



Synthesis and Ion Exchange Characteristics of Cerium (IV) Phosphotungstate

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A new thermally stable three component inorganic ion exchanger cerium (IV) phosphotungstate have been synthesized and the sample with maximum ion exchange capacity and almost total regeneration has been chosen for further studies. The product has been characterized by IR and TGA studies. The chemical composition (Ce : P : W = 3 : 1 : 1), chemical stability, distribution coefficients for ten metal ions, change in its capacity with ionic radii, effect of temperature on ion exchange capacity and effect of electrolyte concentration on distribution coefficients of metal ions have been studied. The quantitative separations like $Pb^{2+} - Hg^{2+}$, $Pb^{2+} - Ni^{2+}$, $Pb^{2+} - Cd^{2+}$ and $Pb^{2+} - Zn^{2+}$ have been achieved on cerium (IV) phosphotungstate columns.

Key words: Cerium (IV) phosphotungstate, Inorganic ion exchanger, Distribution coefficient, Binary separations.

INTRODUCTION

The insoluble salts of heteropolyacids with polyvalent metals are preferred to other ion exchangers as they exhibit selective ion exchange behaviour. Qureshi *et al* have studied Vanadophosphate¹, Vanadotungstate² and Phosphotungstate³ of tin (IV). Studies on Ce (IV) Arsenite⁴ and Ce (IV) Vanadate⁵ were already reported. The Heteropolyacid exchangers based on cerium(IV) have not studied in detail. Phosphosilicate⁶ and phosphomolybdate⁷ of cerium (IV) are some of them. This paper summarises our findings on the synthesis and ion exchange behaviour of Cerium (IV) phospho-tungstate.

EXPERIMENTAL

Two samples of cerium (IV) phosphotungstate were prepared by mixing 0.1M cerium (IV) ammonium nitrate, 0.1M trisodium phosphate and 0.1M sodium tungstate solutions in different volume ratios. The pH was maintained at 1 with dilute H_2SO_4 . The shining yellow crystalline precipitate was kept for 24h and then filtered, washed and dried at room temperature. The dried sample was converted into H^+ form by keeping in 1.0M HCl for 24 h with thorough shaking and intermittent changing of acid. The product was washed, filtered and dried. The bright yellow beads obtained (100-120 mesh) were used for the

investigations. All the chemicals used are BDH chemicals. The 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 TGA7. The absorbance measurements for estimation of tungsten was done in an inductively coupled plasma spectrophotometer.

The composition of the exchanger was determined by dissolving 100mg of the sample in hot Conc. HCl. Cerium (IV) was estimated volumetrically⁸, phosphorous gravimetrically as $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ ⁸ and tungsten was quantitatively precipitated using cupron reagent and then incinerated to WO_3 ⁸ and weighed. The amount of tungsten was also confirmed by direct estimation done with inductively coupled plasma spectrophotometer at a wave length of 207.911nm.⁹

The Ion exchange capacity of the various samples were determined by column operation by eluting with 1.0M sodium chloride solution. The hydrogen ions eluted from the column were determined titrimetrically with standard NaOH. The exchanger could be regenerated three times without appreciable loss of ion exchange capacity. The sample having higher exchange capacity (0.60) is used for further studies.

The effect of temperature on ion exchange capacity was studied by heating samples of materials to various temperatures for 1 hour and ion exchange capacity of the samples were determined after cooling them at room temperature. The effect of electrolyte concentration on i.e.c was studied by determining i.e.c. in presence of electrolytes HNO_3 , NH_4NO_3 in different concentrations.

The distribution coefficients for 10 metal ions were found out by a batch process¹⁰. The exchanger (100mg) was equilibrated with 20ml of 0.005 M metal ion solution for 6h. Each solution was then analysed for metal ion by complexometric titration. The Kd values of the metal ion were calculated using the equation.

$$K_d = \left(\frac{I-F}{F} \right) \frac{V}{m} \text{ where I and F are the initial}$$

and final volumes of EDTA respectively. V is the volume of the metal ion solution and M is the mass of the exchanger taken. The Kd values are given in table 2. Separations of metal ions were carried out on a cerium (IV) phosphotungstate (60-100 BSS mesh) column (5-6x0.5cm i.d.).

Binary separations of synthetic mixtures was performed using column method. The column was having 0.5 cm diameter and was prepared with 5 g of the exchanger. At first, the column washed with DMW and mixture to be separated loaded on the column and metal ions to be separated eluted at a flow rate of 2-3 drops per minute using electrolyte eluents. The metal ions separated were determined quantitatively by EDTA titrations.

RESULTS AND DISCUSSION

The cerium (IV) phosphotungstate sample having maximum ion exchange capacity (0.6 meq/g) was prepared in bulk for investigations. The colour of the exchanger was bright yellow. The exchanger is stable in water, ethanol, acetic acid and in 2.0 M solutions of HCl, HNO_3 and H_2SO_4 and salt solutions. The chemical composition of cerium (IV) phosphotungstate was determined and found to be 1:1:1 (Ce: P:W) with a variation of ± 0.01 % for successive determinations.

The thermoanalytical investigations help us to calculate empirical formula and theoretical exchange capacity of the sample. TGA of the sample showed sharp change at $\sim 110^\circ\text{C}$ due to loss of external water molecules. From the mass loss upto 110°C , the water lost per formula mass of the exchanger can be calculated by the method of

Table 1: Effect of size and charge of exchanging ion on exchange capacity

Exchanging ion	Ionic radiiA°	Exchange capacity meq/g
Li (I)	3.40	0.50
Na(I)	2.76	0.60
K(I)	2.32	0.67
Mg(II)	7.00	0.56
Sr(II)	6.10	0.78
Ba(II)	5.90	0.82

Table 2: Distribution coefficients of some metal ions on cerium (IV) phosphotungstate

Cation	Taken as	Kd (ml/g)
Cd ²⁺	Chloride	25.58
Pb ²⁺	Nitrate	121.60
Zn ²⁺	Sulphate	31.46
Ni ²⁺	Sulphate	24.86
Mg ²⁺	Sulphate	26.89
Co ²⁺	Sulphate	39.59
Cu ²⁺	Sulphate	65.75
Hg ²⁺	Chloride	10.81
Sn ²⁺	Chloride	Precipitated
Bi ³⁺	Nitrate	5.85
Th ⁴⁺	Nitrate	42.03

Alberti *et al.*¹¹ The mass loss is 12%. So $1800n/818+18n = 12$ and $n = 6$. The empirical formula can be written as $3CeO_2 \cdot \frac{1}{2} P_2O_5 \cdot WO_3 \cdot 6H_2O$. The ion exchange capacity calculated on the basis of one proton per formula weight is $1000/926 = 1.073$. The experimental value is 0.6. The slight departure from theoretical value may be due to partial hydrolysis of the salt.

IR spectrum showed a broad peak at 3500 cm^{-1} and 1686 cm^{-1} .¹² This shows the presence of water of crystallization. Peaks at 812 cm^{-1} , 708 cm^{-1} , 619 cm^{-1} etc show the M – O stretching vibrations. The broad peak at 1070.6 cm^{-1} shows the presence of W=O bond. The ion exchanger is stable upto 900°C .

Table 3: Binary separations on cerium (IV) phosphotungstate

Mixtures with eluents	Amount loaded (mg)	Amount recovered (mg)	Efficiency
Hg ²⁺ [0.1M HNO ₃ + 0.1 M NH ₄ NO ₃]	4.53	4.34	95.81
Pb ²⁺ [1.0M HNO ₃ + 1.0 M NH ₄ NO ₃]	4.78	4.58	95.81
Ni ²⁺ [0.1M HNO ₃ + 0.1 M NH ₄ NO ₃]	1.52	1.46	96.05
Pb ²⁺ [1.0M HNO ₃ + 1.0 M NH ₄ NO ₃]	4.88	4.58	93.85
Cd ²⁺ [0.1M HNO ₃ + 0.1 M NH ₄ NO ₃]	2.64	2.54	96.21
Pb ²⁺ [1.0M HNO ₃ + 1.0M NH ₄ NO ₃]	4.88	4.68	95.90
Zn ²⁺ [0.1M HNO ₃ + 0.1 M NH ₄ NO ₃]	1.56	1.27	81.41
Pb ²⁺ [2.0M HNO ₃ + 2.0 M NH ₄ NO ₃]	5.07	5.07	100

The effect of size and charge of the ingoing ion on the capacity of the exchanger was studied. For alkali and alkaline earth metal ions the sequence shown by cerium (IV) phosphotungstate is $K(I) > Na(I) > Li(I)$ and $Mg(II) < Sr(II) < Ba(II)$. The ion exchange capacity increases with decrease in hydrated ionic radii as given in table 1.

The value of ion exchange capacity decreased on heating the compound at higher temperatures. The results indicate that cerium (IV) phosphotungstate retains very little ion exchange capacity (0.06 meq/g) on heating to 200°C . Almost a straight line graph is obtained (Fig. 1).

The distribution studies with II metal ions (table 2) revealed that cerium (IV) phosphotungstate shows high affinity for Pb²⁺, Cu²⁺ and Co²⁺ and least affinity for Hg²⁺, Ni²⁺ and Zn²⁺.

Results of the studies on the effect of solvent (HNO₃, NH₄NO₃) concentrations on the distribution coefficients of some metal ions show that the uptake of ions such as Pb²⁺, Cu²⁺ and Co²⁺ decreases with increase of solvent concentrations due to the competition of cations of the solvent with metal ions.

Results of some important binary separations carried out for the separation of

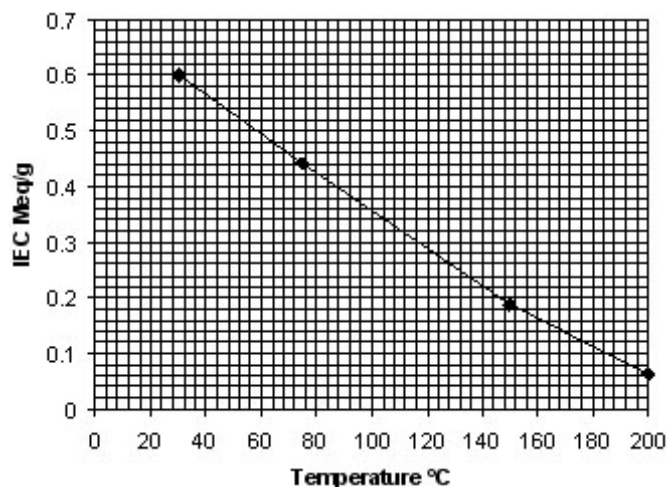


Fig. 1: Effect of temperature on ion exchange capacity of Cerium (IV) phosphotungstate

Pb²⁺ from Hg²⁺, Ni²⁺, Cd²⁺ and Zn²⁺ are given in Table 3. The recovery ranged from 96 to 100 % with the variation of 2% for repetitive determinations

²⁺, Pb²⁺– Cd²⁺ and Pb²⁺– Zn²⁺

CONCLUSION

The studies on the ion exchange properties of cerium (IV) phosphotungstate have shown that this exchanger is suitable for binary separations of metal ions as Pb²⁺– Hg²⁺, Pb²⁺– Ni

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