

Studies on Ceric Tungstate Ion Exchanger

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Synthesis and some interesting ion exchange properties of ceric tungstate are reported. The material, suitable for column operation, was used for the separations of several analytically binary mixtures of cations.

INTRODUCTION

The use of inorganic ion exchanging materials formed by the combination of polybasic acid with multivalent metals have been reviewed extensively in a recent literature¹. Among them zirconium phosphate is the most widely studied one. In our earlier work² we have reported some important ion exchange behaviour of a similar class of compounds *e.g.*, zirconium tungstate and as a continuation of this work with insoluble tungstates, we have described here the synthesis and ion exchange properties of amorphous ceric tungstate. Only a little attention³ has been paid for this material.

EXPERIMENTAL

Ceric sulphate (E Merck) and sodium tungstate (Loba GR) were used without further purification. All other chemicals used were of AR grade. A digital pH meter (Sambros 335 type) was used for pH measurements. Spectrophotometric measurements were carried out using a double beam spectrophotometer (Shimadzu, UV-190). Shimadzu atomic absorption spectrometer (Model 646) with MUV-1 was used for the determination of Hg^{2+} . IR spectrum of ceric tungstate (1A) was recorded by IR spectrophotometer (Shimadzu-IR-408) using standard KBr disc technique.

Preparation of Ceric Tungstate

Samples of ceric tungstate were prepared by mixing hot solution of ceric sulphate in 2N H_2SO_4 with sodium tungstate under different conditions (Table 1). The precipitate so appeared was allowed to settle overnight and then washed with distilled water several times by the method of decantation until the pH of the washing was around 5.0. Finally the yellow product was filtered and dried at room temperature over silica gel. The colour of two products (1A, 3A) gradually changed from yellow to orange during the drying period; these are hard, granular and suitable for column operation. The other two products (2B, 4B) remained yellow even after drying and became soft powder, not suitable for column operation.

TABLE 1
CONDITION OF SYNTHESIS OF CERIC TUNGSTATE

Sample No.	Concentration of starting material (M)		Mixing ratio v/v	Ion exchange capacity for Na ⁺ /meq/gm				Ratio of Ce : W in the product
	*CS	*SW		40°C	Colour	80°C	Colour	
1A	0.10	0.10	1 : 1	0.2	Orange	0.3	Orange	1 : 1
2B	0.10	0.10	1 : 1	0.35	Yellow	0.5	Yellow	1 : 1.9
3A	0.10	0.10	1 : 2	0.2	Orange	0.3	Orange	1 : 1
4B	0.10	0.10	1 : 2	0.28	Yellow	0.4	Yellow	1 : 1.7

*CS = ceric sulphate and *SW = sodium tungstate
A = CS added to SW and B = SW added to CS

The products were analysed by the usual way⁴ and results are reported in Table 1. The samples 1A and 3A were found to have identical compositions.

Thermal Stability

The exchanger (1A) was heated at various temperatures for 1 hr upto 160°C. The colour of the sample did not change during the course of heating. The effects of heating at different temperatures are reported in Table 2.

TABLE 2
EFFECT OF HEAT TREATMENT ON CERIC TUNGSTATE (Sample No. 1A)

Temperature (°C)	% of weight loss	Colour of exchanger	Ion exchange capacity for Na ⁺ /meq/gm
40	0.56	Orange	0.20
80	9.20	Orange	0.30
120	12.8	Orange	0.30
160	15.6	Orange	0.30

Chemical Stability

The orange material (Sample No. 1A) so prepared was found to be chemically stable against all mineral acids upto 2M concentration, concentrated alkali (> 4M) could attack the exchanger, otherwise it was quite stable. The solid was stable in solution of LiCl, NaCl, KCl, MgCl₂, CaCl₂, BaCl₂ etc. and also in alcohol or benzene.

pH Titration

For the amorphous ceric tungstate (1A) pH titration was performed with varying amounts of MOH (M = Li, Na, K) by a method reported earlier⁵ (Fig. 1). The experiment was repeated in presence of a mixture of sodium hydroxide and sodium chloride, the total concentration of sodium ion being kept at 0.1 M (Fig. 2).

Ion Exchange Capacity

Ceric tungstate is a cation exchanger, the capacity of the exchanger was determined by equilibrating 0.5 gm of ceric tungstate (1A) with 50 ml 2M NaCl solution for 16 hrs and the optimum time of equilibration was determined in a preliminary experiment. The liberated acid was titrated with standard sodium hydroxide solution.

$$\text{Capacity} = \frac{\text{Titre of alkali} \times \text{strength of alkali}}{\text{Weight of exchanger}}$$

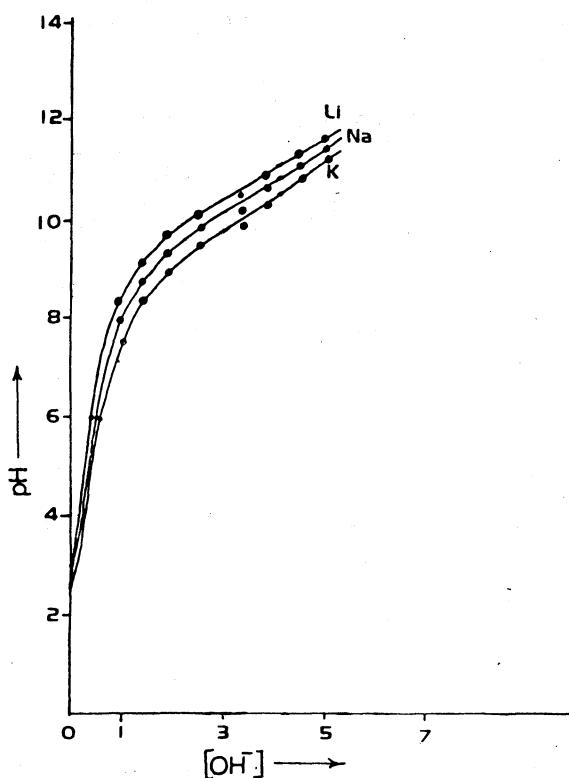


Fig. 1. pH titration curve for Ceric tungstate (Titrants: KOH, NaOH, LiOH)

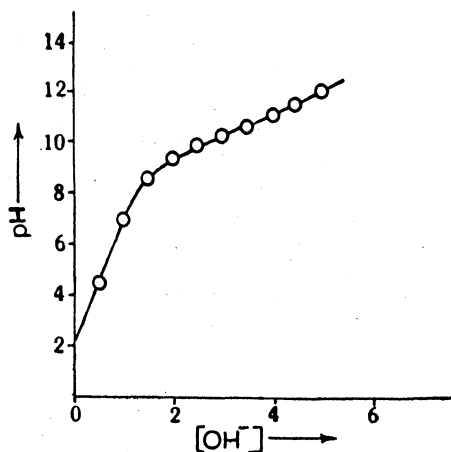


Fig. 2. pH titration curve for Ceric tungstate with NaCl-NaOH.

Similar values for several other cations were determined (Table 3).

TABLE 3
ION EXCHANGE CAPACITY

Metal ion	Hydrated radius (Å ^o)	Ion exchange capacity meq/gm	
		40°C	80°C
Li ⁺	3.4	0.13	0.2
Na ⁺	2.76	0.20	0.3
K ⁺	2.32	0.25	0.4
Mg ²⁺	7.0	0.15	0.22
Ca ²⁺	6.30	0.22	0.32
Ba ²⁺	5.90	0.28	0.40

Distribution Coefficients

In order to examine the affinity of ceric tungstate toward various metal ions, distribution coefficients were determined (Table 4) at pH 2-3 and pH 5-6 by equilibrating 0.5 gm of the exchanger with 50 ml solution of the cations for 16 hrs at room temperature with intermittent shaking.

The ferric ions were determined spectrophotometrically⁴ and mercury by atomic absorption spectroscopy⁶. All other cations were determined by titration with standard EDTA solutions⁷⁻⁹.

TABLE 4
DISTRIBUTION COEFFICIENTS OF METAL
IONS ON CERIC TUNGSTATE AT $30 \pm 2^\circ\text{C}$

Metal ion	Taken as	Kd (ml/g)	
		pH 2	pH 5-6
Mg ²⁺	Sulphate	0	6
Ca ²⁺	Chloride	5	16
Sr ²⁺	Nitrate	7	36
Ba ²⁺	Chloride	25	50
Cu ²⁺	Sulphate	3	14
Zn ²⁺	Sulphate	0	7
Ni ²⁺	Chloride	0	2
Co ²⁺	Sulphate	0	6
Mn ²⁺	Sulphate	2	11
Cd ²⁺	Sulphate	0	4
Hg ²⁺	Chloride	0	3
Pb ³⁺	Nitrate	100	450
Fe ³⁺	Chloride	50	—
Al ³⁺	Chloride	0	—
Bi ³⁺	Chloride	T.A.*	—
La ³⁺	Nitrate	15	21

*T.A. = Total adsorption

Quantitative Separation on Ceric Tungstate

For separation studies (Table 5) glass columns (ID = 1.5 cm) containing 5 gm of ion exchanger (50-100 mesh) in the hydrogen form were used. The rate of flow was kept constant throughout the elution process.

RESULTS AND DISCUSSION

Table 1 shows the condition of synthesis of ceric tungstate. We have concentrated our studies on sample No. 1A because this sample is hard, granular and suitable for use in the column operation. The loss of weight during heating the sample at different temperatures (Table 2) may be attributed to the loss of water molecules. The compound is thermally stable. IR spectrum reveals the similar characteristic features of thorium tungstate¹⁰. The band between 3000 and 3500 cm⁻¹ with a maximum at 3400 cm⁻¹ appears to be characteristic of interstitial water molecules and OH groups, the band between 1500 and 1700 cm⁻¹ with a maximum at

1620 cm^{-1} may be attributed to deformation vibration of interstitial water. The band between 700 and 900 cm^{-1} showing a maximum at 850 cm^{-1} is due to W-O and that at 550 cm^{-1} is due to Ce-O.

TABLE 5
QUANTITATIVE SEPARATIONS OF METAL IONS ON CERIC
TUNGSTATE COLUMNS

No.	Separation achieved	Exchanger/g	Metal ions taken/ μg	Eluent
1.	Pb^{2+} —(Hg^{2+} , Cu^{2+})	5	Hg^{2+} (2106.3) Cu^{2+} (1239) Pb^{2+} (2776.6)	Hg^{2+} ; 0.01(M) HNO_3 , Cu^{2+} ; 0.01(M) HNO_3 , Pb^{2+} ; 0.02(M) HNO_3 ,
2.	Bi^{3+} —(Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+})	5	Cu^{2+} (1239) Zn^{2+} (779) Cd^{2+} (1236.4) Hg^{2+} (2106.3) Bi^{3+} (1964.3)	Cu^{2+} ; 0.01(M) HNO_3 , Zn^{2+} ; 0.01(M) HNO_3 , Cd^{2+} ; 0.01(M) HNO_3 , Hg^{2+} ; 0.01(M) HNO_3 , Bi^{3+} ; 2(M) HNO_3 ,
3.	Fe^{3+} —(Ca^{2+} , Sr^{2+} , Ba^{2+} , La^{3+})	5	Ca^{2+} (352.7) Sr^{2+} (1121.8) Ba^{2+} (1648.3) La^{3+} (1583.7) Fe^{3+} (446.8)	Ca^{2+} ; 0.1(M) NH_4Cl + 0.01(M) HCl Sr^{2+} ; 0.1(M) NH_4Cl + 0.01(M) HCl Ba^{2+} ; 1(M) NH_4Cl + 0.01(M) HCl La^{3+} ; 1(M) NH_4Cl + 0.01(M) HCl Fe^{3+} ; 1(M) HCl

Ion exchange capacity (Table 3) shows sequence of adsorption $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ and $\text{Ba}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$. This is due to the increase in hydrated radii from K^+ to Li^+ and Ba^{2+} to Mg^{2+} . The pH titration (Fig. 1) also confirmed the same adsorption sequence, $\text{K}^+ > \text{Na}^+ > \text{Li}^+$. pH-Titration curves (Fig. 2) also reveal the monofunctional behaviour of ceric tungstate.

The results of distribution co-efficient (Table 4) data indicate high selectivity for few cations like Fe^{3+} , Pb^{2+} , Bi^{3+} and low affinities for others so that the separation of several analytically important binary mixtures of cations could be achieved even at low pH. Quantitative separation of these systems, e.g., Pb(II) from Hg(II) and Cu(II) , Bi(III) from Cu(II) , Zn(II) , Cd(II) and Hg(II) , and Fe(III) from Ca(II) , Sr(II) , Ba(II) and La(III) establishes it as a potential ion exchanging system even at moderately acid medium, the condition which is particularly necessary for Fe^{3+} or Bi^{3+} to prevent their hydrolysis. Studies of some other aspects of ion exchange behaviour of ceric tungstate are in progress.

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