliequivalent of $\bar{O}H$ ion added. The same procedure was adopted for the LiOH-LiCl and KOH-KCl systems, the results being shown in figure 1.

Distribution studies: Metal ion solutions for the distribution studies were prepared in DMW except tri and tetra valent metals, for which minimum amount of corresponding mineral acids were added to prevent

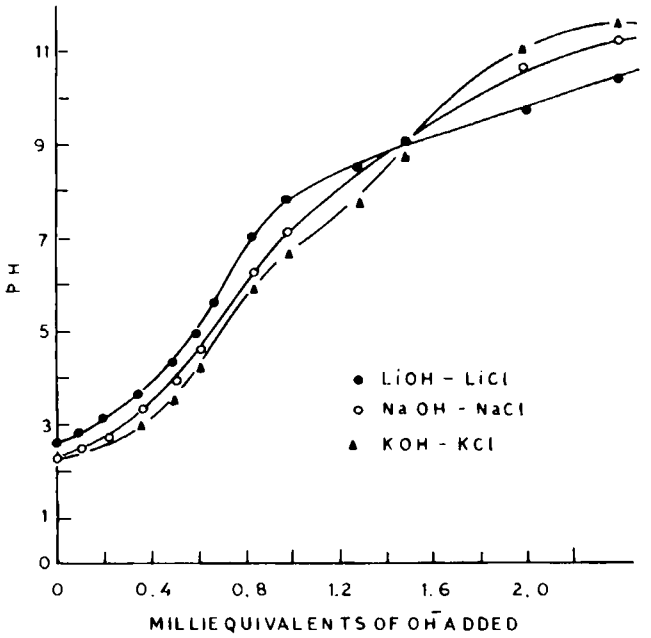

FIGURE 1: pH-titration curves for Sn(IV) phosphosilicate.

TABLE - 2: Kd values of metal ions on Sn(IV) phosphosilicate in different media.

Metal ion	Water	0.01M HNO_3	0.1M HNO_3	0.01M $HClO_4$	0.1M $HClO_4$	0.1M NH_4NO_3	0.1M $NaClO_4$	0.1M HCOOH	0.1M CH_3COOH
Mg(II)	1525	150	0	132	0	8	18	550	1200
Ca(II)	TA	200	0	275	0	20	50	900	2900
Sr(II)	TA	252	9	233	11	50	58	1400	TA
Ba(II)	TA	1060	21	1060	61	61	190	1833	TA
Zn(II)	TA	458	20	378	14	67	139	1575	TA
Cd(II)	TA	560	10	560	10	83	230	1550	TA
Hg(II)	16	0	0	3	0	9	0	16	25
Pb(II)	TA	6600	272	3250	276	1016	1016	TA	TA
Mn(II)	3200	120	0	120	0	10	32	3200	TA
Cu(II)	TA	1066	0	900	13	250	600	3400	TA
Ni(II)	TA	128	0	115	0	23	60	700	TA
Co(II)	TA	1450	94	182	29	48	106	1140	TA
VO(II)	TA	1000	6	842	6	73	136	633	TA
Ag(I)	TA	520	12	430	10	82	88	235	TA
UO_2(II)	TA	1180	88	1550	110	472	480	1200	TA
Al(III)	800	239	69	600	116	170	69	145	TA
Fe(III)	TA	2230	400	2400	455	316	400	1900	2520
Y(III)	TA	2900	100	2282	259	373	542	1185	TA
Th(IV)	610	38	0	40	0	24	27	110	2200
Zr(IV)	580	48	0	56	2	34	39	168	2200

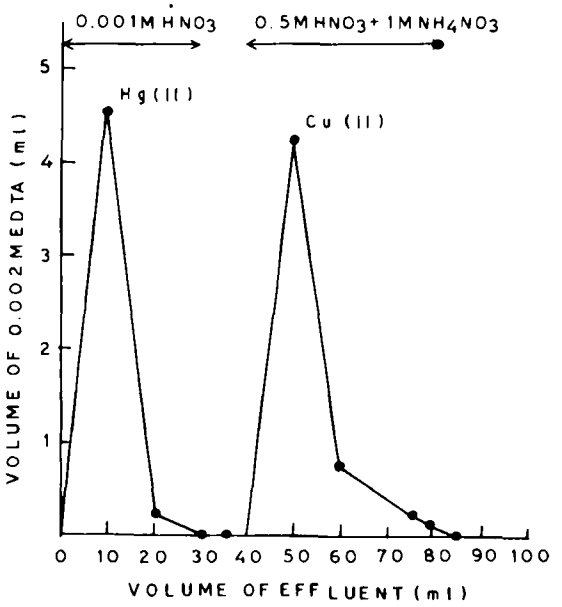

FIGURE 2: Separation of Hg(II) from Cu(II) on Sn(IV) phosphosilicate.

hydrolysis. Molar distribution coefficients (kd in ml g^{-1}) for 20 metal ions were dittermined in different acids and salts media by shaking for 4 hours, 250 mg of the exchanger with 25 ml of the metal solutions containing the metal ion not more than 3% of the total i.e.c. EDTA titrations were performed for all metals, except Ag(I) and UO_2(II), to estimate the amounts of the metal ions initially and after adsorption on the ion exchanger, Ag(I)[15] and UO_2(II)[16] were determined spectrophotometrically. Table 2 shows the Kd values.

Separation studies: A glass column of i.d. 0.6 cm and containing 1 g of the exchanger was used for separating the metal ions. The mixture was loaded on the column bed with a very slow rate (2-3 drops $minute^{-1}$) and the elution was performed with a suitable solvent at a flow rate 0.5 ml $minute^{-1}$. Different amounts of the metal ions were loaded to determine the separation limits. Table 3 summarises the details of the separations achieved, while Fig.2 shows the typical elution curves.

TABLE - 3: Separations of metal ions on Sn(IV) phosphosilicate columns.

Sl. No.	Separation achieved	Amounts loaded μg	Amounts found μg	% of error	Limit of separation in μg on 1 g. exchanger	Eluent used	Volume of eluent (ml)
1.	Hg(II)-Cu(II)	1880 Hg	1880 Hg	0	40 - 2000	0.001M HNO_3	20
		700 Cu	686 Cu	-2	50 - 1900	0.5M HNO_3 + 1M NH_4NO_3	40
2.	Hg(II)-Zn(II)	1880 Hg	1880 Hg	0	40 - 2000	0.001M HNO_3	20
		600 Zn	601 Zn	0	50 - 2100	0.4M HNO_3	30
3.	Hg(II)-Cd(II)	1880 Hg	1880 Hg	0	40 - 2000	0.001M HNO_3	20
		1020 Cd	1033 Cd	+1.3	60 - 2500	0.4M HNO_3	30
4.	Hg(II)-Pb(II)	1880 Hg	1880 Hg	0	40 - 2000	0.001M HNO_3	20
		1800 Pb	1781 Pb	-1.1	80 - 4000	1M HNO_3	50
5.	Hg(II)-Ag(I)	1880 Hg	1880 Hg	0	40 - 2000	0.001M HNO_3	20
		850 Ag	830 Ag	-2.4	60 - 1200	0.2M HNO_3	40
6.	Th(IV)-Y(III)	1300 Th	1300 Th	0	100 - 2200	0.01M HNO_3	30
		900 Y	888 Y	-1.4	60 - 1700	0.5M HNO_3 + 1M NH_4NO_3	40
7.	Th(IV)-UO_2(II)	1300 Th	1300 Th	0	100 - 2200	0.01M HNO_3	30
		1100 U	1070 U	-2.8	60 - 1200	0.05M HNO_3	40
8.	Zr(IV)-Y(III)	856 Zr	856 Zr	0	80 - 900	0.01M HNO_3	30
		900 Y	900 Y	0	60 - 1700	0.5M HNO_3 + 1M NH_4NO_3	40
9.	Zr(IV)-UO_2(II)	856 Zr	856 Zr	0	80 - 900	0.01M HNO_3	30
		1100 U	1080 U	-1.8	60 - 1200	0.5M HNO_3	40

DISCUSSION

Synthesis of a new, reproducible and stable inorganic ion-exchanger is the essential feature of this study. A method of homogeneous phosphatisation has been devised resulting into a material having reproducible characteristics. Addition of an acid like HCl to a clear solution of sodium silicate slowly forms silicic acid, which when treated with $SnCl_4$ at pH$\sim$8 forms a gel which probably consists of flakes of SiO_2 coated with the tin(IV) hydroxide as proposed by Naumann for zirconium phosphosilicate[4]. When this gel is heated at 70°C with H_3PO_4-HNO_3 mixture for 2 hours with a continuous stirring the precipitate of Sn(IV) phosphosilicate is formed showing good reproducibility and ion exchange properties. Cerium(IV) phosphosilicate, prepared earlier by the same method, also showed reproducible ion exchange behaviour, suggesting therefore that a homogeneous phosphatisation occurs due to continuous stirring at a relatively higher temperature ($\sim$70°C). A comparison with the single salts such as Sn(IV) phosphate[17] and Sn(IV) silicate[3] shows that the sample of Sn(IV) phosphosilicate has a higher Na ion-exchange capacity probably due to a better phosphatisation of the Sn(IV) silicate gel. Also, it shows a better thermal stability than Sn(IV) phosphate reported earlier. On heating upto 400°C Sn(IV) phosphate loses its i.e.c. almost completely while Sn(IV) phosphosilicate retains it appreciably. Figure 3 shows the percentage retention of the i.e.c. of this material and other Sn(IV) based double salts such as arsenophosphate[18], tungstoarsenate[19], vanadophosphate[20] and vanadoarsenate[21] along with that of Sn(IV) phosphate[17] at different elevated temperatures. The Sn(IV) phosphosilicate heated at 200°C, 300°C or 500°C for 1 hour do not show any change in its elution behaviour for Cu(II) ion. However the elution becomes weaker on a column of the sample heated at a higher temperature. It, therefore, indicates that the present material is superior to other similar salts in its thermal stability.

pH-titrations (Figure-1) indicate a weak cation exchange behaviour of the material. No sharp inflection is observed either in the acidic or basic pH range, probably because of a wide spread of pKa values.

The IR spectrum taken by the KBr disk technique shows the band maxima[22] at frequencies$\sim$3400, $\sim$ 1600, $\sim$ 1050 and in the range 400-600 cm^{-1}. The first one is due to the stretching vibrations of interstitial water and the more strongly attached OH groups present

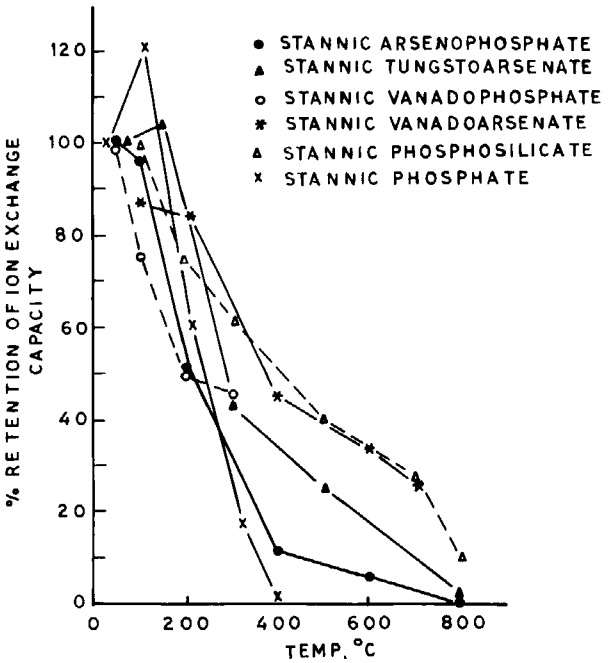

FIGURE 3: A comparison of thermal stability of different Sn(IV) based double salts and Sn(IV) phosphate.

in the material, while the second peak indicates the M-OH deformation vibrations. The broad and strong peak observed at $\sim$ 1050 cm^{-1} is due to the presence of $H_2PO_4^-$, HPO_4^{--}, PO_4^{---} groups which also corresponds to the SiO_3^{--} group. A weak peak ranging between 400 and 600 cm^{-1} is the characteristic of the M-O stretching vibrations.

Distribution studies show that in water almost all metal ions are adsorbed completely. In 0.01M HNO_3 or $HClO_4$ medium the selectivity sequence observed is as Ba > Sr > Ca > Mg. Sn(IV) phosphate on the other hand, adsorbs Ca in preference of Sr. For bivalent transition metals also a reversal in the behaviour is observed when compared with Sn(IV) phosphate. Their adsorption sequence on Sn(IV) phosphosilicate is as Co > Cu > Zn > Ni while on Sn(IV) phosphate it is Cu > Zn > Ni > Co. Tetravalent metals like Th(IV), Zr(IV), Ce(IV) and Ti(IV) are completely eluted through the column of Sn(IV) phosphosilicate using simply 0.01M HNO_3, a behaviour which is surprisingly different to the other

similar salts which are generally known to adsorb these metals strongly. The reason may be the formation of an extra stable Sn(IV) phosphate matrix in presence of SiO_2. On the basis of Kd values some analytically important separations have been achieved as summarized in table-3, on the column of Sn(IV) phosphosilicate. Hg(II) is separated easily from Cu(II), Zn(II), Cd(II), Pb(II) and Ag(I). Similarly Zr(IV) and Th(IV) are separated from UO_2(II) and Y(III). The limits of these separations are wide enough for some useful applications. A typical elution curve showing a sharp and quick separation of Hg(II) and Cu(II) is shown in figure 2. The precision and accuracy of these separations have been tested by achieving them several times.

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REFERENCES

(1). T.P.Tang, P.Sun and K.Y.Chan, Hua Hsueh, 33, (1965).

(2). G.T.Desai and D.R.Baxi, Indian J.Technol., 16, 204 (1978).

(3). G.T.Desai and D.R.Baxi, Ibid, 16, 201 (1978).

(4). D.Naumann, Kernenergie, 6, 173 (1963); CA, 63, 3443g (1965).

(5). S.J.Naqvi, D.Huys and L.H.Baetsle, J.Inorg.Nucl.Chem., 33, 4317 (1971).

(6). K.G.Varshney, A.Maheswari and A.A.Khan, (Unpublished studies).

(7). K.G.Varshney and A.Premadas, (Unpublished studies).

(8). F.J.Welcher, "Standard Methods of Chemical Analysis", VIth Edn., Vol.II, Part B, p.2475 D.Van Nostrand Co., INC., NJ (1963).

(9). I.M.Kolthoff and R.Belcher, "Volumetric Analysis", Vol.3, p.320, Interscience, N.Y.

(10). F.J.Welcher, (Editor), "Standard Methods of Chemical Analysis", VIth Edn., Vol.II, Part B, p.1491, D.Van Nostrand Co., INC. NJ (1963).

(11). E.B.Sandell, "Colorimetric Determination of Traces of Metals", IIIrd Edn., p.864 Interscience Publishers INC, NY (1959).

(12). F.D.Snell and C.T.Snell, "Colorimetric Methods of Analysis", 3rd Edn., Vol.II, p.695, D.Van Nostrand Co., INC, NJ (1959).

(13). F.D.Snell and C.T.Snell, Colorimetric Methods of Analysis", 3rd Edn, Vol.II, p.636, D.Van Nostrand Co., INC, NJ (1959).

(14). N.E.Topp and K.W.Pepper, J.Chem.Soc., 3299 (1949).

(15). E.B.Sandell, "Colorimetric Determination of Traces of Metals", p.812, Interscience Publishers, INC, NJ (1959).

(16). F.D.Snell and C.T.Snell, "Colorimetric Methods of Analysis", 3rd Edn., Vol.II, p.492, D.Van Nostrand Co., INC. NJ (1959).

(17). Y.Inoue, Bull.Chem.Soc.Japan, 36, 1316 (1963).

(18). K.G.Varshney and A.A.Khan, J.Inorg.Nucl.Chem., 41, 241 (1979).

(19). M.Qureshi, R.Kumar, V.Sharma and T.Khan, J.Chromatog., 118, 175 (1976).

(20). M.Qureshi and R.C.Kaushik, Anal.Chem., 49, 165 (1977).

(21). P.S.Thind, S.S.Sandhu and J.P.Rawat, Chim.Analit., 24, 65 (1979).

(22). C.N.R.Rao, "Chemical Applications of Infra Red Spectroscopy, Academic Press, N.Y. (1963).