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Synthesis, characterization and analytical application of zirconium (IV) antimonoarsenate as a potentiometric sensor

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Abstract

A new inorganic ion exchanger, zirconium (IV) antimonoarsenate has been synthesized at different pH values. An amorphous sample prepared at pH 1 having an ion-exchange capacity of 0.40 meq/g was selected for further studies. The material is characterized using various analytical techniques, like XRD, IR, TGA and SEM, in addition to the ion-exchange capacity and distribution coefficient (K_d) studies. Further the exchanger has been used as an electro-active material for the determination of Cerium (III) ions with epoxy resin, PVC and polystyrene as binding materials. A membrane having a composition: ZrSbAs (50%) and polystyrene (50%) gives the best performance. It works well over a wide Ce (III) ion-concentration range of 5×10^{-5}–1×10^{-1} M with a super-Nernstian slope of 52.0 mV/decade. It has a fast response time of 10 s and has an average lifetime of four months. The proposed sensor shows a good selectivity for cerium (III) ions with respect to alkali, alkaline earth, some transition and rare earth metal ions that are normally present along with cerium in its ores. The electrode has also been used as an indicator electrode in potentiometric titrations of Ce (III) ions against oxalic acid.

Keywords: Inorganic ion exchanger; K_d values; Electro-active material; Cerium (III); Selectivity; FIM; Potentiometric titration

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1. Introduction

Inorganic ion exchangers have been synthesized under different conditions of synthesis and characterized for nearly four decades now, since the classical work of Amphlett [1]. Different types of inorganic ion exchangers and their applications in various fields are documented by Clearfield [2]. Inorganic ion exchangers, besides their other advantages, are important in being more stable at high temperature and radiation fields [1–4]. They are stable towards chemical degradation and possess sharp selectivity for metal ions over their organic analogs [5]. Ion-selective electrodes employing inorganic ion exchangers as ion sensors have been reviewed by Arnold and Solsky [6] and Buck [7].

Amorphous and crystalline forms of tetravalent metal acid salts, generally called single salts, with the general formula M (IV) $(HXO_4)_2 \cdot nH_2O$ {where, M represents Sn (IV), Zr (IV), Ti (IV), etc. and X represents P, W, Si, Mo, Se, Sb, As etc.} have been studied. Some single salts of tin (IV), like phosphates and antimonates, have shown some characteristics of ion exchangers [8]. However,

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studies have shown that mixed salts have better ion-exchange capacity, thermal and chemical stability as compared to single salts [9]. These mixed salts may have tetravalent metals such as Sn (IV), Zr (IV), Ti (IV), etc. in combination with any two anions from P, B, W, Si, Mo, Se, Sb, As, etc. These mixed salts are called double salts. Double salts of tin and zirconium [10,11] have shown better ion-exchange characteristics than the corresponding single salts.

Rare earths are slightly toxic [12] in nature. These are dumped in the environment mainly by petrol producing industries. These metal ions gradually accumulate in soils and eventually lead to increasing concentration in human, animals and soil particles. In human beings, these can cause lung embolisms and can be a threat to liver, especially during long-term exposure. With water animals, these metal ions cause damage to cell membranes, which has several negative influences in reproduction and on functions of the nervous system [13].

Available methods for low-level determination of rare earth ions in solutions include spectrophotometry, ICPMS, ICP-AES, isotope dilution mass spectrometry, neutron activation analysis, and X-ray fluorescence spectrophotometry [14–22]. All these methods are too expensive for most analytical laboratories. Potentiometric sensors can offer an inexpensive and convenient method for analysis of rare earth metal ions in solution, provided acceptable sensitivity and selectivity are achieved.

Cerium is the most abundant of rare earth elements and is found in monazite, ceric bastnaesite and silicate rocks. It is widely used in the production of ductile iron, cast iron and some stainless steels [23]. Therefore, the determination of cerium in different samples is of special interest.

Cerium (III) ion sensors have been reported by Shamsipur et al. [24–26] using 1, 3, 5 trithiane as an electro-active material. Recently, a cerium (III)-selective membrane electrode has been reported by Akhond et al. [27] using 2-amino benzothiazole. Tin (IV) antimonoarsenate prepared by Mittal et al. [28] showed selectivity for some rare earth metal ions. So, a novel inorganic ion exchanger zirconium (IV) antimonoarsenate was prepared and characterized by using analytical techniques, like IR, XRD, TGA, SEM and EDS. Distribution coefficient studies showed that it possesses selectivity for cerium (III) ions as compared to other rare earth metal ions. Thus, it was used for preparing a potentiometric sensor for Ce (III) ions.

2. Experimental

2.1. Reagents

Zirconyl oxychloride (LOBA Chemie, India), potassium pyroantimonate (BDH, England) and sodium arsenate (s.d. fine chem., India) were used for the synthesis. Cerium chloride and other rare earth chlorides were purchased from Indian Rare Earth Chemicals Ltd., India. Standard solutions for the analytical work were prepared either by direct weighing of AR grade reagents or by indirect standardization. All stock solutions of rare earth metal ions were standardized with EDTA using xylenol orange as an indicator. Double distilled deionized water was used throughout the experiment.

2.2. Instruments used

An electric thermostated oven was used for drying the sample. An ISFET 701 pH meter (Delta TRAK, INC., USA Model 24003) was used for pH measurements. X-ray powder patterns were obtained with a Rigaku Dmax III C instrument and a Debye Scherrer camera. Infrared studies were made with a Bomem, MB-104 spectrophotometer using the KBr pellet technique. TGA studies were done on Mettler Toledo Star System. SEM images were obtained by using a JEOL JSM 840A electron microscope. Polymer film making machine (Techno Search Instruments, India) was used for making the polymer membranes. EMF measurements were made using a digital potentiometer (Equiptronics EQ-602, Mumbai, India) with an accuracy of ± 0.1 mV.

2.3. Synthesis of zirconium (IV) antimonoarsenate (ZrSbAs)

Five samples of the exchanger were prepared by adding zirconyl oxychloride (0.1 M) solution to a continuously stirred solution of potassium pyroantimonate (0.1 M) and sodium arsenate (0.1 M) at 60 °C, in the volume ratio 2:1:1 under the conditions given in Table 1. Gelatinous white precipitates were obtained and pH of the gel was adjusted by adding either HCl or NaOH solution. Precipitates were filtered, washed with DMW until free from halides. The gel was air dried at 40 °C. Dried products broke down into small granules when immersed in water. The material was converted into the H^+-form by treating it with HCl (0.1 M) for 24 h with occasional