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International Journal of Current Research
Vol. 5, Issue, 08, pp.2176-2178, August, 2013

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

CALCIUM ION SELECTIVE ELECTRODE BASED ON SCHIFF BASE AS AN ELECTRO ACTIVE MATERIAL – ITS PREPARATION AND ANALYTICAL APPLICATIONS

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ARTICLE INFO

Article History:
Received 06th May, 2013
Received in revised form
25th June, 2013
Accepted 08th July, 2013
Published online 23rd August, 2013

Key words:

Calcium ion selective electrode,
Potentiometry, Schiff base,
Poly vinyl chloride.

ABSTRACT

A new schiff base based membrane ion selective electrode has been developed. The ion selective electrode system prepared used without an internal solution contains dioctyl phthalate (plasticizer) and sodium tetra phenyl borate (anion excluder). The electrode reveal a Nernstian behavior in linear concentration range of 1M to $1x10^{-4}M$ with detection limits of the order of $10^{-4}M$. The stable potentiometric signals are obtained within a short time period of 1 minute. The effect of pH, and the effect of medium have been studied to found a better response. Selectively coefficient values were evaluated. The sensors have also been used as an indicator electrode in potentiometric titrations of Ca (II) ions with EDTA and determination of concentration of Ca^{2+} in milk and hardness in water samples.

INTRODUCTION

Calcium is an essential element for humans, and is also responsible for 'water hardness', a water quality parameter frequently tested in industrial plants and municipal water treatment facilities. Calcium is biologically required for numerous functions, such as building and maintaining the bones and teeth, blood clotting, transmitting of the nerve impulses and regulating heart's rhythm (Vickackaite, Tautkus and Kazlauskas, 2007). Milk and dairy products are convenient sources of calcium for many people (Lanou, Berkow and Barnard, 2005). Drinking water is an important source of calcium in the elderly, particularly because of increased needs and decreased consumption of dairy products (Marque, Jacqmin-Gadda, Dartigues and Commenges, 2003). Therefore, low-cost, sensitive and selective methods are necessary to determine this ion. Potentiometry with ion-selective electrodes (ISEs) may be a technique of choice for a continuous and automatic analysis (Alexander, Dimitrakopoutos and Hibbert Electroanalysis, 1998; Di Benedetto, Dimitrakopoutos, Farrell and Iles 1997; Bratov, Abramova, Munoz, Domínguez, Alegret and Bartrolív, 1995). ISEs are extremely simple, cheap, and applicable to in situ measurements. Despite the name, ISEs are often non-selective devices as they are based on ionophores designed for complexing, interacting, holding the analytes in a molecular cavity etc. This type of interactions is actually non-specific so that interference from other species with similar size and charge commonly appear. Thus, the selectivity of measurements is often not sufficient to enable the primary ion to be analyzed without significant errors caused by additional components of the sample matrix, changes in the pH, etc. Great efforts have been expended over the past 25 years to synthesize of more selective ionophore to elaborate sensors. Commercial calcium electrodes also suffer from interferences, matrix effects and lack of day-to-day reproducibility that may affect seriously the accuracy of the analysis (Sales, Callao, Rius, 1999). Today, many techniques have been used for the calcium determination such as mass spectrometry, gas chromatography, atomic absorption spectroscopy. However, the utility of ion-selective electrodes (ISEs) is being increasingly realized by analytical chemists in view of the rapid growth of industry and technology all over the world, as they represent a rapid, accurate and low-cost method of analysis (Faridbod, Ganjali, Dinarvand and Norouzi 2007; Faridbod, Ganjali and Norouzi, 2008; Ganjali, Norouzi, Faridbod, Rezapour and Pourjavid, 2007; Faridbod, Ganjali, Dinarvand and Norouzi, 2007; Javanbakht, Ganjali, Norouzi, Abdouss and Riahi, 2008). Schiff's bases belong to a widely used group of organic intermediates important for a production of chemical specialties, e.g. pharmaceuticals, or additives to rubber. A basic reaction synthesis involves an aromatic amine and aldehydes (Schiff Justus Liebigs, 1867; Cordes, Jenks, 1962; March, 1992). The condensation of primary amines with aldehydes and ketones has a numerous application (Patai,1970), for preparative, detection, determination and purification uses. Potentiometric Sensors prepared by coating polymeric films containing electroactive species on metallic or graphite conductors (Azzouz, 2010) with no internal electrolyte solution are known to be very effective for a varity of cations and anions ;. Electrodes of this type are advantages in terms of simplicity, durability, high mechanical durability, low cost and they are capable of reliable response over a wide concentration range.

Experimental part

Salicylaldehyde (merck), Poly vinyl chloride (PVC), Dioctyl phthalate (DOP) and sodium tetra phenyl borate (NaTBP), tetra hydro furan (THF) were obtained from E.Merck. All other reagents such as calcium chloride ($CaCl_2$), Magnesium chloride ($MgCl_2$) and Sodium chloride (NaCl) were of analytical grade all the solutions were prepared using the deionized water

Preparation of Schiff base

For preparing Schiff base, Salicylaldehyde solution was mixed with glycine and the mixture was stirred. Sodium hydroxide solution (1M)

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is added dropwise to the mixture and the final mixture was left for 15 minutes, filtered, washed with cold ethanol and dried (Azzouz, and Ali 2010). The FTIR spectra of prepared salicylidene glycine were recorded by using Testscan Shimadzu Prestige-21 series and the spectrum illustrates in Fig 1 shows the following wavenumbers:-

1. A broad stretching wavenumbers range between (3385.41-3424.33) cm^{-1} which confirm OH group in the carboxyl group of Schiff bases.
2. A strong to medium intensities bands are assigned to carbon nitrogen double bond i.e C = N, with stretching frequency range between 1618cm^{-1} (R.M.Silverstein and G.C.Bassler).

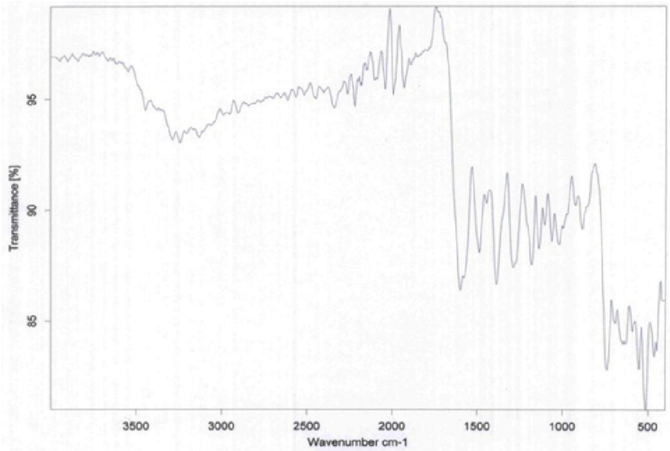

Fig. 1. The IR absorbtion spectrum of salicylidene glycine Electrode Response

Preparation of membrane electrode

0.2g of prepared schiff base and 0.1g of DOP and NaTBP was dissolved in 3 ml of THF and a clear solution was evaporated. A copper wire was polished with emery paper and it was washed with methanol, water and THF.Polished and clean surface end of copper wire was dipped in concentrated solution for a minute, non-transparent coating was formed. The electrode was removed and dried overnight at room temperature. The main advantage of this electrode is no internal solution is required. The membrane was conditioned for 48 hours to attain equilibrium in 1M $CaCl_2$ solution and later the EMF measurements were carried out using the following cell assembly,

Internal reference Electrode Ag/AgCl	Schiff base coated copper wire (working electrode)	Sample Solution	External reference electrode (SCE)

RESULT AND DISCUSSION

The electrode was first conditioned in 1M $CaCl_2$ solution to attain stable equilibrium. In order to test the performance of the electrode; various parameters including response time, selectivity, and the influence of pH were investigated. The electrode was used over a period of 4 month with good reproducibility. The electrode was kept in de ionized water throughout the study.

Response characteristics of the electrode

The electrode potential for a series of standard solution of Ca (II) ions was measured. The electrode gave a linear response to Ca (II) concentration in the range of 1M to 1x 10^{-4} M. The values are given on Table 1. Standard Electrode potential (E^0) determined by extrapolation method was found to be +0.215 V. The slope value was found to be 43 mv/decade. This shows that the electrode behaves according to Nernst equation.

Table 1. Electrode response for Ca^{2+} ions

S.NO	Concentration of $CaCl_2$ solution (M)	EMF (volts)
1	1	0.214
2	$1x10^{-1}$	0.172
3	$1x10^{-2}$	0.111
4	$1x10^{-3}$	0.084
5	$1x10^{-4}$	0.044
6	$1x10^{-5}$	0.044

Effect of pH

To study the effect of pH, a standard solution containing 1M $CaCl_2$ ion were prepared in which a series of buffer solution was added. It was found that the potential remained unchanged with in the pH range of 1 to 6 which is found to be the working pH range for the electrode.

Effect of medium

To study the effect of medium, a standard solution containing 1M $CaCl_2$ ion in a series of 25%, 50%, 75%, ethanol, Acetone and Dimethyl formamide, Dimethyl acetamide was added. It was found that the potential remained unchanged in above medium.

Selectivity

The selectivity which is an important characteristic of a membrane sensor is measured in terms of the potentiometric selectivity coefficient. The reduced form of Eisenman's equation given below is often used to calculate the selectivity co efficient K_{Ca}^{pot}

$$\text{Log } K_{Ca}^{pot} = \frac{(E_1 - E_2)}{S} - \left(\frac{n}{Z} - 1\right) * \text{Log}[a]$$

Where E_1 and E_2 are the potentials measured in 1 M solutions of interfering ion and Ca^{2+}; S is the calibration slope, n and z are the charges of Ca^{2+} and interfering ions respectively and [a] is the concentration of the ions used. In this method, the concentration of primary ion,Ca(II) ion is varied where as the concentration of secondary interfering ions is kept constant in the test solution which is $1x10^{-1}$ M, concentration of interfering ion present case. It was found that the potential remains unaffected in the presence of a series of various cation like Na^+ ,Mg^{2+}, Cu^{2+}, K^+,and anion like I^-, Br^-, Cl^-.

Analytical applications, Potentiometric titration

The practical significance of the sensor was tested by using as an indicator electrode for potentiometric titrations of Ca $^{2+}$ with EDTA solution. Before the end point, the potential shows usual logarithmic change with the volume of the titrant added while the potential response after the end point remains almost constant. It is shown in Figure.3. To asses the applicability of the sensors to real samples an attempt was made to determine calcium ion in real samples like milk, water samples. The recovery of calcium ion in sample analysis was formed to be quantitative with the maximum recovery of 99%.

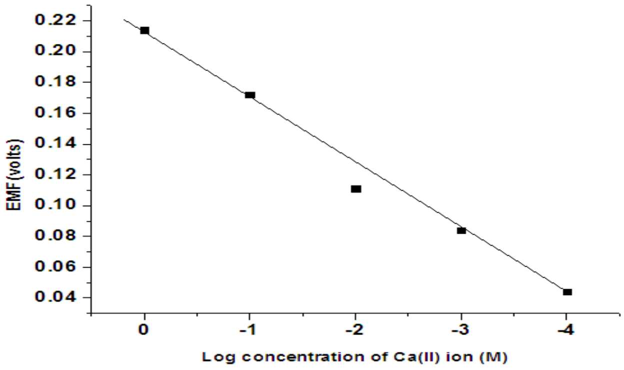

Fig. 2. Plot of log concentration of Ca(II) ion(M) Vs EMF (volts)

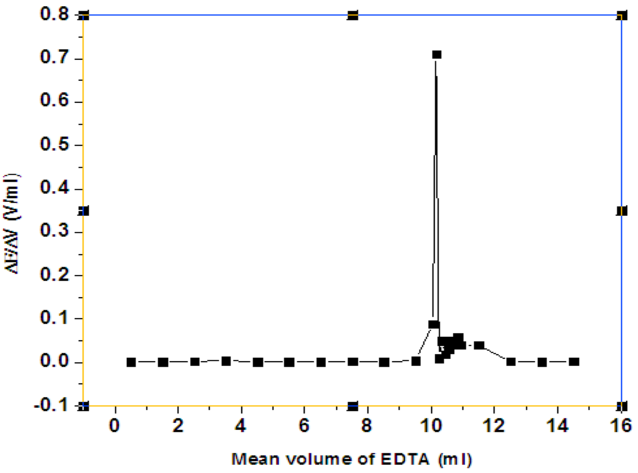

Fig. 3. Plot of mean volume of EDTA (ml) Vs ΔE/ΔV (volts)

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