PHYSICOCHEMICAL SENSORS FOR THE DETERMINATION OF SILVER

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Abstract:

A novel silver sensor based on 3,7- dimethoxy -6-hydroxy benzofuran-5- carboxylic acid as an ionophore for ion-selective polymeric membrane electrode toward Ag^{+1} ions was examined. The sensor showed a near Nernstian response for Ag^{+1} ions over a concentration range $1x10^{-6}$ to 1.0×10^{-2} mol L^{-1} with a slope of 61± 0.4 mV per concentration decade in an acidic solution (pH 5). The limit of detection was 0.47 mg mL^{-1}. It had a response time of < 20 s and can be used for at least 3 months without any divergence in potentials. The influence of plasticizer as well as the amount of lipophilic anionic site additive in the sensing membrane was discussed. It was shown that membrane electrodes formulated with the ionophore and appropriate anionic additive exhibited enhanced potentiometric response toward Ag^{+1} over all other cations tested. Validation of the assay method revealed good performance characteristics, including long life span, good selectivity for Ag^{1+} ions over a wide variety of other metal ions, long term response stability, and high reproducibility. The sensors were used for direct measurement of silver content in different rocks collected from different geological zones. The results agreed fairly well with data obtained using atomic absorption spectrometry.

Key Words: Psysicihemical Sensors, Silver Determination

Introduction

'Heavy metals' is a general collective term applying to the group of metals and metalloids with an atomic density greater than 6 g /cm^3. Although it is only a loosely defined term it is widely recognized and usually applied to the elements such as silver, nickel, iron, lead, copper and zinc which are commonly associated with pollution and toxicity problems. Unlike most organic pollutants, heavy metals occur naturally in rock-forming and ore minerals and so a range of normal background concentrations is associated with each of these elements in soils, sediments, waters and living organisms. On an annual basis, significant quantities of various heavy metals are produced from the mining of their respective ores [1]. Industrial uses of metals and other domestic processes (e.g. burning of fossil fuels, incineration of wastes, automobile exhausts, smelting processes and the use of sewage sludge as landfill material and fertilizer) have introduced substantial amounts of potentially toxic heavy metals into the atmosphere and into the aquatic and terrestrial environments. Electrochemical sensors are simple, sensitive and selective devices for real-time monitoring of analytes of interest when properly designed.The development of chemical sensors for determination of heavy metals in the environment is of great importance from the ecotoxicological point of view [2]. For selective recognition, an efficient molecular receptor which has high potential as a complexing agent for a target heavy metal is required as sensing element [3]. Nowadays many compounds have been designed and synthesized to form remarkably stable and selective complexes with transition metal ions such as Schiffbases [4], podands [5], cyclams [6] and calixarenes [7]. Among them crown ethers containing nitrogen and sulfur donor atoms (i.e. azathiacrown ethers) are of special interest as they exhibit extremely high affinities toward heavy metal ions such as Ag^+, Hg^{2+} and Pb^{2+} [8–10]. Their selectivities and coordination abilities with transition metal ions depend on ring cavity size, ligand rigidity, the nature of donor atoms and their disposition [11]. In recent years, many azathiacrown ethers have been synthesized and successfully utilized for highly selective binding with heavy metals in diversal processes such as ion transports through artificial and natural membranes, liquid–liquid phase-transfer reactions and isotope separations [12–14]. Ion-selective electrodes (ISEs) are most frequently used potentiometric sensors for heavy metals due to high selectivity, good precision, low cost and simplicity. In recent years, the quest for improved lower detection limits of polymeric membrane ISEs has reinvigorated the search for better molecular receptors [3]. Several thiacrown ethers based on calixarenes have been explored as ionophores for heavy metals with lower detection limits [15,16]. Many crown ethers have been utilized as Ag+-ionophores [18,19]. However, most of them suffer from problems of complicated synthesis procedures and poor selectivities. However, so far there has been no report on the characterization of 3,7dimethoxy -6-hydroxy benzofuran-5- carboxy drazide as ionophores for the polymeric membrane ISEs for silver with improved lower detection limits. In the present work, we have designed potentiometric plasticized poly (vinyl chloride) membrane electrodes using this compounds as Ag^+-ionophore in terms of their selectivity coefficients and detection limits for Ag+. The selectivity towards Ag+ is tunable by altering the composition of donor atoms, ring size and ligand geometry [17]. The electrodes based on this ionophore show excellent affinities to Ag+. The effects of flexibilities of these ligands on the response of polymeric membrane Ag+-ISEs have been studied.

Experimental part

Equipments

All potentiometric measurements were made at 25 ± 1C with an Orion digital pH /mV using 3,7- dimethoxy -6-hydroxy benzofuran-5- carboxylic acid membrane sensor in conjunction with an Orion double junction Ag/AgCl reference electrode (Model 90-02) filled with 10 % W/W KNO_3 in the outer compartment, Orion combination pH electrode was used for pH adjustment.

Chemicals and Reagents

Ionophore (3,7- dimethoxy -6-hydroxy benzofuran-5- carboxylic acid) was prepared according to the recommended procedure. Analytical reagent grade chemicals , and bidistilled water were used for preparing all aqueous solutions. High molecular weight carboxylated poly vinyl chloride (PVC-COOH), *o*-, nitropheny octyl ether (*o*-NPOE), Dibutyl sebacate (DBS), Dioctyl phthalate (DOP) and (THF) tetrahydrofuran were obtained from Fluka. Stock solutions (10^{-1} M) of different metal salts (chloride, sulfate, nitrate) were prepared form reagent grade chemicals.

Preparation of 3,7- dimethoxy -6-hydroxy benzofuran-5- carboxylic acid

0.01mmole khellin and 50 ml of 30% of H_2O_2 was mixed and stirred for 30 min. , the resulting compound was completely dissolved. The undissolved residue was Filtered, and the filtrate was acidified by hydrochloric acid to precipitate 3,7- dimethoxy -6-hydroxy benzofuran-5- carboxylic acid and the product was crystallized from ethanol. The structure(Fig. 1) was comfermed by elemental analysis ,I. R spectrophotometry ,HNMRspectra and mass spectra.

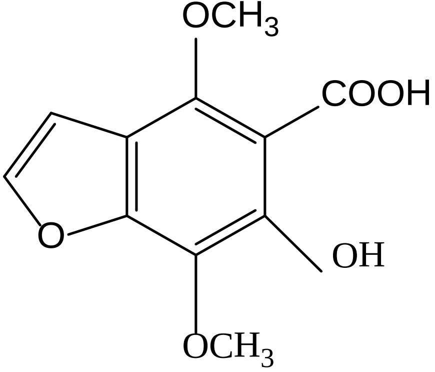


Fig.1 structureormula of 3,7 dimethoxy -6-hydroxy benzofuran-5- carboxylicacid

Construction and characterization of the sensor

PVC-membrane sensor based on 3,7dimethoxy -6-hydroxy benzofuran-5- carboxylic acid as ionophore was prepared as described elsewhere [18] using 3 mg of the ionophore, 130 mg dibutyl sebacate(DBS) as plasticizer, 65 mg PVC as matrix, 1 mg of tetra dedocyl methyl ammonium chloride (TDMAC) as lipophilic anionic site additive and about 3 ml of THF as solvent. The cocktail in a Petri- dish of a diameter 3 cm was mixed well and left to stand overnight at room temperature.

Working sensors were assembled by cutting 5 mm diameter disks of the prepared membrane and mounting these disks into glass electrode bodies (ISE-561, glasblaseri Moller, Zurich). A solution consisting of equal volumes of 10^{-2} M $AgNO_3$ and KNO_3 is adjusted to pH 5.5, and used as internal filling solution. Before use, the membrane sensors were conditioned overnight in 10^{-2} M $AgNO_3$ solution. A standard stock solution of 10^{-1} M $AgNO_3$ was prepared. A series of diluents concentrations prepared with buffer acetate pH = 5 and another series of diluents concentrations prepared by 10^{-3} KNO_3 of pH = 5. The potentials were plotted against concentration for two different buffer solutions for the Ag^+ sensor based on ionophore ,to clarify the effect of type of buffer on the sensor.

EMF measurements

All measurements were carried out at 25ºC with cells of the following type: Ag/AgCl / KCl (0.1 M) / 0.1 M KNO_3 / sample solution //sensor membrane// internal filling solution / AgCl / Ag. Sensors calibrations were carried out by measuring the potential of 10^{-6} – 10^{-2} M $AgNO_3$ solutions starting from the low to high concentration. The sensor in conjunction with a double junction Ag/AgCl reference electrode was immersed in 50 ml beaker containing l ml of 10^{-1} M $AgNO_3$ and 9 ml 10^{-3} KNO_3 of pH = 5 and more diluted solution from 10^{-6} – 10^{-2} M were prepared by the same way. The potential change for each concentration was recorded. A calibration curves were constructed by plotting the potential change against logarithm Ag(I) concentration. The lower detection limits was taken at the point of intersection of the extrapolated linear segments of the silver (I) calibration curve. Sensor life span was examined by repeated monitoring of the slope of silver calibration curve.

The effect of membrane composition

Studies incorporating varying weight of ionophore (20 mg, 15 mg, 10 mg and 5 mg), 190 mg PVC and 350 mg of DBS with 5 ml THF in 50 mm diameter ground glass. The potential of $AgNO_3$ solutions starting from the low to the high concentrations were carried and the potentials were plotted as a function of logarithm silver ion concentrations. Two different types of PVC, PVC-COOH were used in the preparation of two different membranes with the same ionophore and (DBS) as plasticizer. The membranes were prepared as described above and the slope, linear range and the lower limit of detection of each membrane were determined.

Effect of pH and dynamic response time

The effect of pH was tested by measuring the potential at pH values ranged 2-10 in Ag (I) ions solutions of 10^{-4} – 10^{-3} M . The pH was adjusted by NaOH or HNO_3 dilute solutions. The corresponding mV readings were recorded after each addition. The pH dependences on silver sensors were examined by plotting the change of potential against pH values. Dynamic response times of the electrodes were measured in constantly stirred solution of varying Ag (I) concentrations during 180 sec period for each concentration, and examined by plotting potentials as a function of time.

Selectivity of membrane sensor

Selectivity coefficients $K^{POT}_{AgNO_3}$ of $AgNO_3$ sensor were measured using the separate solutions method [19]. In this method the potentials of the cell containing Ag ionophore sensor in conjunction with double junction Ag/AgCl reference electrode were measured independently for each of two separate solutions for all concentrations. Then, the activates that correspond to the same sensor potential were used to determine $K^{POT}_{AgNO_3}$ and can be calculate selectivity coefficient using equation.

$$- \text{Log}\ K^{pot} = E_M - E_{Ag} / s$$

Where E_{Ag} and E_M are the response potentials of the sensor for silver nitrate ion and interference M, respectively at 10^{-3} M and S is the sensor slope (mV/decade $^{-1}$) potentials are recorded for concentration from low to high analytical application.

Analytical Application

Direct Potentiometric determination of silvers

These sensors in conjunction with a double junction Ag/AgCl reference electrode were immersed in a fixed volume of $AgNO_3$ with fixed concentration and 0.1 M of NaCl were successively added and the potential change for each addition was recorded. This process repeated three times with different concentration of Ag^+ in a fixed 10 ml volume. Titrations were plotted for three sensors based on ionophore and the equivalent volumes were determined.

Results and Discussion

Sensor characteristics

Direct potentiometry with chemical sensors provides a selective, precise and fast method for monitoring of various metal ions including silver at low concentrations. Silver **-** ISEs have been intensively studied and extensively used for the formation of coordination networks based on the binding of silver. In preliminary experiments, the new sensitized ligand combined with various plasticizers used to prepare PVC membrane selective for Ag ions. The performance characteristics were evaluated under many different variables such as type of PVC, plasticizer (solvent mediator), the influence of pH, effect of internal solution concentration of the electrode Potentiometric response of sensor based neutral ionophore is greatly influenced by the polarity of the membrane medium, which is in turn defined by the dielectric constants of the major membrane components. Silver PVC-COOH matrix membrane incorporating three different plasticizers having dielectric constants 4-24 namely DBC,DOP and NPOE The results indicate that, Performance characteristics of membrane incorporating PVC-carboxylated with (DBS) plasticizer and 10^{-2} M internal solution showed high sensitivity, wide linear response range and near Nernistian slope at pH 5 as tabulated in table1. The results showed that the sensor displays a linear response for Ag^+ over the concentration range $1x10^{-2}$ $-1x10^{-6}$ M with a detection limit $5.0x10^{-6}$ M and a calibration slope of 61±0.2 mV/decade, the slope of sensor is near to the theoretical Nernstian value. In the light of the soft heavy metal ions displaying great affinity for soft coordination centers like nitrogen, sulfur or oxygen. We try to explain the properties of the electrodes in terms of coordinating ability of the O atoms in ionophore. The coordination interaction between electron donors and acceptors cause the electrode to respond to metal ion.

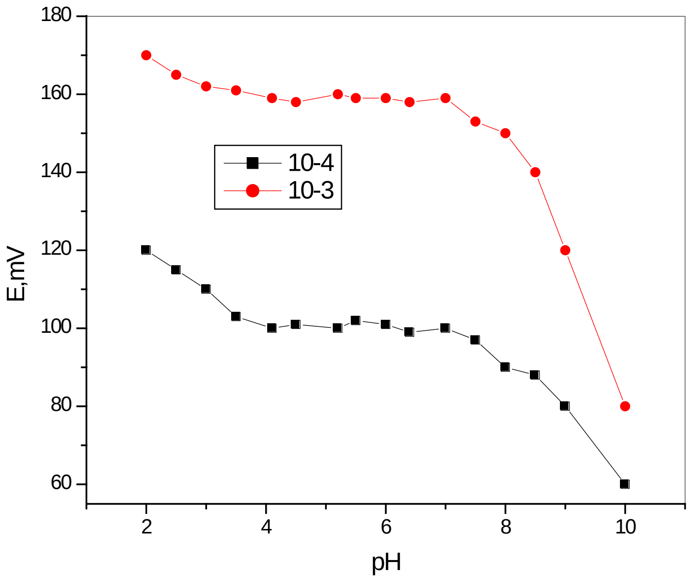


Fig 1. Effect of the pH on the potential of the proposed sensor

Parameter	Silver sensor
Slope,(mV/decade)	61.1
Working concentration range (M)	10^{-6} -10^{-2}
Lower limit of detection, (M)	$5x10^{6}$
pH range	4-7
Correlation coefficient,(r)	0.99994
Standard deviation	0.94868

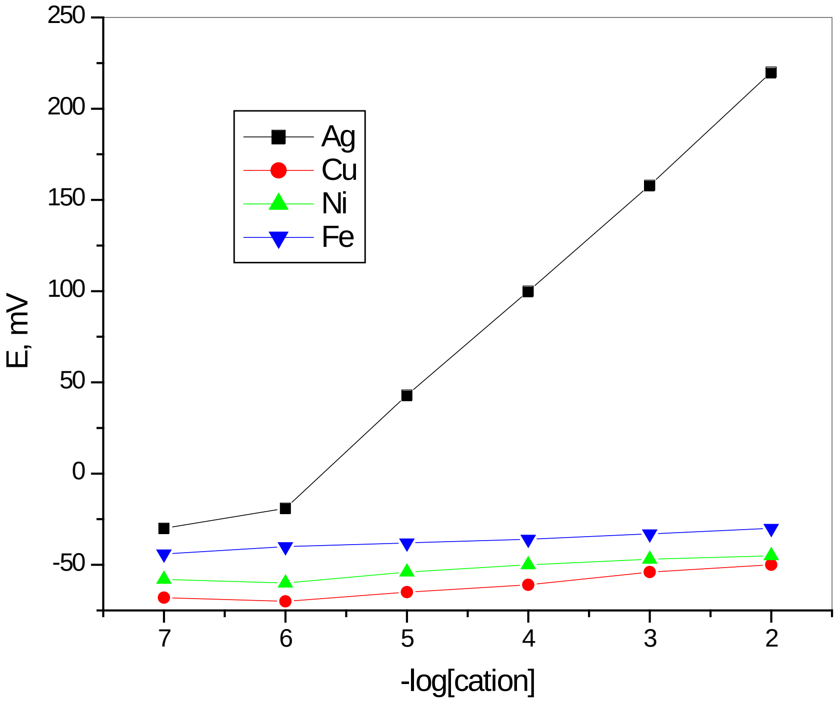
Table 1. Performance characteristics of silver sensor

Selectivity of Sensor

The most important characteristic of a membrane sensor is its response for the primary ion in the presence of other cations. This is measured in terms of the potentiometric selectivity coefficients (Robert et al.,2000)with 10^{-3}M concentration level of alkali, alkaline earth and transition metal ions. The results obtained (Table 2.9) (Fig. 2.17) (Fig. 2.18) (Fig. 2.19) For the ionophore (I) (II) (III) respectively**.**

Potentiometric selectivity coefficients of Ag-sensor (II) membrane based sensor for some common cations were evaluated using the separate solutions method (SSM),(Ma andHassan,1982).It can be seen from Table (2.9) that (I) (II) (III) sensors exhibits high selectivity towards Ag^+ ions over many of the ions under investigation. The selectivity was measured for 10^{-3}M concentration of the analyte and the interferents.

Fig. 2. Comparision of the reponse characteristics of silver sensor with silver and ther cations



Concolution

Silver sensor based on 3,7- dimethoxy -6-hydroxy benzofuran-5- carboxylic acid as an ionophore was constructed. The sensor showed response for Ag^{+1} ions over a concentration range $1x10^{-6}$ to 1.0×10^{-2} mol L^{-1} with a slope of 61± 0.4 mV per concentration decade in an acidic solution (pH 5). The limit of detection was 0.47 mg mL^{-1}. It had a response time of < 20 s and can be used for at least 3 months without any divergence in potentials. The influence of plasticizer in sensing membrane was discussed. It was shown that membrane electrodes formulated with the ionophore and appropriate anionic additive exhibited enhanced potentiometric response toward Ag^{+1} over all other cations tested. Validation of the assay method revealed good performance characteristics, including long life span, good selectivity for Ag^{1+} ions over a wide variety of other metal ions, long term response stability, and high reproducibility. The sensors were used for direct measurement of silver content in different rocks collected from different geological zones. The results agreed fairly well with data obtained using atomic absorption spectrometry.

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