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Zirconium [IV] Antimonoarsanotungstate Zr[SbAsW]: Synthesis and Characterization

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ABSTRACT: In the present research work we concentrated on the structure elucidation of new heteropolyacid salts: Zirconium Antimonoarsanotungstate Zr[SbAsW] salt synthesized at variable pH using sol-gel route. Instrumental technique, FTIR was used to assign the structural aspects to the compound. Physical characterization involve determination of ion exchange capacity and maximum value for this parameter is 0.40mg/eq. Distribution coefficient values showed that the synthesized compound is preferentially selective for Pb^{2+} ion. Membrane composition, where ZrSbAsW was 40% showed linearity in the range of 1.0×10^{-4} M to 1.0×10^{-1} M with slope of 20.0 mV/decade taking 10^{-1} M as internal solution. Above instrumental and analytical studies gave a picture of Pb^{2+} selective electro-active characteristics to the synthesized compound.

Keywords: Zirconium Antimonoarsanotungstate, synthesis, Kd values, ion exchange capacity, ZrSbAsW.

1. INTRODUCTION

Heteropoly acid (HPAs)/ polyoxometalates are composed of multifaceted network of basic unit MO_6, exhibiting a wide range of geometry, compositions and architectures[1-2] and J.F. Keggin was the foremost to conclude the geometry of α-Keggin anions using X-ray diffraction[3]. Various categories of HPA's are described by Clearfield, Vesely, Pekarek and others[4-6]. Heteropolyacid salts are widely used in analytical chemistry as ion exchanger and as catalyst in synthetic chemistry because of their leading properties like wide and desirable variations possible in their compositions, which in turn alters their physical and chemical properties, particularly selectivity. The first commercially available ion exchanger is amorphous aluminosilicate gels[7]. Lun-Yu et al prepared and then characterized tungstophosphate heteropoly complex substituted by titanium and peroxotitanium[8]. Unusual selectivity of titanium antimonite (TiSbA) salt have been reported by Abe et al for alkaline earth metal[9]. Siddiqi and Pathania synthesised titanium (IV) tungstosilicate and titanium (IV) tungstophosphate and then applied these for the separation of metal ions[10]. Nabi et all

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synthesize a new cation exchanger-zirconium(IV) iodotungstate[11] Meanwhile, a new era of higher heteropolyacid salts started and some of the salts of such complexity are (i) Zirconium (IV) tungstoiodophosphate synthesized by S. A. Khan having excellent IEC for Na^+ 2.20 and for K^+ 2.35 meq/g[12], (ii) Zirconiumcerium (IV) arsenotungstate(ZrCeAsW), having IEC as 1.21meq/g and then its analytical importance was certified by the separation of appreciable amount of Pb^{2+} from other metal ions[13]. Ion exchange characteristics of newly Synthesized Ceriumzirconium Phosphotungstate have been synthesised by Preetha et al[14]. Along this track, still there is a wide scope, therefore, we did efforts to synthesize a novel lead selective heteropolyacid salt named Zr[SbAsW].

2. MATERIALS AND METHODS

2.1 CHEMICALS AND APPARATUS

Essential chemicals like sodium arsenate, sodium tungstate and zirconium chloride were procured from HI media. Other required metal ion solutions were developed by taking AR grade reagent and then they were standardized wherever required.

Infrared studies of synthesized Zirconium (IV) antimonoarsanotungstate Zr[SbAsW] were conducted by using a Perkin, ABB spectrophotometer (KBr pellet technique). Digital pH meter and Potentiometer both from Electronic India were used for pH and potential measurements, respectively.

2.2 SYNTHESIS OF ZIRCONIUM (IV) ANTIMONOARSANOTUNGSTATE

Zirconium (IV) antimonoarsanotungstate was prepared by slowly pouring Zirconiumoxychloride (1 M) solution to a mixture

of sodium arsenate, antimony trichloride and sodium tungstate solution. Gelatinous white ppt. were obtained. Precipitates were re-fluxed for three hours to upgrade the characteristics of the synthesized compound. These ppt. were filtered and rinsed to make them free from chloride ions and then dried at 40^{0}C. The dried sticky product acquire the specific geometry of heteropoly compounds when immersed in water. Then, the material was actuated by dipping it in HCl (0.1 M) overnight and then again dried at low temperature to retain the original geometry of compound. As the preparatory conditions is the primary factor to govern the property of the heteropoly compound, therefore various attempts under the conditions as given in table no 1 were tried to get the exchanger of better ion exchange capacity.

Table 1: Preparation of Zr[SbAsW] under different conditions

Sample No.	Respective constituents	Volume ratio	Molar ratio (M)	Temp ^{0}C (reflux)	pH	IEC mg/eq.
1.	Zirconium oxychloride Antimony trichloride Sodium tungstate Sodium arsenate	2:1:1:1	0.1:0.1:0.1:0.1	40	1	0.40
2.	Zirconium oxychloride Antimony trichloride Sodium tungstate Sodium arsenate	2:1:1:1	0.2:0.1:0.1:0.1	60	1	0.35
3	Zirconium oxychloride Antimony trichloride Sodium tunstate Sodium arsenate	1:1:1:1	0.1:0.1:0.1:0.1	25	1	0.32
4.	Zirconium oxychloride Antimony trichloride Sodium tungstate Sodium arsenate	1:1:1:1	0.1:0.1:0.1:0.1	50	1	0.30

3.PHYSICOCHEMICAL CHARACTERIZATION

3.1 DETERMINATION OF ION EXCHANGE CAPACITY

Column operation methodology was exercised to determine the ion exchange capacity of the synthesized sample. Ion exchange capacity of various exchangers synthesized by using different conditions are given in table no. 1.

Table 2: Distribution coefficient values

Sr. No.	Metal ion	Distribution coefficient (Kd)
1.	Cobalt nitrate	32.5
2.	Lead nitrate	53.5
3.	Mercuric chloride	25.5
4.	Nickel sulphate	16.6
5.	Magnesium chloride	47.5
6.	Cupric nitrate	35.0
7.	Cadmium sulphate	33.3
8.	Copper sulphate	50.0

3.2 MEMBRANE DEVELOPMENT

To optimize the membranes component, varying amount of activated exchanger materials were tried with binding materials (epoxy resin). Appropriate quantity of evenly crushed exchanger was homogenized with epoxy resin (w/w) to make a near consistent paste. Then paste was pressed between the folds of butter paper under a weight of 2.0 Kg/cm^2 overnight. These membranes were then mounted to the one end of the glass tube to assemble them in the form of electrode.

3.3 DISTRIBUTION COEFFICIENT (K$_D$)

Distribution coefficients (K$_d$) for different metal ions such as Ni^{2+}, Cu^{2+}, Mg^{2+}, Hg^{2+}, Co^{2+}, Cd^{2+} and Pb^{2+} were determined in aqueous solutions by following Batch Adsorption procedure and applying the formula as given in the previous reports[15].

$$K_d = (I - F) / F . V / W$$

3.4 EMF MEASUREMENT

The membranes were then equilibrated with 0.1 M metal ion solution for 24 hours and immersed in a beaker containing test solution of varying concentrations. Potential measurements were carried out using the cell assemble 1.

Table 3: Different composition of membranes

membrane	Exchanger	Epoxy resin
50 %	0 .50gm	0.50gm
60 %	0.60gm	0.40gm
40 %	0.40gm	0.60gm

3.5 STORAGE OF ELECTRODES

Electrodes can be preserved in distilled water and further can be revitalized by keeping in 0.1 M Pb^{2+} ion solution for two hours.

4 RESULTS AND ANALYSIS

4.1 PHYSICOCHEMICAL CHARACTERISATION

4.1.1 ION EXCHANGE CAPACITY

From the experimental work, we observed that maximum ion exchange capacity is 0.40mg/eq. for sample no. 1 out of various synthesized samples.

4.1.2 DISTRIBUTION COEFFICIENT (K_D)

Distribution coefficient studies helps in drawing the inference that K_d values for Lead (II) ions is maximum and the most promising property of synthesized exchanger was having selectivity towards Pb^{2+} ion, so this exchanger is preferentially selective for Lead metal ions.

Cell Assemble 1: Hg-Hg₂Cl₂(s), KCl (sat.)│0.1M ││membrane││ test solution│ KCl (sat.), Hg₂Cl₂ -Hg

4.2 STRUCTURAL CHARACTERISATION (INFRARED SPECTRA)

IR spectra (fig) of the Zr[SbAsW] represent the following sharp and strong bands (fig 1) at:

Broad band at 3315 cm^{-1} stretching mode of interstitial water molecules.

A flimsy band at 2966 cm^{-1} – deformation vibration of the accommodated water molecules.

Sharp band at 1624 cm^{-1} indicates deformation interstitial water molecules.

Broad band 3179 cm^{-1} stretching mode of M-OH (acidic) group.

Sharp band at 1367 cm^{-1} indicates deformation M-OH bond.

A spurted band at 880-541 cm^{-1} is due to swinging, twisting and rocking modes of metal oxygen and aqua bonds.

Coupling of various types of electronic states with the vibrational states of the molecules shifted the original position of bands from their normal mode. In spite of deviations, various stretching modes correspond to the heteropolyacid geometry having the presence of incorporated water[16].
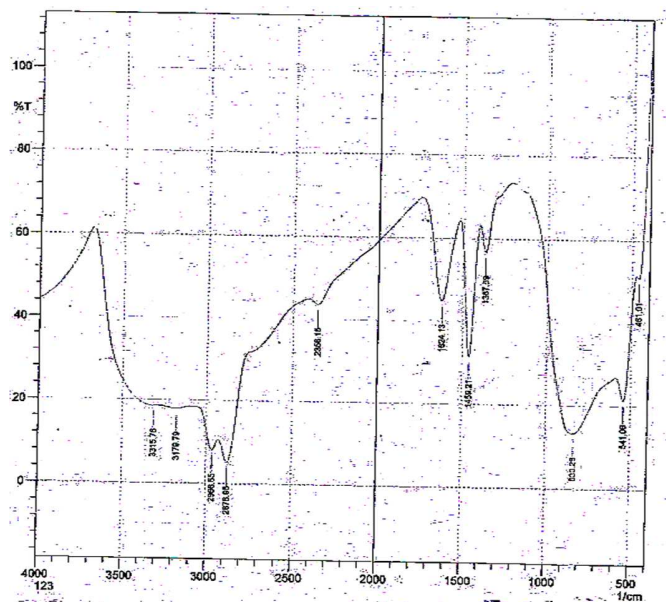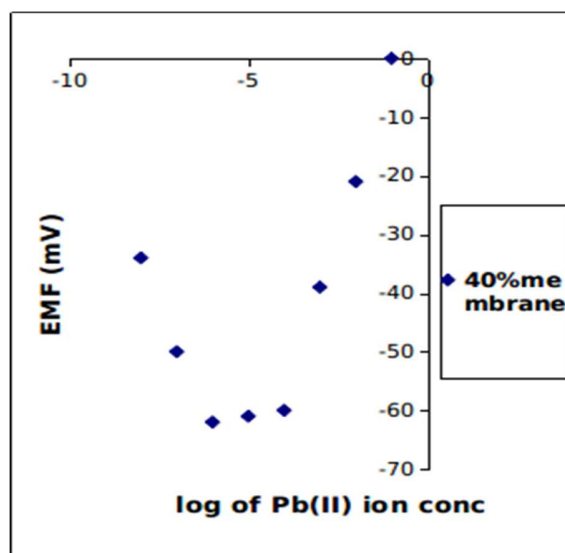

Fig.1: IR Spectra of the exchanger

Fig. 2: Calibration curve for Pb (II) ion selective electrode.

4.3 INFLUENCE OF INTERNAL SOLUTION

Performance of synthesised electrodes were examined by studying potential response of electrodes in Pb(II) ion solutions of varying concentration range (1.0×10^{-8} M to 1.0×10^{-1} M). 40 % membrane expressed linearity from 1.0×10^{-4} M to 1.0×10^{-1} M with a near-Nernstian slope of 20.0 mV/decade, which is supported by literature[17-18]. Response time was very low i.e. 6 sec. Plot of EMF vs log of activities of Pb(II) ions is shown in figure 2.

5. ACKNOWLEDGMENT

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