

Synthesis, Characterization and Ion Exchange Properties of a New Inorganic Ion Exchange Material: Zirconium(IV) Iodo-succinate

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A new three-component inorganic ion exchange material zirconium(IV) iodo-succinate (ZIS) has been synthesized by adding a mixture of 0.2 M potassium iodate and 0.2 M succinic acid to 0.2 M zirconium oxychloride in different volume ratios at pH 1.0. Among several samples synthesized, ZIS-1 is selected for detailed studies owing to its highest ion exchange capacity and chemical stability. The material has been characterized on the basis of chemical composition, fourier transform infra-red and thermogravimetric studies. The ion exchange capacity of the material for Na⁺ ion has been found to be 3.0 meq g⁻¹ dry exchanger. The ion exchange capacity for other ions varies and is found to be depending upon the crystal ionic radius of exchanging cations. The chemical stability of the material has been tested in acidic, neutral and basic media.

Key Words: Zirconium(IV) iodo-succinate, Ion-exchange, FTIR, Thermogravimetric.

INTRODUCTION

Extensive studies on the synthetic inorganic ion exchanger have proved their potential in solving diverse problems of environmental and analytical chemistry. Acidic salts of multivalent metals, prepared in combination with anions of phosphate, tungstate, arsenate, tellurate, etc. as two-component ion exchangers have been studied most intensively^{1,2}. Phosphate and arsenate of zirconium show good thermal and chemical stabilities while little work has been done on zirconium vanadate³. The inorganic ion exchangers based on three components have been found to show relatively increased ion exchange capacity (IEC) and selectivity^{4,5}. Zirconium phosphate type cation exchangers have been extensively studied and are well known for their excellence as inorganic ion-exchangers and for other chemical applications such as separation of rare earth⁶.

In recent years, a large number of zirconium(IV) based inorganic ion-exchangers have been prepared and their applications have been studied by many researchers^{4,7}.

The present study is an attempt to explore the possibility of synthesizing a new inorganic ion-exchanger, zirconium(IV) iodo-succinate providing a better ion exchange material useful in environmental analysis and to check their utilization as a heavy metal remover from wastewater.

EXPERIMENTAL

Zr(IV) oxychloride, potassium iodate and succinic acid used were of GR grades, marketed by E. Merck (India) and were used without further purification. Melting

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point of succinic acid was determined in order to check purity and was found in close agreement with literature value. All other chemicals and reagents used were of analytical grade. pH measurements were performed using an Elico (India) LI-120 model pH-meter. A Bausch & Lomb Spectronics-20 spectrophotometer was used for the determination of iodate. IR studies were made on a Fourier transform infra-red (FTIR) Nicolet 50X model. Thermal stability measurements were performed using a muffle furnace.

Synthesis of the ion exchange material: The ion exchange material was synthesized by mixing 0.2 M Zr(IV) oxychloride solution gradually to a mixture of potassium iodate and succinic acid solution with continuous stirring in various mixing volume ratios and is given in Table-1. The gelatinous precipitate so obtained was allowed to settle down for 24 h at room temperature. The supernatant liquid was removed and the precipitate was washed with de-ionized water and filtered. The product was dried at $70 \pm 2^\circ\text{C}$ in an electric oven. The material was broken down into small graduals by placing in de-ionized water. The granules were converted into H^+ form by treating with 1.5 M HNO_3 solution for 24 h. The material was then washed several times with deionized water to remove any excess of acid and finally dried at $70 \pm 2^\circ\text{C}$.

Determination of ion exchange capacity (IEC) of the material: The ion exchange capacity of the material was determined by the column process. 1.0 g of the exchanger (H^+ form) was packed in a column and washed with distilled water to remove any excess of acid sticking to the particles. 250 mL of 1 mol solution of NaCl was passed through the column maintaining the flow rate 1 mL min^{-1} . The effluent was collected and titrated against a 0.1 M NaOH solution to determine the total H^+ ions released. The results are summarized in Table-1.

TABLE-1
SYNTHESIS AND PROPERTIES OF ZIRCONIUM(IV) IODO-SUCCINATE

Sample	Molar concentration			Mixing ratio (v/v/v) Zr : IO_3 : $\text{C}_4\text{H}_6\text{O}_4$	pH	Appearance of precipitate	IEC in terms of Na^+ ions (meq/g)
	Zr (M)	IO_3 (M)	$\text{C}_4\text{H}_6\text{O}_4$ (M)				
ZIS.1*	0.2	0.2	0.2	1:1:1	1.0	White gelatinous	3.0
ZIS.2	0.2	0.2	0.2	1:2:1	1.0	White gelatinous	1.7
ZIS.3	0.2	0.2	0.2	2:2:1	1.0	White gelatinous	1.9
ZIS.4	0.2	0.2	0.2	2:3:2	1.0	White gelatinous	2.7
ZIS.5	0.2	0.2	0.2	2:2:3	1.0	White gelatinous	2.3

*Selected for detailed study

To determine the chemical stability, 0.50 g of the exchanger was equilibrated with 50.0 mL of solutions of interest for 24 h at room temperature. The zirconium and iodate were determined spectrophotometrically using alizarin red-S and pyrogallol as colouring reagents, respectively, and succinic acid was determined by subtracting the zirconium and iodate from total weight.

Chemical composition: For the determination of the chemical composition of the sample ZIS-1, 0.10 g of exchanger was dissolved in minimum amount of concentrated H_2SO_4 . The solution was diluted to 100 mL with distilled water. The zirconium and iodate were determined using the methods described earlier. The

mole ratio of Zr, IO₃ and succinic acid was found to be 0.99 : 1.01 : 1.0, which is very near to 1 : 1 : 1. On the basis of chemical analysis it is also found that the molar ratio of ZIS-1 and ZIS-4 is approximately same, *i.e.*, 1 : 1 : 1.

The distribution studies of various metal ions in distilled water and nitric acid were carried out by the batch equilibrium technique. For this purpose, 0.50 g of the exchanger in H⁺ form was equilibrated with 25.0 mL of 0.05 M solutions of different metal ions. The mixture was shaken for 6 h to attain equilibrium. The amount of metal ions left in the solution was then determined by titrating against 0.01 M EDTA solution using appropriate indicators. The K_D values of the metal ions were calculated using the following equation:

$$K_D = (I_R - F_R) \times V / (F_R \times M)$$

Here I_R and F_R denote the volume of EDTA solution required before and after equilibrium respectively, V is the solution volume in mL and M is the mass of the exchanger in grams.

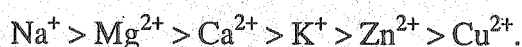
RESULTS AND DISCUSSION

Zirconium iodo-succinate appears to be a promising ion exchange material with good ion exchange capacity. Table-1 describes the preparation and properties of the ion exchange material. Sample ZIS.1 was chosen for detailed study owing to its higher ion exchange capacity and stability. The ion exchange capacity was measured with different uni- and bivalent metal ions. The results are summarized in Table-2.

TABLE-2
ION EXCHANGE CAPACITY (meq g⁻¹ DRY
ION EXCHANGER) OF ZIRCONIUM(VI)
IODO-SUCCINATE FOR VARIOUS CATIONS

Cations	Ion exchange capacity (meq g ⁻¹ dry exchanger)
Na ⁺	3.00
K ⁺	1.50
Mg ²⁺	1.76
Ca ²⁺	1.58
Zn ²⁺	0.24
Cu ²⁺	0.15

These results indicate that ion exchange selectivity of the material is different for different cations. The IEC in meq g⁻¹ dry exchanger for various metal ions follows the order:



The material was found to be fairly stable in lower concentration of mineral acids such as HCl, H₂SO₄, and HNO₃. The ion exchanger completely dissolved in 3 M H₂SO₄ and 3 M NaOH solution.

The chemical composition data of the material suggest the molar ratio of Zr(IV), IO₃ and H₆C₄O₄ as 1 : 1 : 1 which may point to the following tentative formula:



where $n = 2.06$ as calculated in thermogravimetric analysis.

Thermogravimetric analysis: The thermogravimetric analysis was done and Fig. 5.2 shows the results. On the basis of thermogravimetric analysis, it is clear that the weight loss up to 145°C is approximately 8.5%, which is due to the presence of external water molecules in the material. The number of such molecules (n) per mol of the exchanger can be determined on the basis of Alberti's equation as follows:

$$18n = \frac{x(M + 18n)}{100}$$

Here, x is the % water content and $M + 18n$ is the molecular weight of the material. It gives the value of n as 2.06.

Further, the loss in weight is observed from 145 to 450°C , which is due to condensation of IO_3 into I_2O_5 . Lastly; there is an abrupt weight loss from 450 – 530°C indicating the volatilization of inorganic groups. Beyond this temperature the weight becomes constant owing to the formation of zirconium oxide.

FTIR Study of the ion exchanger: In order to further characterize the material, its FTIR studies were performed at room temperature using KBr disc method. The strong and broad band in the region 3600 – 3000 cm^{-1} may be assigned to interstitial and coordinated water molecule and $-\text{OH}$ group. The presence of water molecule was again confirmed by the presence of $\text{H}-\text{O}-\text{H}$ bending vibration in the region 1600 – 1540 cm^{-1} . Presence of succinic acid in the compound is shown by the presence of $(\text{C}=\text{O})$ stretching vibration in the region of 1770 – 1700 cm^{-1} and the presence of CH_2 group of succinic acid was shown by a $-\text{CH}$ vibration at 2361 cm^{-1} and $-\text{CH}$ bending doublet at 1445 – 1339 cm^{-1} . $\text{C}-\text{O}$ stretching vibration of succinic acid in the region 1233 – 1176 cm^{-1} is also found in the spectrum. The spectrum also shows a strong absorption in the region 772 – 500 cm^{-1} indicating the presence of iodate and metal oxide.

The distribution studies indicate that the material is selective for $\text{Ca}(\text{II})$ in comparison to other metal ions studied. The decreasing order of K_D values for various bivalent metal ions in distilled water and 0.10 M HNC_3 is given as follows:



The K_D values decrease as concentration of nitric acid increases. This behaviour can be useful for the separation of $\text{Ca}(\text{II})$ from other metal ions in environmental analysis.

REFERENCES

1. V. Vesley and V. Pekarek, *Talanta*, **19**, 224 (1972).
2. A. Clearfield, *Chem. Rev.*, **88**, 125 (1988).
3. V.A. Shiehko and E.S. Biochinova, *Zh. Pirk. Khim.*, **41**, 326 (1968).
4. A. Dyer, T. Shaheen and Z. Mohammad, *J. Mater. Chem.*, **7**, 1895 (1997).
5. S.A. Nabi, A. Islam and N. Rahman, *Adsorp. Sci. Technol.*, **17**, 629 (1999).
6. A. Clearfield, CRS Press, Boca Raton, FL (1982).
7. O.K. Singh, S. Singh and B. Srivastava, *Indian J. Chem.*, **41A**, 2526 (2002).