2636 © 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 2636—2641 (1982) [Vol. 55, No. 8

# Synthesis, Ion Exchange Properties, and Analytical Applications of a Novel Tin(IV)-edta Ion Exchanger

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Tin(IV)-edta compound has been synthesized by mixing aqueous solutions of tin(IV) chloride and disodium salt of ethylenediaminetetraacetic acid (EDTA=$H_4$ edta) in different conditions. The most stable sample is prepared by mixing 0.1 mol dm$^{-3}$ solution of tin(IV) chloride with 0.1 mol dm$^{-3}$ solution of disodium salt of edta in the volume ratio of 3:2 at pH 2.5 and refluxing the mixture for 16 h. Ion exchange capacities of the material for alkali metals are significantly smaller (0.26—0.20 mequiv./g) than for alkaline earths (0.74—0.40 mequiv./g). The thermal and chemical stability of this material has been compared with amine-tin hexacyanoferrate(II). Analytical importance of this material has been established by achieving a number of quantitative separations on its columns.

The advancement in the field of synthetic inorganic ion exchangers has been reviewed by various authors.[1,2] Their importance in analytical chemistry has been firmly established. It has been found that inorganic ion exchangers often exhibit their own characteristic properties. It is therefore, always of interest to synthesize new ion exchange materials and to utilize them to solve analytically difficult problems of specific nature.

Of the various ion exchangers studied earlier, have been synthesized either by interaction of pure organic or inorganic compounds. As far as we are aware only limited efforts have been made to develop this new class of ion exchange material which is based on the interaction of metal ions with organic compounds. Amine-tin hexacyanoferrate(II) and zirconium(IV)-bis(carboxymethanephosphonate)[3,4] have been found to exhibit exchange properties. However, detailed studies have not been made on these materials due to their limited chemical and thermal stability.

Crystalline edta complexes of zirconium, hafnium, thorium and tin at pH 1.5 have been described fairly stable.[5] However these compounds have not been studied for their ion exchange properties. In continuation to our studies in these directions we have been able to synthesize amorphous tin(IV)-edta compound as a new cation exchanger. EDTA has been chosen because of its enormous usefulness as an analytical reagent. The present paper deals with the preparation, properties and applications of tin(IV)-edta compounds.

## Experimental

*Reagents.* Tin(IV) chloride pentahydrate (Poland) and ethylenediaminetetraaceticacid disodium salt (E. Merck, Germany) were used. All the other chemicals were of reagent grade.

*Apparatus.* pH was measured with an Elico LI-10 pH meter. A spectronic 20 colorimeter and a Perkin Elmer 137 spectrophotometer were used for spectrophotometric and IR studies respectively. An electric temperature controlled shaker (SICO) was used for shaking. X-Ray studies were performed on a philips diffractometer and Stanton-Thermobalance type $H_4$ was used for thermogravimetric studies.

*Synthesis.* Tin(IV)-edta precipitates were prepared by mixing 0.1 mol dm$^{-3}$ aqueous solution of ethylenediaminetetraacetic acid disodium salt to 0.1 mol dm$^{-3}$ aqueous solution of tin(IV) chloride in different volume ratio as indicated in Table 1. The desired pH was adjusted by adding either dilute hydrochloric acid or dilute sodium hydroxide solution. The precipitate formed, was allowed to settle for 24 h at room temperature. It was then filtered off, washed with distilled water and dried at 40 °C. Sample 1, 2, and 3 so prepared were powder like and yellowish white in appearance. Sample 4 was prepared by adding 0.1 mol dm$^{-3}$ aqueous solution of disodium salt of edta gradually to 0.1 mol dm$^{-3}$ aqueous solution of tin(IV) chloride in volume ratio 2:3 while continuously stirring the mixture. The pH was adjusted to 2.5 by adding dilute solution of sodium hydroxide. The white precipitate obtained was refluxed for 16 h with mother liquor. It was then filtered off under suction, washed several times with distilled water and then dried at 40 °C. This dirty yellow substance when immersed in water, broke down into smaller particles with cracking. Out of these four samples, sample 4 was found to be fairly stable in water and some mineral acids and further studies were therefore, performed on sample 4. The material was immersed in 1 mol dm$^{-3}$ nitric acid solution for 24 h to convert it into $H^+$ form. Excess of acid was removed by repeated washing with demineralized water. The conditions of synthesis and few properties are summarized in Table 1.

*Chemical Stability.* Sample 4 was washed several times to remove excess of tin or EDTA adhered to the surface of the particles. 0.5 g of the material was then treated with 50 cm$^3$ of the solvent in a 250 cm$^3$ Erlenmeyer flask. The mixture was shaken for 6 h in a shaker incubator at 25±2 °C and then kept for 24 h. Tin released was determined spectrophotometrically using hematoxylin as a colouring reagent[6] and edta in the solution was determined volumetrically using magnesium nitrate solution.[7] These results are given in Table 2.

*Chemical Composition.* Since the material is not completely soluble in concentrated hydrochloric acid and EDTA is damaged by hot concentrated sulfuric acid, potassium hydroxide was utilized for its dissolution. A 0.2 g of the exchanger was dissolved in 1.0 mol dm$^{-3}$ potassium hydroxide solution. The pH of the solution was decreased by adding hydrochloric acid drop by drop till precipitation was complete. It was then filtered off. The precipitate was dried and tin was estimated as tin dioxide. The filtrate left was made to 100 cm$^{-3}$ and edta was determined titrimetrically against a standard solution of magnesium nitrate.[7]

*Ion Exchange Capacity.* Ion exchange capacities of some uni- and bivalent ions are shown in Table 3. 0.5 g

TABLE 1. SYNTHESIS OF TIN(IV)-edta

| Sample No. | Conditions of synthesis | | | Adjusted pH | Time of refluxing / h | Appearance $H^+$ form | Chemical composition Tin/edta |
|---|---|---|---|---|---|---|---|
| | $SnCl_4 5H_2O$ (mol $dm^{-3}$) | edta (mol $dm^{-3}$) | Mixing ratio (v/v) | | | | |
| 1 | 0.1 | 0.1 | 1 : 1 | 2.0 | — | Yellow powder | — |
| 2 | 0.1 | 0.1 | 2 : 1 | 2.1 | — | Yellowish white powder | — |
| 3 | 0.1 | 0.1 | 3 : 2 | 2.0 | — | Yellowish white powder | 1.0 |
| 4 | 0.1 | 0.1 | 3 : 2 | 2.5 | 16 | Dark yellow shiny particles | 2.5 |

TABLE 2. COMPARISON OF FEW PROPERTIES OF TIN(IV)-edta AND AMINE-TIN HEXACYANOFERRATE(II)

| Effect of drying temperature on ion exchange capacity (meqiv./g) | | | Chemical stability | | | | |
|---|---|---|---|---|---|---|---|
| | | | | Tin(IV)-edta | | Amine-tin hexacyanoferrate(II) | |
| Temp / °C | Tin(IV)-edta | Amine-tin hexacyanoferrate(II) | Solvent | Tin released (mg/50 $cm^3$) | edta released (mg/50 $cm^3$) | Iron released (mg/50 $cm^3$) | Tin released (mg/50 $cm^3$) |
| | | | $H_2O$ | 0.00 | 0.00 | 0.10 | 0.20 |
| 60 | 0.74 | 1.2 | 0.05 M $HNO_3$ | 0.00 | 0.00 | 0.25 | 0.00 |
| 100 | 0.74 | 1.2 | 0.1 M $HNO_3$ | 0.00 | 0.00 | — | — |
| 200 | 0.48 | 0.8 | 0.5 M $HNO_3$ | 0.00 | 0.00 | 0.20 | 0.10 |
| 300 | 0.24 | — | 1.0 M $HNO_3$ | 0.00 | 0.00 | 0.40 | 0.15 |
| 400 | 0.13 | 0.10 | 0.1 M NaOH | 6.00 | 6.50 | Complete dissolution | |
| 500 | 0.12 | 0.00 | | | | | |
| 600 | 0.10 | 0.00 | | | | | |

TABLE 3. ION EXCHANGE CAPACITY (pH=6) OF TIN(IV)-edta (SAMPLE 4) AT ROOM TEMPERATURE

| Exchanging ion | Solution used | Ion exchange capacity (mequiv./g) |
|---|---|---|
| $Li^+$ | Lithium chloride | 0.20 |
| $Na^+$ | Sodium nitrate | 0.20 |
| $K^+$ | Potassium nitrate | 0.24 |
| $Rb^+$ | Rubidium chloride | 0.20 |
| $Mg^{2+}$ | Magnesium nitrate | 0.70 |
| $Ca^{2+}$ | Calcium nitrate | 0.74 |
| $Sr^{2+}$ | Strontium nitrate | 0.60 |
| $Ba^{2+}$ | Barium chloride | 0.40 |

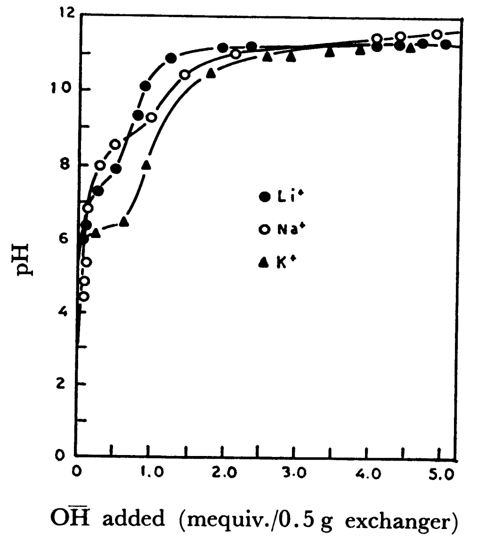

Fig. 1. pH titration curves of tin(IV)-edta.

of the exchanger in $H^+$ form was taken into the column with glass wool support. The $H^+$ ions eluted by passing 1 mol $dm^{-3}$ of the electrolyte solutions (pH=6) through the column. The eluted $H^+$ ions in the effluent were determined volumetrically using standard sodium hydroxide solution as titrant.

*pH Titrations.* pH titrations were performed using Topp and Papper's method[8] for LiCl–LiOH, NaCl–NaOH, and KCl–KOH systems at 25±2 °C (Fig. 1).

*Distribution Coefficient.* The $K_d$ values of metal ions in different solvent systems were determined with the method reported earlier.[9] The results are given in Tables 4 and 5.

*Quantitative Separations of Metal Ions.* Quantitative separations of some metal ions were achieved on a 0.3 cm diameter (id) glass column using 2.0 g of exchanger (mesh size 100—200) in $H^+$ form. The cation mixture was poured on the top of the column. The stop cock open so that the mixture passed through the column with a very slow rate. The column was rinsed with distilled water. The cations adsorbed were then eluted with suitable eluting agents. The flow rate during elution was maintained 1.0 $cm^3$/min. The 10 $cm^3$ fraction of the effluent was collected and the metal ions were determined by standard methods.[6,7] Quantitative separations of metal ions achieved on the columns of tin(IV)-edta are summarized in Table 6.

*X-Ray Analysis.* Nickel-filtered Cu $K\alpha$ radiation was used for X-ray analysis of sample 4.

*Infrared Spectra.* IR spectrum of tin(IV)-edta compound in $H^+$ form was performed using Nujol technique and compared with IR spectrum of disodium salt of EDTA (Fig. 2).

*Thermal Treatment.* Thermogravimetric analysis of 0.3310 g of sample 4 in $Mg^{2+}$ form was performed at a heating rate of 10 °C/min (Fig. 3). To examine the effect of

TABLE 4. DISTRIBUTION COEFFICIENTS OF METAL IONS ON TIN(IV)-edta SAMPLE 4 IN DIFFERENT SOLVENT SYSTEMS

| Metal ions | $K_d$/cm$^3$ g$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | Water pH=6 | $10^{-3}$ mol dm$^{-3}$ HNO$_3$ | $10^{-2}$ mol dm$^{-3}$ HNO$_3$ | $10^{-1}$ mol dm$^{-3}$ HNO$_3$ | $10^{-1}$ mol dm$^{-3}$ NH$_4$Cl | $10^{-1}$ mol dm$^{-3}$ NH$_4$Cl + $10^{-2}$ mol dm$^{-3}$ HNO$_3$ |
| Mg$^{2+}$ | 308±17 | 85±1 | 45±2 | 27±2 | 70±3 | 36±1 |
| Ca$^{2+}$ | 270±8 | 120±2 | 90±2 | 32±2 | 38±2 | 18±2 |
| Sr$^{2+}$ | 140±6 | 78±1 | 45±2 | 22±1 | 28±3 | 32±8 |
| Ba$^{2+}$ | 100±8 | 65±1 | 36±1 | 19±1 | 22±2 | 20±1 |
| Al$^{3+}$ | 117±12 | 52±2 | 17±1 | 00±0 | 52±1 | 00±0 |
| Fe$^{3+}$ | 1080±134 | 880±9 | 200±33 | 74±4 | 85±4 | 64±6 |
| Co$^{2+}$ | 448±17 | 284±7 | 140±3 | 65±2 | 67±2 | 20±1 |
| Ni$^{2+}$ | 970±92 | 430±15 | 270±2 | 165±4 | 93±5 | 31±2 |
| Zn$^{2+}$ | 316±16 | 240±1 | 178±1 | 12±1 | 246±5 | 43±1 |
| Pb$^{2+}$ | 1900±182 | 640±29 | 263±3 | 77±1 | 400±2 | 176±4 |
| Cd$^{2+}$ | 526±6 | 410±2 | 88±2 | 21±1 | 120±7 | 17±5 |
| Mn$^{2+}$ | 1660±73 | 190±2 | 91±1 | 25±2 | 63±2 | 76±2 |
| VO$^{2+}$ | 8100±400 | 1210±56 | 550±7 | 64±1 | 370±8 | 134±1 |
| Cu$^{2+}$ | 2020±82 | 2020±43 | 430±8 | 92±1 | 324±2 | 35±2 |
| Zr$^{4+}$ | 120±10 | 110±2 | 68±4 | 00±0 | 86±22 | 60±5 |
| Hg$^{2+}$ | 368±18 | 64±1 | 36±1 | 6±1 | 157±3 | 32±2 |
| Ce$^{4+}$ | 320±36 | 210±3 | 77±2 | 61±1 | 310±6 | 40±2 |
| Ho$^{3+}$ | 1280±120 | 1020±20 | 530±30 | 200±4 | 530±30 | 510±10 |
| Dy$^{3+}$ | 3580±130 | 720±22 | 600±5 | 140±6 | 4330±20 | 360±3 |
| Sm$^{3+}$ | 660±33 | 620±2 | 230±2 | 82±3 | 420±9 | 196±5 |
| La$^{3+}$ | 286±24 | 200±4 | 130±1 | 100±5 | 110±5 | 58±4 |
| Tm$^{3+}$ | 496±28 | 460±4 | 440±7 | 350±10 | 200±32 | 230±8 |
| Eu$^{3+}$ | 220±14 | 210±3 | 170±1 | 94±2 | 210±62 | 200±12 |
| Pr$^{3+}$ | 450±12 | 430±1 | 280±5 | 140±4 | 270±10 | 150±7 |
| Nd$^{3+}$ | 428±28 | 330±24 | 250±7 | 210±6 | 431±31 | 271±4 |

TABLE 5.

| Metal ions | $K_d$/cm$^3$ g$^{-1}$ | | | |
|---|---|---|---|---|
| | $10^{-2}$ mol dm$^{-3}$ HClO$_4$ | $10^{-1}$ mol dm$^{-3}$ HClO$_4$ | $10^{-1}$ mol dm$^{-3}$ NaClO$_4$ | $10^{-2}$ mol dm$^{-3}$ HClO$_4$ + $10^{-1}$ mol dm$^{-3}$ NaClO$_4$ |
| Mg$^{2+}$ | 51±1 | 46±1 | 70±1 | 36±2 |
| Ca$^{2+}$ | 70±3 | 46±2 | 70±6 | 42±1 |
| Ba$^{2+}$ | 80±4 | 50±3 | 80±6 | 63±5 |
| Al$^{3+}$ | 20±2 | 3±1 | 260±20 | 00±0 |
| Fe$^{3+}$ | 526±15 | 10±1 | 660±5 | 276±36 |
| Co$^{2+}$ | 29±1 | 10±1 | 57±2 | 10±3 |
| Ni$^{2+}$ | 86±2 | 24±1 | 348±4 | 80±6 |
| Zn$^{2+}$ | 340±7 | 100±6 | 1750±40 | 214±11 |
| Pb$^{2+}$ | 12000±1200 | 104±4 | 15200±101 | 508±2 |
| Cd$^{2+}$ | 700±11 | 60±1 | 220±1 | 200±8 |
| Mn$^{2+}$ | 72±3 | 32±5 | 55±2 | 40±6 |
| VO$^{2+}$ | 71±9 | 33±3 | 1100±23 | 60±36 |
| Cu$^{2+}$ | 2040±20 | 850±13 | 9450±545 | 881±79 |
| Th$^{4+}$ | 60±5 | 31±1 | 210±10 | 50±1 |
| Hg$^{2+}$ | 12200±300 | 1400±51 | 11250±100 | 1900±140 |
| Ce$^{4+}$ | 20±1 | 15±1 | 53±3 | 15±1 |
| UO$^{2+}$ | 11±2 | 00±0 | 40±2 | 22±6 |
| Ho$^{3+}$ | 61±4 | 22±2 | 82±2 | 66±1 |
| Dy$^{3+}$ | 30±3 | 11±3 | 39±5 | 22±1 |
| Sm$^{3+}$ | 65±1 | 24±3 | 120±1 | 53±2 |
| Pr$^{3+}$ | 28±1 | 20±4 | 45±5 | 28±2 |
| Nd$^{3+}$ | 20±1 | 14±1 | 44±13 | 17±1 |

Table 6. Separations of metal ions achieved on tin(IV)-edta columns

| Sample No. | Separations achieved | Amount loaded µg | Total elution volume[a)] ($cm^3$) | % of metal ion eluted | Eluent used |
|---|---|---|---|---|---|
| 1 | $Ca^{2+}$ | 240 | 30 | 98 | 0.01 M $HNO_3$ |
| | $UO_2^{2+}$ | 2000 | 30 | 95 | 0.05 M $HNO_3$ |
| 2 | $Ba^{2+}$ | 520 | 30 | 96.1 | 0.01 M $HNO_3$ |
| | $UO_2^{2+}$ | 2000 | 30 | 95 | 0.05 M $HNO_3$ |
| 3 | $UO_2^{2+}$ | 2000 | 30 | 95 | 0.05 M $HNO_3$ |
| | $Cu^{2+}$ | 370 | 50 | 95.5 | 1.0 M $HClO_4$+0.1 M $NaClO_4$ |
| 4 | $Mg^{2+}$ | 134 | 40 | 95.5 | 0.01 M $HNO_3$ |
| | $UO_2^{2+}$ | 2000 | 30 | 95.5 | 0.05 M $HNO_3$ |
| 5 | $Ni^{2+}$ | 293 | 60 | 98.6 | 0.05 M $HClO_4$+0.1 M $NaClO_4$ |
| | $Pb^{2+}$ | 1035 | 50 | 96.2 | 0.5 M $HClO_4$+0.1 M $NaClO_4$ |
| 6 | $Mn^{2+}$ | 265 | 50 | 97 | 0.05 M $HClO_4$+0.1 M $NaClO_4$ |
| | $Pb^{2+}$ | 1035 | 50 | 96.4 | 0.5 M $HClO_4$+0.1 M $NaClO_4$ |
| 7 | $Mg^{2+}$ | 134 | 50 | 97 | 0.01 M $HNO_3$ |
| | $Pb^{2+}$ | 952 | 60 | 97 | 0.1 M $HNO_3$ |
| 8 | $Ca^{2+}$ | 240 | 40 | 95.8 | 0.01 M $HNO_3$ |
| | $Pb^{2+}$ | 952 | 60 | 96.1 | 0.1 M $HNO_3$ |
| 9 | $Zn^{2+}$ | 340 | 50 | 94.7 | 0.05 M $HClO_4$+0.1 M $NaClO_4$ |
| | $Pb^{2+}$ | 1035 | 50 | 97.2 | 0.5 M $HClO_4$+0.1 M $NaClO_4$ |
| 10 | $Cd^{2+}$ | 562 | 40 | 97.5 | 0.05 M $HClO_4$+0.1 M $NaClO_4$ |
| | $Pb^{2+}$ | 1035 | 50 | 96.6 | 0.5 M $HClO_4$+0.1 M $NaClO_4$ |
| 11 | $Ba^{2+}$ | 520 | 30 | 94.6 | 0.01 M $HNO_3$ |
| | $Pb^{2+}$ | 952 | 60 | 92.4 | 0.1 M $HNO_3$ |
| 12 | $Ba^{2+}$ | 520 | 30 | 98 | 0.01 M $HNO_3$ |
| | $Cu^{2+}$ | 330 | 50 | 100 | 1.0 M $HClO_4$+0.1 M $NaClO_4$ |
| 13 | $Ca^{2+}$ | 240 | 40 | 96.6 | 0.1 M $HNO_3$ |
| | $Cu^{2+}$ | 330 | 50 | 98.4 | 1.0 M $HClO_4$+0.1 M $NaClO_4$ |
| 14 | $Mg^{2+}$ | 134 | 50 | 97 | 0.01 M $HNO_3$ |
| | $Cu^{2+}$ | 330 | 50 | 99 | 1.0 M $HClO_4$+0.1 M $NaClO_4$ |
| 15 | $Co^{2+}$ | 280 | 50 | 92.8 | 0.05 M $HNO_3$ |
| | $Cu^{2+}$ | 330 | 50 | 99.6 | 1.0 M $HClO_4$+0.1 M $NaClO_4$ |
| 16 | $Zn^{2+}$ | 340 | 50 | 98.5 | 0.05 M $HClO_4$+0.1 M $NaClO_4$ |
| | $Cu^{2+}$ | 330 | 50 | 100 | 1.0 M $HClO_4$+0.1 M $NaClO_4$ |
| 17 | $Pb^{2+}$ | 950 | 60 | 94.6 | 0.1 M $HNO_3$ |
| | $Cu^{2+}$ | 330 | 50 | 96.4 | 1.0 M $HClO_4$+0.1 M $NaClO_4$ |
| 18 | $Cd^{2+}$ | 562 | 40 | 99.6 | 0.05 M $HClO_4$+0.1 M $NaClO_4$ |
| | $Cu^{2+}$ | 330 | 50 | 98.4 | 1.0 $HClO_4$+0.1 M $NaClO_4$ |
| 19 | $Ni^{2+}$ | 293 | 60 | 95.2 | 0.05 M $HClO_4$+0.1 M $NaClO_4$ |
| | $Cu^{2+}$ | 330 | 50 | 100 | 1.0 M $HClO_4$+0.1 M $NaClO_4$ |
| 20 | $Mn^{2+}$ | 265 | 50 | 94.3 | 0.05 M $HClO_4$+0.1 M $NaClO_4$ |
| | $Cu^{2+}$ | 330 | 50 | 95.4 | 1.0 M $HClO_4$+0.1 M $NaClO_4$ |

Cation mentioned first has been eluted first. a) Volume of eluent for total elution of metal ions.

drying temperatures on the ion exchange capacity, the material was dried at various temperatures in a muffle furnace for 1 h. The exchange capacities at various temperatures are given in Table 2.

## Discussion

It is apparent from Tables 1 and 2 that the mixing ratio of the reactants and conditions of reaction greatly affects the chemical stability and physical appearance of the product. It has been observed that when the precipitate is refluxed for several hours, the chemical stability of the product is significantly increased. The optimum pH for the precipitation of the material which can exhibit exchange properties has been found to be 2.5. However, if the precipitation is done below this pH value, the product obtained is

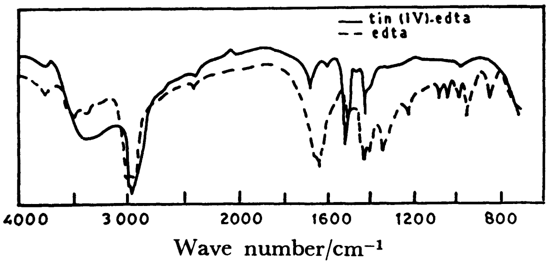

Fig. 2.

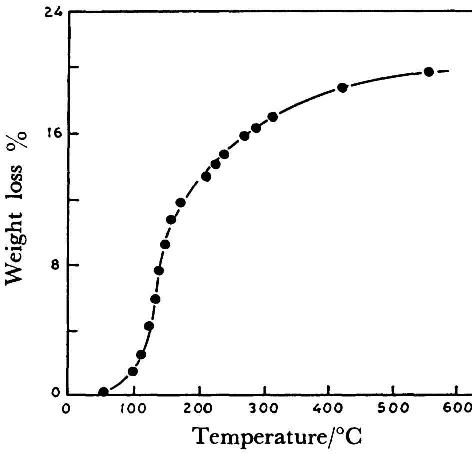

Fig. 3. Thermogram of tin(IV)-edta in $Mg^{2+}$ form.

unstable and therefore has not been studied in detail.

The ion exchange capacities of tin(IV)-edta sample 4 varies with different metal ions (Table 3). The maximum ion exchange capacity is recorded as 0.74 mequiv./g for $Ca^{2+}$ ion. The values of ion exchange capacity for alkali metals are almost constant and small as compare to the ion exchange capacities for alkaline earth metals. However, the ion exchange capacities for alkaline earths has been found to be in the order $Ca^{2+} \geqslant Mg^{2+} > Sr^{2+} > Ba^{2+}$. The peculiar feature which has been noticed regarding this material is that the ion exchange capacities for the univalent ions differ significantly from the ion exchange capacities for the bivalent ions. These data (Table 3) suggest the potentiality of the ion exchanger for the separation of almost all the alkali metals from alkaline earth series.

The pH-titration curves reveal some interesting features regarding the uptake of alkali metals which is affected by pH. The uptake of these metals below pH 6 is almost equal which is supported by ion exchange capacity data (Table 3). However, in the pH range 6 to 8.5 the uptake order is $K^+ > Li^+ > Na^+$. In the pH range 8.5 to 11.2, $Na^+$ ions are more strongly adsorbed than $Li^+$ ions and beyond pH 11.2 again the uptake of $Li^+$ ions becomes higher than $Na^+$ ions. The two inflection points in all the curves show the bifunctional behaviour of the ion exchanger.

The specificity of inorganic ion exchangers for metal ions is greatly dependent on the nature of the material. Thus tin(IV) antimonate[10)] and titanium(IV) antimonate[11)] are selective for alkaline earths while zirconium(IV) antimonate[12)] and tin(IV) selenite[13)] for alkali metals. Tin(IV)-edta is found to be selective for alkaline earth metals when compared to alkali metals as it is evident from ion exchange capacity data. $K_d$ values of some important metal ions on tin(IV)-edta in different solvent systems are given in Tables 4 and 5. The adsorption sequence for some metal ions in water is found to be $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$: $Pb^{2+} > Mn^{2+} > Fe^{3+} > Ni^{2+}$: $Sm^{3+} > Pr^{3+} > Ce^{4+}$. It is clear from Table 4 that $K_d$ values decreases gradually with the increase in nitric acid concentration as expected. A marked difference in $K_d$ values of metal ions has been observed in perchloric acid and sodium perchlorate system. $K_d$ values for bivalent ions in general, are found to be higher then ter and quadrivalent ions. The sequence of adsorption in 0.01 mol dm$^{-3}$ perchloric acid is found to be $Hg^{2+} > Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+} > Mn^{2+} > Co^{2+} > Al^{3+}$: $Sm^{3+} > Ho^{3+} > Dy^{3+} > Pr^{3+} > Ce^{4+} > UO_2{}^{2+}$. $K_d$ values reveal the possibility of numerous separations of metal ions. Some of the binary separations achieved on the columns of tin(IV)-edta are listed in Table 6.

The usual interferences which are encountered in the determination of Mg are Fe, Cu, Co, Ni, Zn, Pb, *etc*, and are frequently removed by precipitation with diethyldithiocarbamate.[14)] However, separation of Mg from these metal ions using this ion exchange material offers additional advantages being a simple and inexpensive method.

The X-ray analysis of sample 4 in $H^+$ form indicates amorphous nature of the material.

The infrared absorption spectrum of tin(IV)-edta in $H^+$ form when compared with infrared spectrum of disodium salt of EDTA, tin(IV) selenite and those explained by Sawyer and Paulsen[15)] yield the following interpretations.

IR spectrum of disodium salt of EDTA shows four important peaks. The different peaks at 1630 cm$^{-1}$, 1390 cm$^{-1}$, 1360 cm$^{-1}$ to 1310 cm$^{-1}$, and 1000 cm$^{-1}$ to 900 cm$^{-1}$ are due to –COO– groups. Infrared spectrum of tin(IV)-edta shows three strong peaks. A broad peak in the 3400—3000 cm$^{-1}$ region represents the interstitial water and OH groups. Another strong peak in the 1700—1500 cm$^{-1}$ region with a maximum at 1650 cm$^{-1}$ may be due to interstitial water molecules. The peaks appearing at 1380, 1500, and 3000 cm$^{-1}$ are also the standard peaks of nujol mull.

The thermogram of tin(IV)-edta sample 4 in $Mg^{2+}$ form (Fig. 3) shows that there is continuous loss in weight upto 170 °C which can be attributed to loss of water molecules. If temperature is raised further, decomposition of the material starts which continues upto 550 °C. This conclusion is also confirmed by the ion exchange capacity data (Table 2). The exchange capacity decreases gradually as the drying temperature is increased. The capacity of the exchanger however completely lost beyond 500 °C.

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