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Short Review Paper

Lead(II)-selective Ionophore based electrochemical sensors - A mini review

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Abstract

The recent advances in lowering the detection limits of ISEs, including fresh methodologies of emerging electrochemical sensors and advances in detecting ultra-small amounts of ions at low concentrations. These progresses have covered the mode to use polymeric membrane based ion selective electrode as in ultra-sensitive affinity bio analysis in aggregation with nanoparticle because of the toxic effect of lead (II) ion, it is needed to examine lead(II) spreading in water resources. This may be accomplished by execution of electrochemical sensors with low detection limit and greater selectivity towards lead(II) ion. Number of ionophores were created and studied for lead(II) ion detection. In this paper Pb(II) ion-selective ionophores based on last 6 year work are collected and gives a general explanation and review on the developed and existing ionophores for Pb(II)-selective electrochemical sensors.

Keywords: Electrochemical sensors, Lead, Ion selective electrode(ISE), Nanoparticle, Ionophore.

Introduction

As compared to optical methods electrochemical techniques deals with numerous benefits associated to their simplicity, price and in-field application probability. The electrochemical methods like potentiometric and voltammetric methods are the highly described for the detection of heavy metals ion[1]. Potentiometry, records on the sample conformation is gained and identified by the change in potential at the two electrodes. Most common methods of potentiometric sensors are field-effect transistors (FETs) and ion selective electrodes (ISEs) sensors, having longest history. These are associated with the fundamental membrane science and related to the host–guest chemistry. Numerous developed ISEs have been used for the determination of activities of heavy metal ions at ultra-low level[2]. The main point to achieve a consistent and good electrochemical sensor fabricate on that type of substance which creates the finding raised area. With advancement in the progress of innovative electrochemical transducing display nanomaterials have carried many benefits on next to their application as electrochemical markers or labels for improvement in signal with curiosity for sensor technologies[3]. Due to the exclusive characterstics of nano materials like chemical, electronic and mechanical (e.g. graphene, metal nanoparticles, carbon nanotubes,) create the electrochemical sensors exceptionally eye-catching in contrast to conventional ingredients[4]. using nano structured Sensing constituents proceeds improvement of the enlarged surface are aelectrode, fast electron transfer, better mass-transport rate, and associated to bulk constituents based electrodes[5]. The collaboration between nano materials technology and electrochemical sensors techniques is supposing to fetchattention-grabbinggains in the field of detection of heavy metals and consequently an encouraging development and research area. The aim of this review is to provide an outline on the up-to-date trends in the growth of electrochemical sensors for the detection of Lead during the previous few years even though their comparatively having a longer history.

Lead ions

The contamination of environment by toxic metal ions in ecosystems has been increased with industrial progress and enlargement in recent years[6]. Lead(Pb) is one of the element which has a large scale industrial use and is broadly used in paints, alloys, storage batteries, in solder for electronics, high quality glass and is used for radiation shielding. Lead is generally recognized as highly toxic and non-biodegradable. It is a effective neurotoxin and a carcinogen, also causes lung disease, stroke, high blood pressure, kidney problems etc. Plumlee et al. reported instantaneous and severe consequence of Pb toxicity in young children viaPb-contaminated soil, food and water. So, it is important to detect and sensibly monitor the total amount of Pbexisting in drinking water. Prolonged Pb intoxication destructively disturbs the biosynthesis ofhemoglobin[7]. The reason of the dementia that influences various Roman Emperors was because of lead acetate (called as lead sugar) swallowing as a sweetener for wine by the Roman Empire. The US Environmental Protection Agency (EPA) and the World Health Organisation (WHO) bear a maximum amount of Pb in drinking wateris 0.05 mg. The Pb(II) ion in solution existing in forms as $PbOH^+$, $Pb3(OH)_4^{2+}$, $Pb_4(OH)_4^{4+}$, $Pb_6(OH)_8^{4+}$ and $Pb_9(OH)_{12}^{6+}$ have been found and they are easily molded in neutral and slightly alkali solution. Therefore the trace level determination of Pb is persistent research attentiveness due to its harmful effects and accumulation in the biological system and environment[8,9]. The numerous approaches such as Spectrophotometric techniques, atomic absorption spectroscopy–electro thermal atomization (AAS–ETS), chromatography photometry, inductively coupled plasma–optical emission spectroscopy (ICP–OES) and inductively coupled plasma–atomic emission spectroscopy (ICP–AES) are applied for the low to low level detection of Pb(II) ions in solution[10,11]. However these approaches generally wants sample pre-treatment and provision back up so, these are not appropriate for repetitive analysis. The potentiometric sensors are very appropriate due to its benefits such as simplicity, good precision, high selectivity, sensitivity, and low price. Ion selective electrodes (ISEs) are versatile equipments with astonishing analytical procedures[12,13]. Maximum existing potentiometric sensors are constructed as ion selective electrodes based on ionophores[14,15]. Numerous neutral complexes used as ionophores have been with nitrogen, sulphur and oxygendon or atoms for Pb(II) ion selective sensors[16].

Overview of Pb(II) ionophores

Presently the well-known commercially available thioamide derivative lead(II) selective ionophore is *p-tert*-butylcalix[4] arene which is commercialized as *lead ionophore IV* [17] (Structure of Ionophore Figure-1).

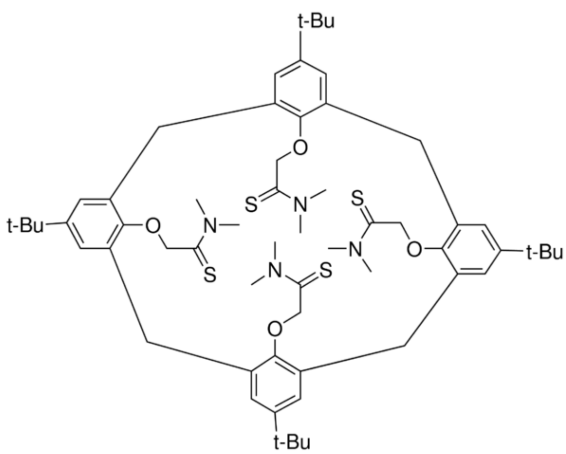

Figure-1: Lead ionophoreIV(22).

We all know that sulphur atom containing ionophore show more affinity towards Pb(II) ions and lead(II) cations fits into the chelation of calix[4]arene. But these type of ionophores affecting by choosiness over silver (Ag) (II) ion since the Ag(II) ions having a more affinity compared to Pb(II) ionsthioamide derivatives having this characteristic. One more type of ionophore (butyl-3-(2-phenylhydrazono) indolin-2-one) used for Pb(II) ion which was considered with near to Nernstian response of 31.0 mV dec^{-1} toward Pb(II) ion and it is fairly better selectivity toward lead(II) as compared to the other ions[18]. Thision selective electrode was apply to detectlead(II) in real sample (mineral rock). (Ionophore structure in Figure-2).

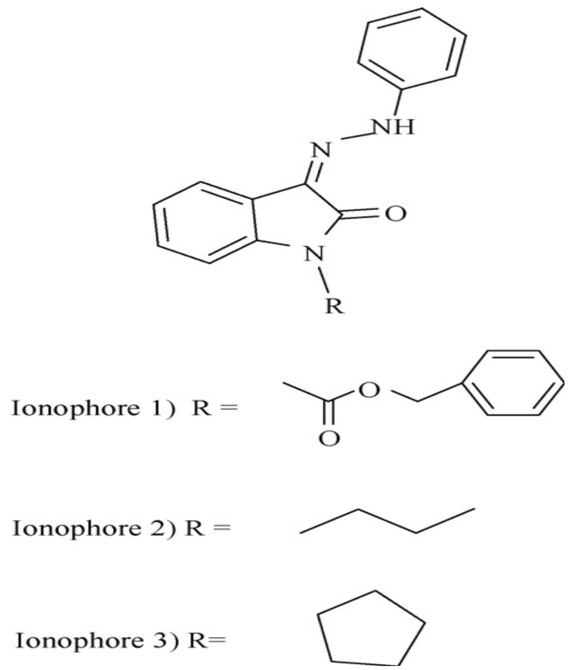

Figure-2: Chemical structure of ionophores butyl-3-(2-phenylhydrazono) indolin-2-one(24).

Lead(II) were also examined by using Bis-thiourea[19]. 1,3-bis (N-benzoylthioureido) benzene ionophore and 1,3-bis(N-furoylthioureido) benzeneionophore were worked as electrochemical sensors (Figure-3). The Nernstian response is (31.5 mV dec^{-1} and 30.0 mV dec^{-1}, respectively). These electrodes were apply to detect Pb(II) in sample of soil. This gave a good accord with ICP-MS.

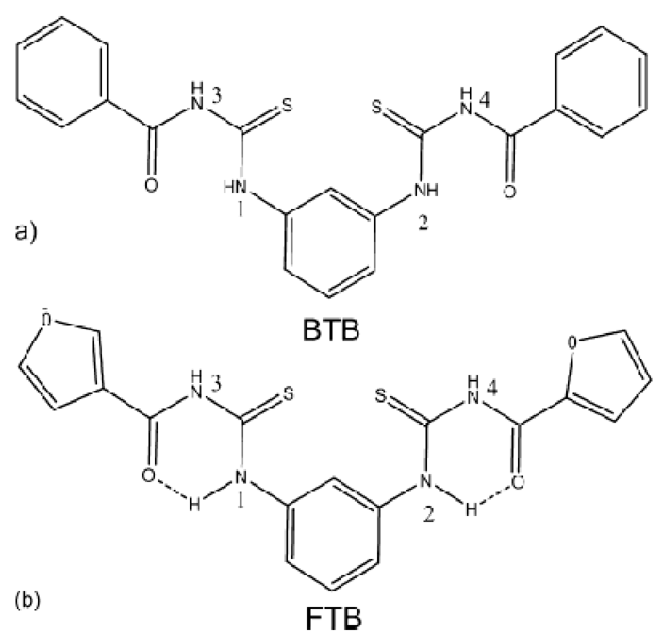

Figure-3: Structure of bis-thioureas used as ionophores. (a) 1,3-bis(N-benzoylthioureido) benzene (BTB) and (b) 1,3-bis(N-furoylthioureido) benzene(FTB).

Singh et. al investigated derivatives of two podand, one is 1,5-bis(2'-hydroxy-4'-nitrophenoxy)-3- thiapentane (L1) and other is 1,5-bis(8'-oxybenzopyridine)-3-thia pentane (L2), ionophoresused as Pb(II) selective[20]. The electrodes response near to Nernstain slope and shows good selectivity towards lead(II) ion. These electrodes applied to tested lead(II) ion in real sample (Industrial waste water sample and Hindon River). The obtained results shows good agreement with ICP-MS and AAS methods. Huang et.al was proposed a solid ionophore based on semi-conducting poly (mphenylenediamine) microparticles[21]. The copolymer microparticles comprising many ligating functional groups including amino, imino and sulfonic groups were synthesized by a chemical oxidative copolymerization of m-phenylenediamine (mPD) and p-sulfonic-m-phenylenediamine (SPD) in pure water. Due to the presence of –NH–, –N], $-NH_2$, and $-SO_3H$ ligating groups on the microparticles, a linear Nernstian response is obtained. The proposed electrode could make for a robust sensor performing credible analysis of Pb(II) concentration in real-world samples at trace levels. The acquired selectivity coefficients indicated realistic selectivity towards lead(II) ion. In potentiometric titration these electrodes were also worked as indicator electrodes and were applied to examines real samples (river and tap water, human urine). Inamuddin et al. proposed Pb(II) ion-selective electrode membranes were fabricated by using solution casting method using carboxymethyl cellulose Sn(IV) phosphate composite cation-exchange material[22]. The membrane electrode showed near Nernstian response of 28.05 mV decade^{-1}. The proposed electrode was found selective for Pb(II) in the existence of alkali and alkaline earth metal ions.

It was also active as an indicator electrode. Guo and co-workers investigate ionophore multi-walled carbon nanotubes (2-aminothiophenol (MWCNTs) derivative as Pb(II) selective. The membrane configuration of the ion selective was improved with near Nernstainslope. The electrode was effectively used to detect the Pb(II) ions concentration in real samples, e.g. Pb(II) waste accumulator, soils, black tea, and waste waters. The obtained data were good agreement with AAS method. Pazik et. al investigate dionophoresbis (phenylhydrazono-1H-tetrazol-5-yl-acetonitriles) derivatives as Pb(II)ion selective[23]. This work was concentrated on metal-ligand interactions by spectrophotometrically. The electrodes observed near to Nerstianslope for Pb(II) ion. Kumar P. et. al developed the Glassy carbon electrodes (GCE) and carbon paste electrodes (CPE) were modified with imidazole functionalized polyaniline for lead (II) in both acidic and basic aqueous solution[24]. The limit of detections obtained with glassy carbon electrode and carbon paste electrode are 20 ng mL^{-1} and 2 ng mL^{-1} of lead ion, respectively. An interference study was carried out with Cd(II), As(III), Hg(II) and Co(II) ions. Cd(II) ions interfere significantly (peak overlap) and As(III) has a depressing effect on the lead signal. The sensing performance of Pb(II)-ion selective membrane sensors has not been investigate properly until date, is not predominantly remarkable, further investigations on its sensing capacity as Pb(II) ionslectiveionophore are significance implement taking into account its outstanding lower limit of detection. Several Pb(II)ion selective sensor response behaviour are mentioned in the Table-1.

Table-1: Response characteristics of lead(II)-selective electrodes based on some porphyrins as ionophores.

Ionophore	Linear Range (M)	Slope (mV decade^{-1})	Detection limit (mol·L^{-1})	References
Polyaniline–titanium(IV)phosphate	1.0×10^{-8} - 1.0×10^{-1}	29.48	1.0×10^{-8}	25
1-((3-((2-Hydroxynaphthalen-1-yl)Methyleneamino)-2,2-Dimethylpropylimino) Methyl) Naphthalen-2-ol	1.0×10^{-6} - 1.0×10^{-1}	25.79	4.0×10^{-7}	26
Schiff base complex [Co-(E)-(3-aminopyridin-4-ylimino)methyl) -phenol(ClO4)·(C3H6O)·(H2O)	7.9×10^{-5} - 1.0×10^{-2}	23.9	4.6×10^{-6}	27
1, 2-bis(N'-benzoylthioureido) benzene	6.3×10^{-8} - 3.9×10^{-2}	30.37	2.5×10^{-8}	28
Ionic liquid	1.0×10^{-8} - 1.0×10^{-1}	29.80	4.3×10^{-9}	29
3,7,11-tris (2-pyridylmethyl)-3,7,11,17-tetraazabicyclo [11.3.1] heptadeca-1(17),13,15-triene	10^{-6}-10^{-1}	28.50	8.0×10^{-7}	30
Polyphenylenediamine	3.1×10^{-6} - 3.1×10^{-2}	29.80	6.3×10^{-7}	31
Multi-walled carbon nanotubes	5.9×10^{-10} - 1.0×10^{-2}	29.50	3.2×10^{-7}	32
Multi-walled carbon nanotubes (MWCNTs) and nanosilica	1.0×10^{-7} - 1.0×10^{-2}	29.80	7.3×10^{-8}	33
Phenyl hydrazone derivative–carbon composite	7.7×10^{-7} - 1.0×10^{-1}	29.46	3.2×10^{-7}	34
Copolyaniline Nanoparticles	1.0×10^{-10} - 1.0×10^{-3}	29.30	2.2×10^{-11}	35
2,20-[1,3-Phenylenbis(methylidynenitrilo)]bis-[benzenethiol] (C20H16N2S2)	1.5×10^{-6} - 1.3×10^{-1}	29.10	9.0×10^{-7}	36

Liquid-state-contact based sensors are credible to substitute by Solid-state-contact based sensors and improve sensors of the next-generation. Even though 30 years ago a solid-state-contact based sensor was described, and primarily used as a Pb(II) ion-selective sensors merely in current years. It was noted that Pb(II) ion selective sensors based on solid-state-contact have quiet problems, e.g., the transducer film is liable to immersion of wetness to build up a layer of water; due to which inside the membrane sensor the redox reactions occurs very fastly. These type of difficulties continually drops the potential and bound the lifetime and reproduciability of the membrane sensors in valuable uses. Whenever these difficulties are conquer positively, solid-state-contact based type sensors can completely show their valuable potential benefits, like simplicity of reduction, great sensitivity, movability, and will unquestionably grow into the chief kind of Pb(II)ion slectivesensors. Nanoparticle-modified electrodes possess higher surface area, improved electron transfer rate, increased mass-transport rate, lower solution resistance, and higher signal-to-noise ratio[37,38]. Au NPs have been used to modify bulk electrodes[39,40]. It has been demonstrated that Au NP-modification of glassy carbonelectrodes eliminated the memory effect and interferences of other ions from intermetallic compounds. So authors used nanomaterial based electrode for the detection of lead ion. Bagheri et al. utilized MWCNTs with triphenylphosphine and ionic liquid for sensitive and real-time analysis of Pb(II)[41]. 4-methoxybenzylideneamino-2-thioxothiazolodin-4-one as a newly synthesized Schiff base with MWCNTs was constructed and suitably performs the accurate detection of Pb(II) and Hg(II) ions in various real samples up to nano-molar levels[42].

Conclusion

Comparison to those instruments which are used for large-scale investigation such as inductively coupled plasma mass spectrometry(ICPMS), fluorescence spectrometry, atomic absorption spectrometry(AAS) and potentiometry has lower selectivity and sensitivity. Nevertheless, the great tolerance to the analysed sample; low-priced, easy to maintenance and operate and movability of the potentiometric ion selective ionophore based sensors simplify its wide-ranging application in the areas such as medical treatments, mass-oriented regulations and scientific research. Moreover, these remarkable features will enterprise the electrochemical sensors to advance improvement of its qualities. The ionophores used in ion selective membrane sensors are the significant elements defining the feature of electrochemical sensors. Consequently, emerging noval and outstanding ionophores for the association of exclusive Pb(II) ion selective sensors is essential and required. Though, they fascinate much concern because of their great potential sloperesponse, short time response, low limit of detection, and easy preparation of sample. These kind of sensors development could be advanced to a innovation with characteristics: (1) Production of noval ionophores which can chelate Pb(II) to make aring types or even a number of ring clusters to significantly improve the ionophore coordination capability, consequently that can be satisfactorily sensitive to seizure Pb(II) ions in a trace amounts. Turn out the existing sensors that are boundless to the system of three-component "ionophore + plasticizer + PVC," by doping procedure of an ionic liquid advances in the procedure giving the lower limit of detection. Apply of nanoparticle and multi walled carbon nano tubes enhance the electrodes having the features of flexibility, integration and reduction. When certain innovations in the overhead inquiries of electrochemical sensors for Pb(II)ion have been attained and larger-respose sensors are gained, in biological materials and environmental samples these can be effectively useful to the examine of Pb(II) ions at trace levels.

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