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SYNTHESIS, CHARACTERIZATION AND ION EXCHANGE PROPERTIES OF A NEW ION EXCHANGE MATERIAL: BISMUTH (III) IODOPHOSPHATE

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Abstract

Eight samples of the three component cation exchanger [Bismuth(III)iodophosphate] has been synthesized by mixing different ratio of 0.1M bismuth nitrate, 0.1M potassium iodate, 0.1M orthophosphoric acid at pH between 0-1. The material shows ion exchange capacity for Na⁺ ion of 0.5meq/g. It has been characterized using I.R., X-ray, TGA studies. A number of ion exchange studies like pH titration, chemical stability, thermal stability and distribution behaviour were studied. Ion exchange capacity has also been determined for various metal ions such as K⁺, Mg²⁺ etc. pH titration method was also used for the determination of ion exchange capacity. On account of the K_a values and elution pattern, the cation exchanger is found to be selective for Pb²⁺.

Keywords: Ion exchange capacity, Thermal and Chemical stability, Distribution

Introduction

A description of ion exchange process can be cited in the most ancient literature following a paragraph written in holy Bible. Now-a-days the ion exchange has come to be recognized as an extremely valuable technique. Ion exchange is a process in which "an insoluble (or immiscible) material, when come in contact with an electrolyte solution takes up stoichiometrically ions of positive or negative charge and release other ions of like charge from the exchanger phase into the solution phase". Carriers of these exchangeable ions are called "ion exchangers". The resurgence of interest in synthetic inorganic ion exchangers has largely stemmed from the fact that these materials can be used under conditions unfavorable towards organic resins. Their resistance towards heat and ionizing radiation makes them attractive to organic resins in the field of radiochemical technology. Some three component synthetic inorganic ion exchangers are: Iron(III) antimonosilicate¹, Zirconium iodooxalate², Antimony(III) tungstovanadate³, Zirconium(IV) sulphosalicylate⁴, Titanium molybdophosphate⁵, Zirconium(IV) tungstomolybdate⁶, Zirconium(IV) iodotungstate⁷, Stannic silicomolybdate⁸ and Zeolite A(SiO₂:Al₂O₃:H₂O:Na₂O)⁹. Bismuth based exchangers have not been studied very much. Bismuth tungstate¹⁰, Bismuth nitrate¹¹, Bismuth tellurate¹² and Bismuth silicate¹³ have been reported to show ion exchange properties. In this paper we have reported the synthesis, characterization and ion exchange behavior of a new three component inorganic ion exchanger based on Bismuth(III). The exchanger is Bismuth(III) iodophosphate. Ion

exchanger was characterized on the basis of ion exchange capacity, pH titration, thermal stability, chemical stability, IR spectrum, TGA curve, XRD pattern and distribution studies.

Experimental

Reagents and chemicals-

Bismuth nitrate, potassium iodate and orthophosphoric acid were Qualigens (India) products. All other reagents and chemicals used were also of analytical grade.

Instrumentation-

pH measurements were performed using a 'Toshniwal Research pH Meter' (model pH-110) for equilibrium studies. 'Tanco's Electric Rotary Shaker' was used for shaking the solutions for different studies. Thermal studies were carried out by using 'Tanco's Electric Muffle Furnace'. For drying samples, 'NSW India's Oven' was used. 'Samson S-300D Electric Balance' was used for weighing. All glass wares used in this work were of 'Borosil' make. For XRD and FTIR 'Philips Analytical X-ray B.V. diffractometer' and 'Thermonicolet IR Spectrophotometer' were used respectively. TGA was obtained with the help of 'Perkin Elmer' (Pyris Diamond) in alumina pan from IIT Roorkee (U.K.).

Synthesis-

Eight samples or matrices were precipitated by adding a mixture of 0.1M potassium iodate and 0.1M orthophosphoric acid solution to 0.1M bismuth nitrate solution with continuous stirring in different volume ratios (table-1). The desired pH was adjusted by

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adding dilute HNO₃. The precipitates were aged in the mother liquors for 24 hours at room temperature. The precipitates of different eight samples were filtered. After filtration continuous washing of all the eight samples was done to remove excess acid, with distilled water. pH of the effluents was checked with the help of pH paper. When the effluent become

neutral, then precipitates were assumed to be free from excess acid. Now these eight different samples were kept in an oven at 40±1°C for drying. After about more than 24 hours precipitates become dry and ready for further treatment i.e. granulization. The colour of the precipitates were recorded (table-1).

Table – 1

Sl. No.	Sample No.	Molar Concentration of Solution			Mixing Volume Ratio			pH Value	*Appearance of Precipitate
		BN	PI	OPA	BN	PI	OPA		
1	BIP-I	0.1	0.1	0.1	2	1	1	0-1	white
2	BIP -II	0.1	0.1	0.1	2	2	1	0-1	white
3	BIP-III	0.1	0.1	0.1	2	1	2	0-1	white
4	BIP-IV	0.1	0.1	0.1	3	1	1	0-1	white
5	BIP-V	0.1	0.1	0.1	3	1	3	0-1	white
6	BIP-VI	0.1	0.1	0.1	3	3	1	0-1	white
7	BIP-VII	0.1	0.1	0.1	1	3	3	0-1	white
8	BIP-VIII	0.1	0.1	0.1	1	2	2	0-1	white

BIP Bismuth(III)iodophosphate, BN Bismuth nitrate,

PI Potassium iodate, OPA Orthophosphoric acid

*The Colour of ppt is after drying them at 40±1°C

For granulization the materials were cracked when they were immersed in to hot water. Now granules of eight samples were ready for generation. Generation of granules into the H⁺ form was done by treating them with molar HNO₃ solution. For this, granules of eight samples were kept separately in acid solution taken in eight different conical flasks and 15 minutes continuous shaking was done with the help of Electric Rotary

Shaker. The same process was repeated several times with fresh acid solution each time. After settlement of granules decant the acid and kept the granules in fresh acid solution and leave them as such for 24 hours. After 24 hours decant the acid and filter them. Granules are finally washed with distilled water to remove excess acid and dried them in an oven at 40±1°C.

Table – 2

S.No	Sample No	COBBG	COBAG	I.E.C. (meq/g)
1	BIP-I	white	white	0.132
2	BIP -II	white	white	0.220
3	BIP-III	white	white	0.220
4	BIP-IV	white	white	0.154
5	BIP-V	white	white	0.220
6	BIP-VI	white	white	0.264
7	BIP-VII	Yellow white	Yellow white	0.220
8	BIP-VIII	white	white	0.501

BIP

COBBG

COBAG

I.E.C.

- Bismuth(III) iodophosphate

- Colour of beads before generation

- Colour of beads after generation

- Ion exchange capacity

Determination of Ion Exchange Capacity-

2.4a Column method : 0.50g (dry mass) of Bismuth(III) iodophosphate in H⁺ form was packed in glass column having a glass wool support at the base. M NaNO₃ solution was passed through the column slowly by adjusting the effluent rate at 9-10 drops per

minute. The effluent was carefully collected in a 250 ml. conical flask. The complete replacement of H⁺ from the ion exchanger by Na⁺ was checked by comparing the pH of the eluent (M NaNO₃) and the effluent with the help of pH paper. The collected effluents were titrated

against a standard NaOH solution. Then I.E.C. was calculated using a suitable formula.

Sample (BIP VIII) was selected for detailed study on account of its higher ion exchange capacity in comparison to others. The sample was synthesized in bulk to fulfill the purpose of detailed study.

Bulk synthesis was done by mixing 0.1M potassium iodate solution, 0.1M orthophosphoric acid solution and 0.1M bismuth nitrate solution with continuous stirring in 1:2:2 ratios respectively. The pH was adjusted to 0-1 by adding dil HNO₃. The precipitate was aged in the mother liquor for twenty four hours at room temperature and filtered. The matrix so obtained was washed to remove the excess acid with distilled water and it was kept in an oven at 40±1°C for drying. After drying, the matrix was converted to granules as described earlier. After generation of granules excess acid was removed by washing them with distilled water and acid free granules were dried at 40±1°C in an oven. Now these granules are ready for detailed study.

The ion exchange capacity was determined once again by column method using molar NaNO₃ solution. The ion exchange capacity value was found to be 0.51 meq/g which is nearly equal to the previous value. Similarly the ion exchange capacity of the synthesized material in bulk was also determined by the same column process for different alkali and alkaline earth metals. Six equal parts of 0.50 g each of the exchanger were packed in six different columns and passed some distilled water through them to wash and settle the granules in the form of a bed. Six different metal ion solutions of 0.1molar concentration were prepared. Each column was treated with a particular salt solution to occur the ion exchange. The flow rate was maintained as one millilitre per minute. The effluents were collected and titrated against standard sodium hydroxide solution separately to determine the hydrogen ion concentration. The ion exchange capacity was calculated again (table-3).

Table – 3: I.E.C. of Bismuth(III) iodophosphate for various cations

Cations	Salt of Cation	Solution Concentration	Hydrated Radii (Å)	IEC (meq/g)
Na ⁺	NaNO ₃	0.1M	7.90	0.50
Li ⁺	LiCl	0.1M	10.0	0.54
Na ⁺	NaCl	0.1M	7.90	0.52
K ⁺	KBr	0.1M	5.30	0.49
Mg ²⁺	MgCl ₂	0.1M	10.80	0.42
Ca ²⁺	CaCl ₂	0.1M	9.60	0.40
Ba ²⁺	BaCl ₂	0.1M	8.80	0.38

I.E.C. :- Ion exchange capacity.

pH titration method- This is an another method of determining ion exchange capacity of the exchanger. In this method 0.5g of the exchanger was treated with 50ml of the NaCl-NaOH solution. Eleven different samples were prepared by varying NaCl-NaOH solutions ratios separately. Six hours continuous

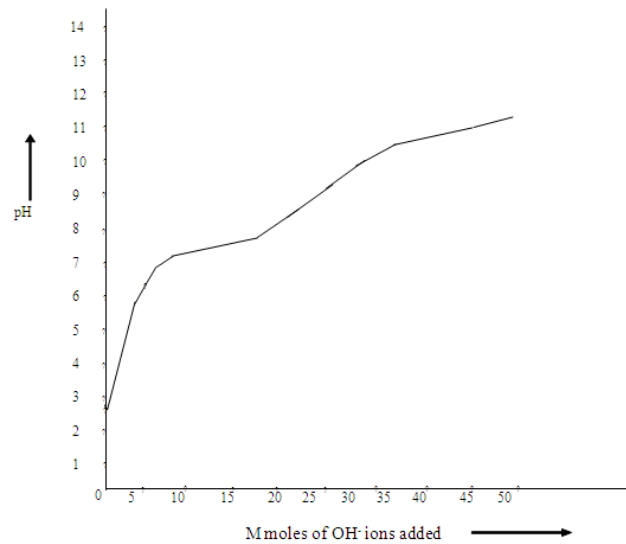
shaking was done with the help of electric rotary shaker and then kept them as such for twenty four hours to maintain the equilibrium. After twenty four hours pH of different samples were measured with the help of pH meter. Please refer table 4 and figure 1.

Table – 4

Sl. No.	Sample No.	NaCl –NaOH System		pH Value
		NaCl Solution (ml)	NaOH Solution (ml)	
1	BIP	50	0	2.79
2	BIP	45	5	6.48
3	BIP	40	10	8.00
4	BIP	35	15	8.36

5	BIP	30	20	8.80
6	BIP	25	25	9.44
7	BIP	20	30	9.75
8	BIP	15	35	10.30
9	BIP	10	40	10.66
10	BIP	5	45	10.70
11	BIP	0	50	10.80

BIP – Bismuth(III) iodophosphate



Thermal Treatment-

Heating effect on weight and ion exchange capacity of the ion exchanger was studied using a muffle furnace in which a temperature up to 900°C can be maintained. To find the stability against temperature, different samples of same amount were heated at different temperatures. For thermal stability seven equal parts of 0.50g each of the exchanger were heated in

different crucibles for one hour at different temperatures from 50°C to 700°C in a muffle furnace. After heating crucibles were removed from the furnace with the help of a tong and cooled them in desiccators. The cooled crucibles were weighed to find the weight loss. I.E.C. of all the samples was also determined by the usual column method using molar sodium nitrate solution (table-5).

Table – 5: Thermal Stability

Sl. No.	Sample No.	Temp (°C)	WBH (g)	WAH (g)	LIW (g)	CAH	I.E.C. (meq/g)
1	BIP	50	0.50	0.50	0.0	white	0.500
2	BIP	100	0.50	0.50	0.0	white	0.500
3	BIP	200	0.50	0.49	0.01	light yellow	0.384
4	BIP	300	0.50	0.48	0.02	blackish yellow	0.280
5	BIP	400	0.50	0.47	0.03	blackishyellow	0.219
6	BIP	500	0.50	0.45	0.05	black	0.219
7	BIP	600	0.50	0.38	0.12	black	0.120
8	BIP	700	0.50	0.30	0.20	black	0.120

WBH- Weight before heating, WAH- Weight after heating, LIW- Loss in weight, CAH – Colour after heating, I.E.C. – Ion exchange capacity

Chemical Stability

To see the effect on ion exchange capacity of the exchanger in different chemical solutions of different concentrations, the study was done. The extent of dissolution of the material in different mineral acids, organic acids and bases was recorded. 0.50g of material was equilibrated with 25ml of the solution of interest for

twenty four hours at room temperature. The remaining amount of material was filtered and washed by DMW. After removal of excess acid or base, it was dried in oven at $40 \pm 1^\circ\text{C}$. The ion exchange capacity of remaining material was determined by usual column method (table-6).

Table-6: Chemical stability

Solution	Wt. Before Treatment (g)	Wt. After Treatment (g)	I.E.C. (meq/g)
DMW	0.50	0.500	0.50
1M HCl	0.50	0.280	0.10
2M HCl	0.50	0.217	0.06
1M HNO ₃	0.50	0.15	0.08
2M HNO ₃	0.50	Dissolve completely	-
1M H ₂ SO ₄	0.50	0.260	0.12
2M H ₂ SO ₄	0.50	0.170	0.08
2M CH ₃ COOH	0.50	0.260	0.12
2M HCOOH	0.50	0.217	0.10
2M NaOH	0.50	Dissolve completely	-
2M KOH	0.50	Dissolve completely	-

I.E.C.- Ion exchange capacity

Distribution studies-

Distribution studies were carried out for nine metal ions by batch process. The metal ion solutions were treated with the fixed amount of the exchanger separately. For maintaining the equilibrium, 6 hours shaking of solutions was done with the help of Electric Rotary Shaker. Then solutions were kept as such for a definite time at room temperature. After it, a definite volume of the solution is taken into conical flask with the help of a pipette and titrated against EDTA solution. The used metal ion solutions were also titrated against EDTA solution without ion exchanger treatment. The

distribution coefficient (K_d) values were calculated for metal ions using the following equation:

$$K_d = \frac{I-F}{F} \frac{A}{W}$$

Where I - Burette Reading for the metal ion solutions before treatment with ion exchanger.

F - Burette Reading for the metal ion solutions after treatment with ion exchanger.

A - Volume of metal ion solution taken.

W- Weight of the ion exchanger.

Table -7: K_d Values of Metal Ions on BIP in DMW

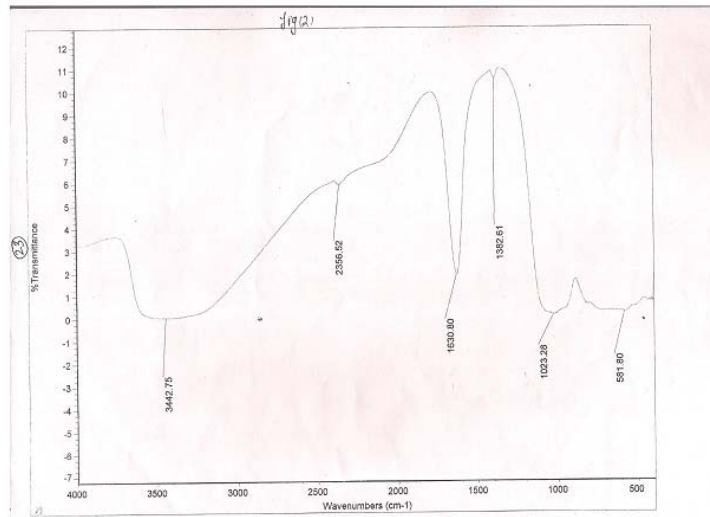
Metal Ion	Taken as	K _d (ml/g)
Mg (II)	Acetate	1.134
Zn (II)	Acetate	10.240
Cu (II)	Acetate	5.590
Mn (II)	Acetate	3.262
Co (II)	Acetate	11.519
Ni (II)	Sulphate	16.519
Pb (II)	Nitrate	21.300
Cd (II)	Chloride	7.010
Ca (II)	Carbonate	0.890

FTIR Study-

FTIR spectrum of the sample was obtained from Instrumentation Centre, IIT Roorkee where Thermo Nicolet IR Spectrophotometer was available.

KBr disc method was used to get the spectrum. The IR absorption spectrum was recorded between 400 and 4000cm⁻¹(Figure-2).

Fig. 2

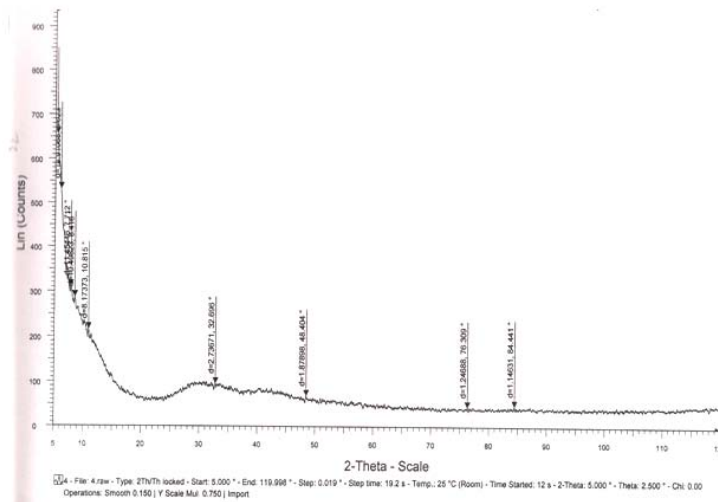


XRD-

The X- ray diffraction pattern of the exchanger was also obtained from the Instrumentation Centre,

IIT Roorkee where Philips Analytical X- ray B.V. Diffractometer was available. The diffraction pattern is exhibited in figure 3.

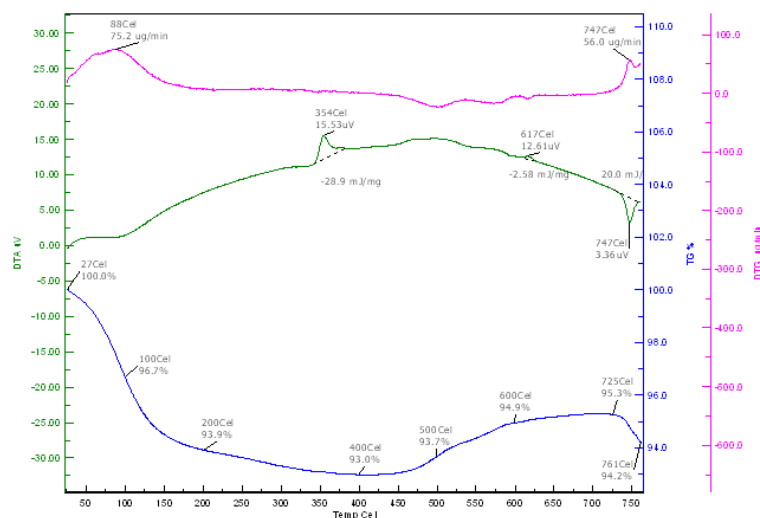
Fig. 3



TGA Curve-

TGA curve of Bismuth(III) iodophosphate was also obtained from IIT, Roorkee. The TGA curve is shown in (figure-4).

Fig-4



Results and Discussion

Bismuth(III) iodophosphate obtained as a white amorphous powder was found to be stable in water, quite soluble in 2M HCl, 2M H₂SO₄, 2M CH₃COOH, 2M HCOOH and fairly soluble in 2M NaOH, 2M HNO₃ and 2M KOH.

The maximum ion exchange capacity for Na⁺ ion was found to be 0.50 meq/g. The ion exchange capacity of Bismuth tungstate¹⁰ is also 0.50 meq/g for Na⁺. The effect of size and charge of the metal ion on the exchange capacity was studied. For the alkali and alkaline earth metal ions, the sequence shown by the exchanger is as follows: K⁺ > Na⁺ > Li⁺ & Ba²⁺ > Ca²⁺ > Mg²⁺ respectively. The trend in ion exchange capacity confirms that the ion exchange takes place with the hydrated form of the ions. The ion exchange capacity varies from 0.38-0.54 meq/g, similarly the ion exchange capacity of Bismuth tungstate¹⁰ varies from 0.30-0.50 meq/g for alkali and alkaline earth metal ions.

The pH titration curve (figure-1) was obtained under equilibrium conditions for NaOH-NaCl system. It appears to be strong cation exchanger as indicated by a low pH (-2.79) of the solution when no OH⁻ ion were added. As the volume of NaOH added to the system is increased, more OH⁻ ions are consumed suggesting in the increase of the rate of ion exchange in basic medium due to the removal of H⁺ ions from the external solution.

The study of thermal effect on ion exchange capacity of Bismuth(III) iodophosphate shows that the ion exchange capacity decreases with increase in temperature, although the sample retains a small exchange capacity 0.12 meq/g even at 700°C. A reported ion exchanger Bismuth antimonate¹⁵ shows complete loss of exchange at > 200°C.

The spectrum has intensity band at 1023.28cm⁻¹ and 1382.61cm⁻¹ that shows the presence of PO₄³⁻ groups and P=O groups attached to the compound respectively. The spectrum has an intense band at 581.06cm⁻¹ that shows the presence of Bi-O group and iodate band falls at frequency 817.68cm⁻¹.

X-ray diffraction pattern of Bismuth(III) iodophosphate does not show sharp peak. It revealed the fact that the exchanger in H⁺ form is amorphous.

The thermogram of the Bismuth(III) iodophosphate is shown in figure 4. The curve shows the weight loss from 0°C to 800°C. There is 3.3% loss at 100°C, 6.1% loss at 200°C, 7% loss at 400°C, 6.3% loss at 500°C, 5.1% loss at 600°C, 4% loss at 725°C and 5.8% loss at 761°C. The 3.3% loss of weight at 100°C may be attributed to the loss of external water molecule from the exchanger. From 100°C to 200°C, 2.8% loss may be attributed to the loss of water of crystallization. Beyond 200°C the loss may be attributed to the effect on component and loss of coordinated water and hydroxyl groups. It also involves the production of Bi₂O₃. These losses follow the regular trend of inorganic ion exchanger.

Distribution behaviour of nine metal ions in DMW were studied (table-7). The study revealed that the material, in DMW showed high preference in the following order: Pb²⁺ > Ni²⁺ > CO₂⁺ > Zn²⁺ > Cd²⁺ > Cu²⁺ > Mn²⁺ > Mg²⁺ > Ca²⁺, so the exchanger is lead selective. Reported ion exchanger Bismuth tungstate¹⁰ also shows a very high selectivity towards Pb²⁺ ions over other ions.

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