

Synthesis and Characterization Of Bismuth (Iii) Iodotungstate, an Exchanger

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Abstract: A number of samples of Bismuth(III) iodotungstate were prepared by mixing the solutions of Bismuth nitrate, Potassium iodate and Sodium tungstate in varying ratios. One of the samples was selected for study because the ion exchange capacity and the yield of the exchanger was found to be satisfactory. The characterization of the exchanger included the determination of the ion exchange capacity of the exchanger by downflow column method and P^H titration method. Both the methods exhibited the ion exchange capacity to be 1.0 meq/g. Further studies included the study of IR, TGA, XRD and Distribution studies. IR of the exchanger indicated the presence of the expected components of the exchanger. Thermal gravimetric analysis has clearly shown the loss of weight of exchanger due to the loss of water molecules & other components at different temperatures. X-Ray diffraction pattern proved the exchanger to be amorphous in nature. Chemical stability of the exchanger was studied in different acid and base solutions of different concentrations. The exchanger was heated at different temperatures and after every heating the ion exchange capacity of the exchanger was determined. This shows the decline in the ion exchange capacity on increasing the temperature. Kd values for different metals ion were determined and found the maximum value for Ni^{++} . Where as minimum value was found to be for Zn^{++} . The results appeared to be satisfactory.

Keywords: Inorganic cation-exchanger, Ion-exchange capacity, Chemical stability, Thermal stability, Distribution studies.

I. Introduction

An ion-exchange reaction may be defined as the reversible interchange of ions between a solid phase (the ion exchanger) and a solution phase. The ion exchanger is usually insoluble in the medium in which the exchange is carried out.¹ In recent years, synthetic inorganic ion exchange have drawn the attention of analytical chemists due to their extraordinary thermal stability and chemical stability.² Inorganic ion exchangers have established³⁻⁵ their place in analytical chemistry due to their differential selectivity for metal ions. Synthetic inorganic ion exchangers have growing interest in the field of separation science.⁶⁻⁷ A long number of studies have been made for their preparation, properties and application to simple binary and ternary separation of metal ions. Every synthetic inorganic ion exchanger has specific selectivity towards one or two metallic species.

They are also highly stable to a wide range of pH. However, their real analytical application in various fields are still lacking.⁸ Inorganic ion exchangers have been found more successfully than adsorbents for the removal and recovery of toxic metal ions from dilute aqueous solutions due to their specific selectivity⁹. In the present work a new inorganic ion exchanger Bismuth(III) iodotungstate is synthesized by mixing the solutions of bismuth nitrate, potassium iodate and sodium tungstate in 1:2:2 ratio respectively. The synthesized exchanger is found to possess 1.0 meq/g ion exchange capacity. The stability of the exchanger against temperature & different chemical solutions of different strength is studied. The exchanger is found to be selective for Ni^{2+} and Zn^{2+} as per distribution studies done.

II. Experimental

Reagents & Chemicals: - Bismuth nitrate, Potassium iodate and Sodium tungstate (all CDH of AR grade) were used. All other reagents used were also of analytical or chemically pure grade.

Instrumentation :- Toshniwal Research pH meter model pH 110, Oven NSW (INDIA) (model - I 43) Rotary Shaker Tanco, Muffl Furnace (Digital temp controller) Shivaki T-701 and Magnetic stirrer with hotplate, Samson Electronic weighing balance (Model - 300 D) were used in the research laboratory, chemistry department, Meerut College Meerut. TGA, XRD and IR were obtained from IIT, Roorkee where Perkin Elmer (Pyris Diamond) in alumina pan with a current of nitrogen Thermo Nicolet for TGA, Thermo Nicolet IR-spectrophotometer for IR and Philips Analytical X-ray B.V. diffractometer for XRD were available.

Synthesis

Six samples of Bismuth(iii) iodotungstate were synthesized by mixing 0.1 M bismuth nitrate solution gradually to a mixture of 0.1 M potassium iodate and 0.1 M sodium tungstate solutions with continuous stirring

in various mixing volume ratios (Table 1). The pH was adjusted to 1 of all the six solutions. The six gelatinous precipitates so obtained were allowed to settle down for 24 hrs at room temperature. The supernatant liquid was removed and the precipitates were washed with distilled water and filtered. The precipitate was dried at $40 \pm 1^\circ\text{C}$ in an electric oven. The materials were broken down in to small granules by placing them in distilled water just after removing them from the oven. The materials were than converted to H^+ form by treating them with 1.0 M HNO_3 for 24 hrs with occasional shaking and intermittently changing the acid. All the six samples of Bismuth(iii) iodotungstate so obtained were separated from the acid solution and washed with distilled water and finally dried in oven.

Determination Of Ion Exchange Capacity

Ion-exchange capacity (IEC) of all the six samples were determined by column method (Table 1). On the basis of IEC sample No. 2 was selected for detailed study and therefore was synthesized in bulk by the procedure as adopted earlier. p^{H} titration method was also followed for the determination of IEC of the exchanger synthesized in bulk.

Column Operation :- The ion-exchange capacity of the selected sample was also determined for different metal ions by column operation method using 0.50g of the exchanger maintaining the flow 0.1 ml min^{-1} of the different metal salt solutions The hydrogen ions eluted were determined titrimetrically with standard sodium hydroxide solution. The results are summarized in Table 1.

p^{H} Titration :- p^{H} titration using the exchanger was performed by batch process. Equal portions (0.50 gm each) of the exchanger were equilibrated with different volume mixtures of 0.1 M NaCl and 0.1 M NaOH solutions. The graph was plotted between pH and OH^- ion concentration (Fig1).

Thermal Studies

In thermal stability determination several portions (0.50g each) of the exchanger were heated at various temperatures in muffle furnace for 1 hr and their ion exchange capacity was determined by the column method after cooling them to room temperature. The results are summarized in Table 3. The graph was plotted between temperature and I.E.C. (Fig 2). TGA of the exchanger shows the loss of water molecules and other components at different temperatures. Finally the weight of the material becomes constant (Fig- 3)

Chemical Stability

Equal amounts (250 mg each) of the exchanger were kept in 25 ml of the various mineral acid solutions, base solutions and salt solutions of different concentration for 24 hrs with intermittent shaking. The results are summarized in Table 4.

Distribution Studies

Distribution studies were carried out for several metal ions by using batch method¹⁰. Seven equal portions (200 mg each) of the exchanger in H^+ form were equilibrated with 20 ml solutions of different metal ions in aqueous medium. The mixture was shaken for 6 hrs continuously and then kept for 24 hrs to maintain the equilibrium. After 24 hrs the amount of the metal ions left in the solution were determined by titrating against 0.01 M EDTA solution¹¹ using appropriate indicators. The distribution coefficient (kd) for different metal ions were calculated (Table 5). Kd values were calculated using the following expression:

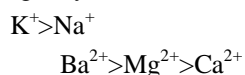
$$\text{Kd} = \frac{I - F}{f} \times \frac{V}{w} \text{ (m/g)}$$

Where

I	=	Initial amount of the ion in the solution phase.
F	=	Final amount of the ion in the Solution phase.
V	=	Volume of the solution (ml).
W	=	Weight of the ion exchanger (g).

III. Results And Discussion

Bismuth(iii) iodotungstate is obtained in a white amorphous form. The maximum ion exchange capacity for Na^+ ion is found to be 1.0 meq/g. The sequence of ion-exchange capacity for the alkali and alkaline earth metal ions as shown by the ion exchanger by column method is as follows (Table 2).

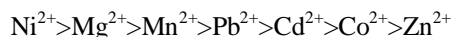


Ion exchange capacity for sodium ions is found to be 1.0 meq/g by p^H titration method too (Fig -1)

The study including the effect of temperature on ion exchange capacity of Bismuth(iii) iodotungstate shows that the ion-exchange capacity decreases with increase in temperature. The exchanger retains a small ion exchange capacity (0.17 meq/g) even at 500⁰c (Table -3 & fig - 2).

The exchanger is found to be stable in water, 0.05 M H₂SO₄, 0.05 M HCl and 0.05 M HNO₃ solutions. It is found partly soluble in H₂SO₄ (0.1M, 0.2M, 1.0M, 2.0M) solutions. It is also found partly soluble in HNO₃ (0.1M, 0.2M, 1.0M, 2M), HCl (0.1M, 0.2M, 1.0M, 2.0M), NaNO₃ (0.2M, 1.0 M, 2.0M), NaOH (0.1M, 0.2M, 1.0M) and KOH (0.2M, 1.0M) solutions. The exchanger become completely soluble in 2 M KOH and 2 M NaOH solutions.

The distribution studies of the exchanger for seven metal ions shows ion-exchange affinity for the ion in the following order (Table 5):



TGA Curve of the exchanger shows that the weight becomes constant at 802⁰C Sharp change in the curve observed at about 400⁰C shows the rapid loss of the components of the exchanger. Above 100⁰C the loss of water is well evident from the curve (Fig-3).

Amorphous form of the exchanger is shown by the X-ray diffraction pattern as no sharp peaks are observed (Fig-4).

The FTIR spectrum of Bismuth(iii) iodotungstate is given in fig-5. The spectrum can be explained on the basis of infrared data. The peak at 1616.65 cm⁻¹ is associated with metal-oxygen band. The band at 3433.97 cm⁻¹ indicates the presence of water molecules. The band at 711.66 cm⁻¹ shows the iodate component. The peak at 935.30 cm⁻¹ shows the presence of tungstate group.

IV. Conclusion

The present study clearly indicates that the synthesized exchanger can be used successfully in acid solutions of 0.05 M strength. The study also shows the selectivity of the exchanger towards nickel ions.

Further study of the exchanger may include the application of the exchanger in removing the nickel ions from the different mixtures.

Acknowledgement

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TABLE – 1

SYNTHESIS OF BISMUTH(III) IODOTUNGSTATE

Sample No.	Molar Conc.			Mixing Ratio			pH of the mixture	Appearance of the precipitate	Appearance of beads after drying at 40±1 ⁰ C	I.E.C. for Na ⁺ (meq gm ⁻¹)
	B	I	T	B	I	T				
1	0.1M	0.1M	0.1M	1	1	1	1	White	White	0.56
2	0.1M	0.1M	0.1M	1	2	2	1	White	White	1.2
3	0.1M	0.1M	0.1M	2	1	1	1	White	White	0.28
4	0.1M	0.1M	0.1M	2	2	1	1	White	White	0.48
5	0.1M	0.1M	0.1M	3	1	1	1	White	White	0.34
6	0.1M	0.1M	0.1M	3	2	2	1	White	White	0.6

B – Bismuth Nitrate Solution
 I – Potassium Iodate Solution
 T – Sodium Tungstate Solution

TABLE – 2

I.E.C. of Some Monovalent and Bivalent Cations

Sl.No.	Cation	I.E.C. (meq gm ⁻¹)
1	Na ⁺	0.76
2	K ⁺	0.78
3	Mg ⁺⁺	0.88
4	Ca ⁺⁺	0.58
5	Ba ⁺⁺	0.98

Alkali earth metal ions – K⁺ > Na⁺

Alkaline earth metal ions – Ba⁺⁺ > Mg⁺⁺ > Ca⁺⁺

**TABLE – 3
THERMAL STABILITY**

Sl.No.	Temperature (°C)	wt. before heating (g)	wt. after heating (g)	Loss in wt. (g)	Colour after heating	I.E.C. (meq gm ⁻¹) after heating
1	50 ⁰ C	0.50	0.50	-	White	0.91
2	100 ⁰ C	0.50	0.49	0.01	White	0.81
3	150 ⁰ C	0.50	0.47	0.03	White	0.80
4	200 ⁰ C	0.50	0.46	0.04	White	0.78
5	250 ⁰ C	0.50	0.46	0.04	White	0.72
6	300 ⁰ C	0.50	0.46	0.04	Light Pink	0.57
7	350 ⁰ C	0.50	0.46	0.04	Light Pink	0.43
8	400 ⁰ C	0.50	0.37	0.13	Pinkesh Yellow	0.41
9	450 ⁰ C	0.50	0.36	0.14	Light Yellow	0.25
10	500 ⁰ C	0.50	0.35	0.15	Dark Yellow	0.17

**TABLE – 4
CHEMICAL STABILITY**

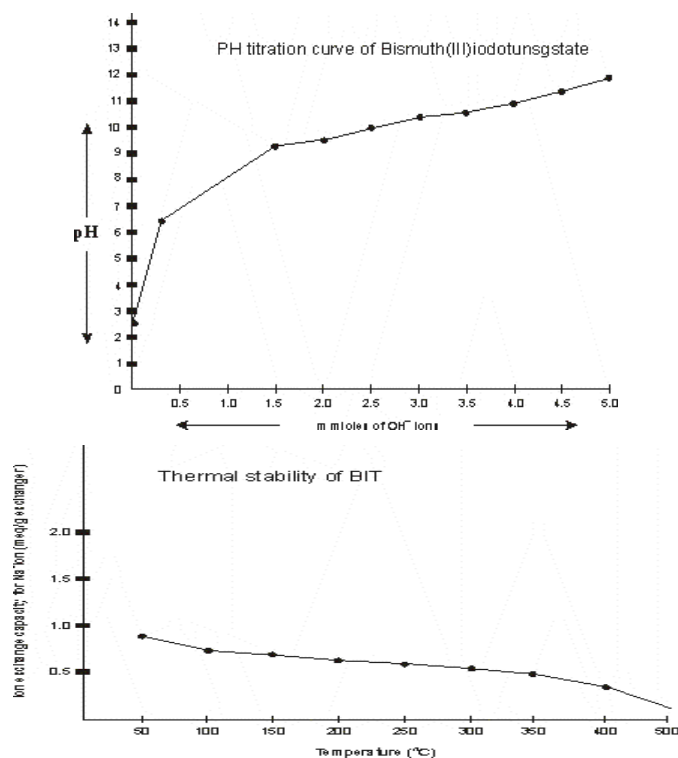
Sl.No.	Solution	Effect of Solution on BIT				W ₁ = weight of IE before treating with solution W ₂ = weight of IE after treating with solution NE = No Effect PD = Partly dissolved CD = Completely dissolved BIT – Bismuth(III) iodotungstate
		W ₁	W ₂	Inference	Colour	
1	0.05 M H ₂ SO ₄	0.25	0.25	NE	White	
2	0.1 M H ₂ SO ₄	0.25	0.20	PD	White	
3	1M H ₂ SO ₄	0.25	0.19	PD	White	
4	0.2 M H ₂ SO ₄	0.25	0.19	PD	White	
5	2 M H ₂ SO ₄	0.25	0.10	PD	White	
6	0.05 M HNO ₃	0.25	0.25	NE	White	
7	0.1 M HNO ₃	0.25	0.20	PD	White	
8	1 M HNO ₃	0.25	0.18	PD	White	
9	0.2 M HNO ₃	0.25	0.19	PD	White	
10	2 M HNO ₃	0.25	0.10	PD	White	
11	0.05 M HCl	0.25	0.25	NE	White	
12	0.1 M HCl	0.25	0.19	PD	White	
13	1 M HCl	0.25	0.08	PD	Yellow	

14	0.2 M HCl	0.25	0.13	PD	Yellow
15	2M HCl	0.25	0.10	PD	Yellow
16	1 M KOH	0.25	0.09	PD	Yellow
17	0.2 M KOH	0.25	0.06	PD	White
18	2 M KOH	0.25	CD	CD	Yellow
19	0.1 M NaOH	0.25	0.06	PD	White
20	1 M NaOH	0.25	0.08	PD	Yellow
21	0.2 M NaOH	0.25	0.08	PD	White
22	2 M NaOH	0.25	CD	CD	Yellow
23	1 M NaNO ₃	0.25	0.17	PD	Light Yellow
24	0.2 M NaNO ₃	0.25	0.18	PD	White
25	2 M NaNO ₃	0.25	0.19	PD	White

TABLE – 5
DISTRIBUTION STUDIES

Sl.No.	Cation	Takes as	Kd (ml/g)
1	Zn ²⁺	Sulphate	12.73
2	Mg ²⁺	Chloride	57.78
3	Pb ²⁺	Nitrate	40.74
4	Cd ²⁺	Nitrate	39.39
5	Co ²⁺	Sulphate	34.84
6	Mn ²⁺	Sulphate	75
7	Ni ²⁺	Sulphate	111.25

Fig-1



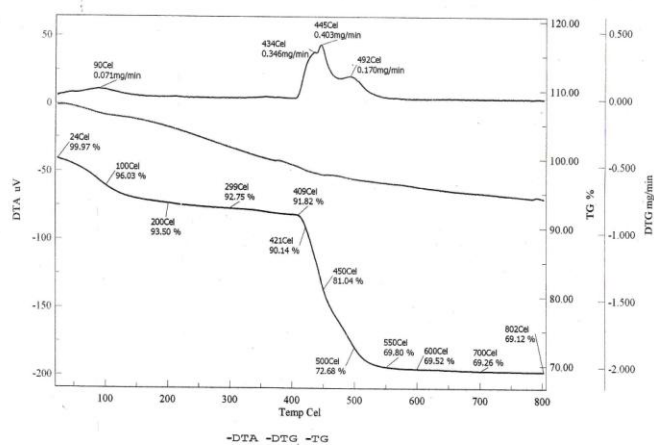
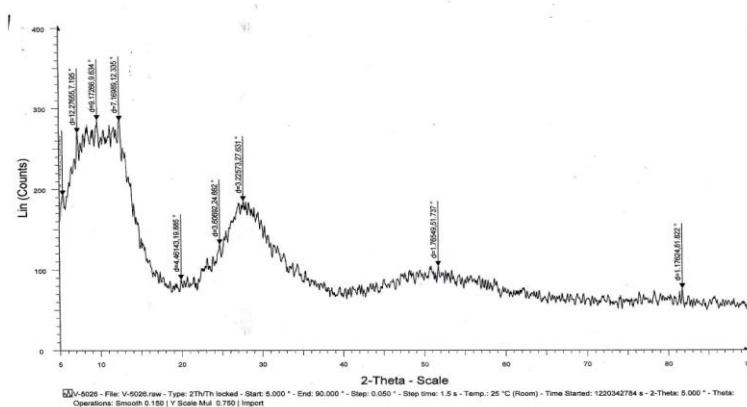


Fig. 3-TGA curve of Bismuth(iii) iodotungstate.



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