Synthesis, Ion-Exchange Properties, and Analytical Applications of Anilinium Tin(IV) Phosphate

Dhruv Kumar Singh* and Anjana Darbari
Department of Chemistry, Harcourt Butler Technological Institute, Kanpur-208002, India

(Received January 13, 1987)

A new inorganic ion-exchanger anilinium tin(IV) phosphate (ATP) has been synthesized under varying conditions. The effects of mixing ratio of reagents and the pH of the mixture on the properties of the material have been studied. The sample ATP_1 has been chosen for detailed studies, such as ion-exchange capacity, chemical and thermal stabilities, chemical composition, pH titration, break-through curve, and IR analysis. Distribution coefficients of 16 metal ions have been studied in water, hydrochloric acid and acetone-hydrochloric acid media. On the basis of K_d values some analytically important separations of metal ions have been achieved on the small columns of anilinium tin(IV) phosphate.

There have been continuous efforts to improve the chemical, thermal, and mechanical stabilities of ion-exchangers and to make them highly selective for particular metal ions. Hahn and Klein[1)] introduced organic ammonium ions in place of inorganic ammonium ion in ammonium hexacyanoferrate(II) compound of cobalt(II) and reported that the ammonium compounds have excellent exchange properties for ^{137}Cs. Ammonium tin(II) hexacyanoferrate(II),[2)] ammonium tin(IV) hexacyanoferrate(II),[3)] tin(IV) diethanolammonium,[4)] iron(III) diethanolammonium,[5)] and tin(IV) phosphate[6,7)] have already been reported and utilized for the separations of metal ions. Anilinium tin(IV) phosphate has not been studied so far. The present paper summarizes the synthesis, ion-exchange properties and analytical applications of anilinium tin(IV) phosphate as a new inorganic ion-exchanger.

Experimental

Reagants. Tin(IV) chloride pentahydrate (Poland), aniline, and orthophosphoric acid (BDH, India) were used. All other reagents were of analytical grade.

Apparatus. Bausch and Lomb Spectronic 20 for spectrophotometry, Systronic digital pH meter for pH measurements and Perkin Elmer model 599 B Spectrophotometer for IR studies, were used. An electric rotary shaking machine IEC-56 was used for shaking purpose.

Synthesis. An excess of aniline (ca. 5 cm^3) was added dropwise to 10 cm^3 of 1 mol dm^{-3} orthophosphoric acid solution with constant stirring to prepare dianilinium hydrogenphosphate [$(C_6H_5NH_3)_2HPO_4$]. It was dissolved in demineralized water (DMW) and diluted up to 200 cm^3. This solution was added to 0.1 mol dm^{-3} tin(IV) chloride solution with constant stirring as outlined in Table 1. The pH of the sample solution in each case was adjusted by adding hydrochloric acid solution dropwise. After 24 h the product was filtered, washed with DMW and dried at 40 °C. The material broke into small particles when immersed in DMW and was converted into H$^+$ form on treatment with 1 mol dm^{-3} nitric acid for 24 h with occasional shaking and renewal of the acid. The excess of the acid was removed after several washings with DMW. The samples were dried at 40 °C.

Ion-Exchange Capacity. The ion-exchange capacity of various samples of anilinium tin(IV) phosphate was determined by the column method (Tables 1 and 2). One gram exchanger in H$^+$ form was taken in the column of 7.2 mm (i.d.). The H$^+$ ions were eluted by percolating the required 1 mol dm^{-3} cationic solution through the column. The feed was passed until its pH became equal to that of the effluent collected. The hydrogen ions so eluted were titrated against standardized 0.1 mol dm^{-3} NaOH. The neutral salt decomposition capacity with different uni- and bivalent ions is reported in Table 3.

Chemical Composition. The well-powdered material (0.5 g) was fused with a 1 : 1 mixture of potassium and sodium carbonates. The fused mixture was extracted with hot water, the undissolved portion was ignited and weighed as SnO_2. The diphosphorus pentoxide present in the disslove portion was precipitated as ammonium molybdophosphate, filtered and determined gravimetrically.[8)] For the determination of aniline, another 0.5 g sample of the exchanger was introduced into a Kjeldahl digestion flask. After digestion 25 cm^3 potassium hydroxide solution (50%) was added dropwise. The amine distilled into 50 cm^3 boric acid solution (1%) was titrated with 0.1 mol dm^{-3} HCl using a mixed indicator (Bromocresol Green and Methyl Red).[9)]

Chemical Stability. A 0.2 g of the material (sample ATP_1) was shaken with 20 cm^3 of the solution concerned at 30±2 °C for 6 h. Tin, phosphorus, and aniline were determined spectrophotometrically with phenylfluorone,[10)] molybdovanadophosphoric acid,[11)] and iron(III) nitrate[12)] respectively.

pH Titration. Topp and Peppers'[13)] method was used for pH titrations using NaOH-NaCl system. A quarter gram samples of dry exchanger (ATP_1) in H$^+$ form were shaken with 25 cm^3 portions of 0.1 mol dm^{-3} (NaCl+NaOH) cationic solution in different conical flasks at 30±1 °C. The concentration ratio of NaCl/NaOH was varied from 0.096 mol dm^{-3}/0.004 mol dm^{-3} to 0.004 mol dm^{-3}/0.096 mol dm^{-3} in the equilibrating solution of the flasks. After 24 h pH of the supernatant solution of each flask was recorded and plotted against the mEq of OH$^-$ added per 0.25 g of dry exchanger (Fig. 1).

Break-through Curve. The break-through curves[14)] were observed for Zn^{2+}, Cd^{2+}, and Hg^{2+} by passing 0.02 mol dm^{-3} solution (pH≈6) of each metal ion through a glass column, i.d. 7.2 mm and 30 cm length packed with 4 g of anilinium thin(IV) phosphate in H$^+$ form (Sample ATP_1). The flow rate was maintained 1 cm^3 min^{-1}. The results are presented in Fig. 3.

Table 1. Synthesis and Properties of Anilinium Tin(IV) Phosphate[a, b)]

Sample No.	Volume of 0.1 mol dm^{-3} Tin(IV) chloride/cm^3	pH	Ion-exchange capacity for K$^+$ meq (dry g)$^{-1}$	Composition Sn: $C_6H_5NH_2$: PO_4^{3-}	Yield g
ATP_1	50	1	1.68	4:2:1	1.06
ATP_2	100	1	1.52	—	—
ATP_3	200	1	1.40	—	—
ATP_4	50	2	1.53	—	—
ATP_5	50	3	1.44	4.6:2:1	—
ATP_6	50	5	1.30	5:2:1	—

a) Tin(IV) chloride solution was added to 200 cm^3 of 5X10^{-2} mol dm^{-3} $(C_6H_5NH_3)_2HPO_4$ solution.
b) Appearance of precipitate was white gelatinous and appearance of beads after drying at 40 °C was white.

Table 2. Reproducibility of the Synthesis

Batch No.	Ion-exchange capacity for K$^+$ meq (dry g)$^{-1}$	Composition Sn : $C_6H_5NH_2$: PO_4^{3-}
1	1.68	4 : 2 : 1
2	1.70	4 : 2 : 1
3	1.68	4.02 : 2 : 1
4	1.66	4 : 2 : 1
5	1.70	4.02 : 2 : 1

Distribution Coefficient. Distribution coefficients (K_d values) of a number of metal ions in water, hydrochloric acid and acetone-hydrochloric acid systems were determined by a batch process.[15)] A quarter gram of the exchanger in H$^+$ form (50—100 mesh) was equilibrated with 25 cm^3 cation solutions (4X10^{-3} mol dm^{-3}) at 30±1 °C for 6 h in a 100 cm^3 Erlenmeyer flask. The amount of cation in the solution after and before the treatment with the exchanger was determined by EDTA titration except Pt^{4+} which was determined with tin(II) chloride[16)] spectrophotometrically. K_d values were calculated from

$$K_d(\mathrm{cm^3\,g^{-1}}) = \frac{\text{Amount of metal ion in exchanger phase per gram}}{\text{Amount of metal ion in solution phase per cm}^3}$$

The results are presented in Table 5.

Quantitative Separations. Quantitative separations of some important metal ions of analytical utility were achieved on the columns of anilinium tin(IV) phosphate. Two grams of the exchanger in H$^+$ form (50—100 mesh) was taken into a glass column of i.d. 3.9 mm. The column was first washed with about 20 cm^3 of 80% acetone-hydrochloric acid (0.01 mol dm^{-3}) and then the mixture of metal ions having concentration 0.644 to 1.044 mg/10 cm^3 was introduced into the column and allowed to be adsorbed. The metal ions were then eluted separately using suitable eluting reagents and determined by EDTA titrations except Pt^{4+} which was determined spectrophotometrically.[16)] The flow rate was maintained about 0.2 cm^3 min^{-1} throughout the elution process. Results of separations achieved have been reported in Table 6.

Table 3. Ion-Exchange Capacity of Anilinium Tin(IV) Phosphate (Sample ATP_1) for Various Cations

Cation[a)]	pH	Hydrated radii/nm	I.E.C. meq (dry g)$^{-1}$
Li$^+$	6.8	0.340	1.28
Na$^+$	6.8	0.276	1.64
K$^+$	6.8	0.232	1.70
Mg^{2+}	6.5	0.700	1.00
Ca^{2+}	6.5	0.630	1.46
Sr^{2+}	6.2	—	1.50
Ba^{2+}	6.2	0.590	1.62

a) Used as chloride (1 mol dm^{-3}).

Table 4. Chemical Stability of Anilinium Tin(IV) Phosphate (ATP_1)

Solvent	Solubility (mg/20 cm^3)		
	Sn released	$C_6H_5NH_2$ released	P released
Demineralized water	0.00	0.02	0.06
1 mol dm^{-3} Nitric acid	0.06	0.04	0.12
4 mol dm^{-3} Nitric acid	1.30	0.84	1.86
1 mol dm^{-3} Hydrochloric acid	0.20	0.37	0.28
4 mol dm^{-3} Hydrochloric acid	2.58	2.14	3.60
0.1 mol dm^{-3} Sodium hydroxide	0.04	3.00	1.62
Acetone	0.00	0.00	0.10
Methanol	0.00	0.04	0.16

Results and Discussion

The ion-exchange capacities and the compositions of the samples of anilinium tin(IV) phosphate are presented in Table 1. In the synthesis of anilinium tin(IV) phosphate, increased pH and volume of 0.1 mol dm^{-3} tin(IV) chloride results in decreased ion-exchange capacity. The maximum ion-exchange capacity (1.7 meq (dry g)$^{-1}$) is observed for sample ATP_1 prepared by mixing 50 cm^3 of 0.1 mol dm^{-3} tin(IV) chloride solution to the anilinium phosphate solution at pH 1. The ion-exchange capacity of ATP_1 is higher than the reported capacity, 1.4 meq (dry g)$^{-1}$

of tin(IV) phosphate.[6,7] ATP_1 shows reproducible properties as is evident from data presented in Table 2.

The ion-exchange capacity measured for various cations is given in Table 3. The data show that ion-exchange capacity for alkali metals are higher than alkaline earths. In both cases the capacity increases with the decrease in hydrated radii of ions. The effect of drying temperature on the ion exchange capacity was studied. The results shown in Fig. 2 indicate that this exchanger can be used up to 100 °C without loss in ion-exchange capacity; above 100 °C there is a decrease in ion-exchange capacity but the decrease is much less than in anilinium hexacyanoferrate(II) of tin(II) and tin(IV).

The results of chemical stability measurements (Table 4) indicate that the product is fairly stable in water, acetone, ethanol, 0.1 mol dm^{-3} NaOH and up to 1 mol dm^{-3} nitric acid and hydrochloric acid.

Analytical data of sample ATP_1 are as follows: amount of exchanger taken, 1.000g; $C_6H_5NH_2$ obtained after distillation, 0.217±0.003 g (2.333 mmol); amount o Sn(IV) found, 0.544±0.002 g (4.583 mmol); amount of PO_4^{3-} found, 0.108±0.002 g (1.137 mmol); molar ratio of Sn(IV): $C_6H_5NH_2$: PO_4^{3-}, 4 : 2 : 1. The products prepared at pH values greater than one contained more tin.

The capacity which is utilized until break-through occurs is called break-through capacity. The break-through behavior of anilinium tin(IV) phosphate for Zn^{2+}, Cd^{2+}, and Hg^{2+} was studied. The results are plotted in Fig. 3.

The results of pH titrations indicate that ATP_1 in

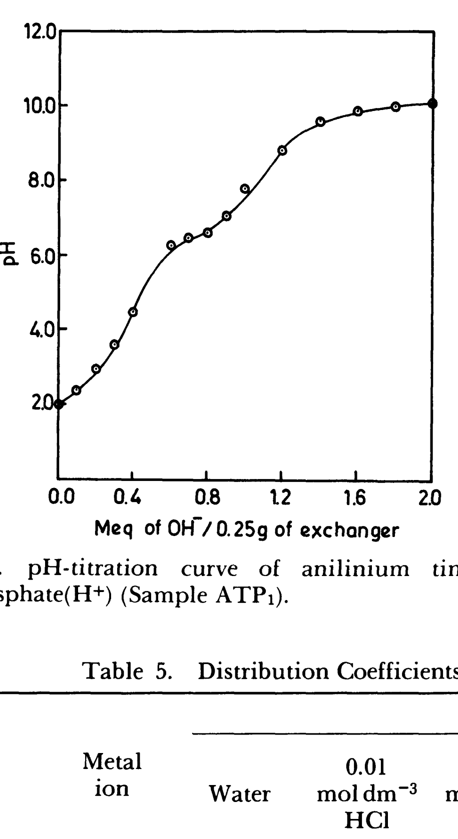

Fig. 1. pH-titration curve of anilinium tin(IV) phosphate(H^+) (Sample ATP_1).

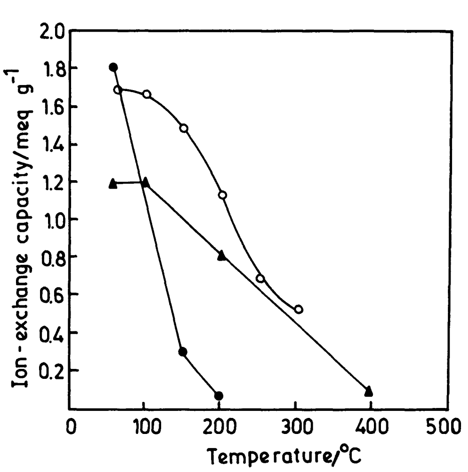

Fig. 2. Ion-exchange capacity of various aniline complexes as a function of drying temperature.
▲ Anilinium tin(II) hexacyanoferrate(II).
● Anilinium tin(IV) hexacyanoferrate(II).
○ Anilinium tin(IV) phosphate (Sample ATP_1).

Table 5. Distribution Coefficients of Some Metal Ions on Anilinium Tin(IV) Phosphate

Metal ion	K_d/cm^3 g^{-1}						
	Water	0.01 mol dm^{-3} HCl	0.1 mol dm^{-3} HCl	80% 0.01 mol dm^{-3} HCl-20% acetone	60% 0.01 mol dm^{-3} HCl-40% acetone	20% 0.01 mol dm^{-3} HCl-80% acetone	Acetone
Zn^{2+}	40	11	3	6	9	13	39
Cd^{2+}	87	49	11	51	81	190	380
Hg^{2+}	580	370	280	1200	5700	7900	9800
Mn^{2+}	40	26	6	21	28	40	63
Fe^{3+}	58	42	26	53	68	110	220
Co^{2+}	69	59	50	350	440	580	900
Ni^{2+}	68	56	43	68	78	110	220
Cu^{2+}	70	17	9	160	250	260	370
Pb^{2+}	410	350	320	360	410	430	500
Mg^{2+}	19	7	1	9	11	26	78
Ca^{2+}	99	55	20	70	95	130	300
Ba^{2+}	110	50	28	86	100	150	330
Al^{3+}	85	60	44	300	470	900	1200
Th^{4+}	22	19	10	35	79	98	110
Pt^{4+}	780	—	210	—	600	750	1300
Zr^{4+}	310	220	130	230	300	—	510

Table 6. Quantitative Separations of Metal Ions on Anilinium Tin(IV) Phosphate (Sample ATP_1) Columns

Sample No.	Separation	Amount fed to the column	Amount found after elution	Percent of metal ions eluted	Total elution volume	Eluent used
		μg	μg		cm³	
1	Zn^{2+}	327	326	99.7	30	60% 0.01 mol dm^{-3} HCl-40% acetone
	Cd^{2+}	225	223	99.4	50	80% 0.01 mol dm^{-3} HCl-20% acetone
	Hg^{2+}	400	388	97.0	70	80% 0.5 mol dm^{-3} HCl-20% acetone
2	Zn^{2+}	327	326	99.6	30	60% 0.01 mol dm^{-3} HCl-40% acetone
	Ni^{2+}	427	421	98.7	50	80% 0.2 mol dm^{-3} HCl-20% acetone
	Pt^{4+}	145	141	96.8	70	80% 0.5 mol dm^{-3} HCl-20% acetone
3	Zn^{2+}	327	326	99.7	30	60% 0.01 mol dm^{-3} HCl-40% acetone
	Cu^{2+}	317	313	98.9	40	80% 0.1 mol dm^{-3} HCl-20% acetone
	Hg^{2+}	400	389	97.2	70	80% 0.5 mol dm^{-3} HCl-20% acetone
4	Zn^{2+}	327	326	99.7	30	60% 0.01 mol dm^{-3} HCl-40% acetone
	Fe^{3+}	280	275	98.2	40	80% 0.2 mol dm^{-3} HCl-20% acetone
	Pb^{2+}	401	394	98.4	50	80% 0.5 mol dm^{-3} HCl-20% acetone
5	Mg^{2+}	243	242	99.8	30	80% 0.01 mol dm^{-3} HCl-20% acetone
	Th^{4+}	232	230	99.1	40	80% 0.1 mol dm^{-3} HCl-20% acetone
	Pt^{4+}	380	372	97.9	70	80% 0.5 mol dm^{-3} HCl-20% acetone
6	Th^{4+}	232	230	99.0	40	80% 0.1 mol dm^{-3} HCl-20% acetone
	Zr^{4+}	450	441	98.0	60	80% 0.5 mol dm^{-3} HCl-20% acetone
7	Mn^{2+}	540	536	99.3	30	60% 0.1 mol dm^{-3} HCl-40% acetone
	Co^{2+}	431	424	98.5	50	80% 0.5 mol dm^{-3} HCl-20% acetone
8	Mg^{2+}	243	242	99.8	30	80% 0.01 mol dm^{-3} HCl-20% acetone
	Ca^{2+}	401	394	98.4	50	80% 0.2 mol dm^{-3} HCl-20% acetone

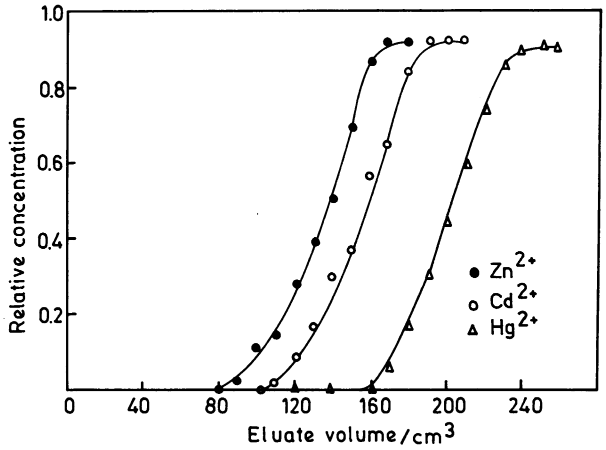

Fig. 3. Break-through curves of ATP_1 for three bivalent cations.

H^+ form behaves as a diprotic acid (Fig. 1). The total ion-exchange capacity is 3.6 meq g^{-1} calculated at the neutralization point. This gives the maximum number of replaceable counter ions and is independent of the nature of the cation.

The IR spectrum of anilinium tin(IV) phosphate is in accord with the proposed composition.

In order to study the analytical potentialities of the ion-exchanger the distribution coefficients of 16 metal ions in seven systems were determined, the results are shown in Table 5. Anilinium tin(IV) phosphate shows selective behavior (higher K_d values) for Hg^{2+}, Pb^{2+} and Pt^{4+}. The data in Table 5 show that K_d values decrease with the increase in concentration of hydrochloric acid and increase in solutions with greater percentage of acetone. On the basis of this behavior (K_d values) separations were tried. Those experimentally successfully achieved are reported in Table 6. The relative order of elution for Zn^{2+}-Cd^{2+}-Hg^{2+} is similar to that of break-through curves (Fig. 3). It is interesting that no significant tailing was observed during the elution of various metal ions and only small volumes of eluents were required to give compact chromatograms.

Mg^{2+} is eluted ahead of Ca^{2+} (binary separation of Mg^{2+}-Ca^{2+}) with suitable hydrochloric acid-acetone solution, hence the columns of anilinium tin(IV) phosphate may be utilized to separate magnesium from calcium in dolomite.[17] Usually, 0.1 to 0.5% cadmium is present in zincblende (Sphalerite) and Calamine.[18] The ternary separation of Zn^{2+}-Cd^{2+}-Hg^{2+} may be utilized to recover Cd^{2+} from these ores using suitable eluents. Zircon contains usually less than 1 per cent of thorium oxide.[19] The binary separation of Th^{4+}-Zr^{4+} can be applied for the recovery of Th^{4+} from Zr^{4+}. Iron and lead occur in major to trace concentrations in zinc bearing ores.[20] Zn^{2+}, Fe^{3+}, and Pb^{2+} can be eluted by different hydrochloric acid-acetone solutions using anilinium tin(IV) phosphate columns.

Authors thank Prof. A. K. Vasishtha, Director and Prof. R. S. Tewari, Head, Department of Chemistry, H. B. Technological Institute, Kanpur for research facilities. Financial assistance from U.G.C. is also gratefully acknowledged.

References

1) R. B. Hahn and H. C. Klein, *Anal. Chem.*, **40**, 1135 (1968).

2) K. G. Varshney and S. Naheed, *J. Inorg. Nucl. Chem.*, **39**, 2075 (1977).

3) K. G. Varshney, A. A. Khan, and S. S. Varshney, *Indian J. Chem.*, **21A**, 398 (1982).

4) J. P. Rawat and M. Iqbal, *Ann. Chimica,* **1981**, 431.

5) D. K. Singh, R. R. Bhatnagar, and A. Darbari, *Indian J. Tech.*, **24**, 45 (1986).

6) Y. Inoue, *J. Inorg. Nucl. Chem.*, **26**, 2241 (1964).

7) Y. Inoue, *Bull. Chem. Soc. Jpn.*, **36**, 1316 (1963).

8) N. H. Furman, "Standard Methods of Chemical Analysis," 5th ed, (1939), Vol. 1, p. 694.

9) J. J. Mitchell, I. M. Kolthoff, E. S. Proskauer, and A. Weisberger, "Organic Analysis," Interscience, New York (1956), Vol. 3, p. 140.

10) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience, New York (1959), p. 862.

11) F. B. David, "Colorimetric Determination of Nonmetals, Chemical Analysis," Interscience, New York (1958), Vol. 8, p. 36.

12) J. P. Rawat and J. P. Singh, *Anal. Chem.*, **47**, 738 (1975).

13) N. E. Topp and Pepper, *J. Chem. Soc.,***1949**, 3299.

14) J. Inczedy, "Analytical Applications of Ion-Exchangers," Pergamon Press (1966), p. 126.

15) J. P. Rawat and D. K. Singh, *Anal. Chim. Acta,* **87**, 157 (1976).

16) E. B. Sandell, "Colorimetric Determination of Traces of Non-metals," Interscience, New York (1959), p. 726.

17) N. H. Furman, "Standard Methods of Chemical Analysis," 6th ed, D. Van Nostrand, Inc., Princeton, New Jersey (1962), Vol. 1, p. 585.

18) I. M. Kolthoff, P. J. Elving, and E. B. Sandell, "Treatise on Analytical Chemistry," Interscience Publishers, New York, London (1961), Part 2, Vol. 3, p. 173.

19) Ref. 18, Vol. 5, p. 143.

20) Ref. 18, p. 99.