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ORIGINAL PAPER

Selective and sensitive lead (II) solid-contact potentiometric sensor based on naphthalene-sulfonamide derivative

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Abstract A new naphthalene-sulfonamide (NS) derivative has been used as ionophore to construct the polyvinylchloride-based lead (II) solid-contact (SC) coated graphite electrode modified with conducting polymer poly(3,4-ethylenedioxythiophene)/polystyrene sulfonate (PEDOT/PSS). The lead-NS derivative complex shows 1:1 stoichiometry with the maximum stability constant of 5.75 as compared to other metal ions that is determined by sandwich membrane method. The proposed membrane morphology has been analyzed by scanning electron microscopy. The proposed lead (II) SC-PEDOT/PSS-coated graphite electrode-1 (Pb(II) SC-PEDOT/PSS-CGE-1) shows the detection limit of 5.62×10^{-8} M (56.2 nm) with Nernstian slope of 29.21 mV/decade within the pH range of 2.0–7.0 and exhibits small response time of <10 s. It has been used as indicator electrode for the potentiometric titration of lead (II) with ethylenediaminetetraacetic acid and successfully applied for the determination of lead (II) ions content in various environmental and ayurvedic medicines sample matrices with very good performance (0.999 correlation coefficients in the comparison against atomic absorption spectroscopy method).

Keywords Naphthalene-sulfonamide · Coated graphite electrode · Stability constant · Scanning electron microscopy · Environment

Introduction

Lead is a universal and versatile metal, which has been used by mankind for many years. It is the most serious environmental pollutant among the toxic heavy metals all over the world. The common sources of its exposure are use of certain products such as paints, cosmetics, environmental emission containing lead, lead acid batteries, Indian manufactured ayurvedic medicines (Saper et al. 2008; Gunturu et al. 2011). Lead has no biological benefit to human and wildlife. World Health Organization (WHO) has recommended a limit of 10 μgL^{-1} (4.80×10^{-8} M) of Pb(II) in potable water (Baird 1999). When lead starts accumulating gradually in human blood, they induce abdominal cramps, reproductive toxicity, learning disability, attention deflect disorder, and brain damage. Due to environmental and biological toxicity of lead, the detection of lead at low level especially in drinking water has forced particular attention of analytical chemists. Presently, the most common analytical methods used for the determination of lead in different samples are atomic absorption spectrophotometry (AAS) and inductively coupled plasma mass spectroscopy (ICPMS). Although both these techniques show good selectivity and low detection limit to lead ions, both of these methods are expensive and complicated to perform online and inline determination of lead in drinking water. Conversely, electrochemical techniques are cheap, portable, robust, and easy to handle. These techniques provide a crucial

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analytical tool for selective detection of various metal ions, drugs, and biomolecules (Sanghavi et al. 2013; Gupta et al. 2000, 2002, 2003, 2005, 2006a, b, c, d, 2007, 2011a, b, c, 2012, 2013; Mobin et al. 2010; Goyal et al. 2007, 2008a, b, c. 2009; Sanghavi et al. 2014).

The certain problems related to conventional polymeric ion-selective electrodes made with inner filling solutions such as drying out of the inner solution (need for maintenance), limitation of applications (electrode orientation, temperature, and pressure), unable to remote sensing, and deep sea measurements automatically disappear with solid-contact ion-selective electrodes (SC-ISEs) (Bobacka 2006; Chumbimuni-Torres et al. 2006; Lindner and Gyurcsanyi 2009). SC-ISEs make their applications in clinical diagnosis, industrial process control, in environmental monitoring and are the best alternative of the above-mentioned complicated method for the estimation of Pb(II) ions.

Many efforts have been made to construct Pb(II) ISEs by using different organic and inorganic compounds (Srivastava et al. 1995; Jain et al. 2006, Chen et al. 2006, Soleymanpour et al. 2012; Wardak 2011; Elmosallamy et al. 2008; Li et al. 2009; Michalska et al. 2009; Kazemi et al. 2009; Wilson et al. 2010; Abbaspour et al. 2010; Huang et al. 2011; Zamani et al. 2011; Yin et al. 2012; Lisak et al. 2012; Guzinski et al. 2013). Very recently, the Rong et al. (2012) reviewed the Pb(II) ISEs based on ionophores bearing oxygen/sulfur functional groups. They have also reported different applications of Pb(II) ISEs and drawbacks of methods used to calculate the selectivity coefficient. Recently, solid-contact Pb(II) ISEs prepared on screen-printed substrate was reported by Anastasova et al. (2012) with tremendous nanomolar detection of Pb(II) ions in local rivers water samples. Yuan et al. (2012) reported a schiff base complex that exploited as Pb(II) ISE with slope of 23.9 mV/decade and detection limit of 4.6×10^{-6} M.

It is well known that low detection limit can also be achieved using solid-contact ISEs based on conducting polymers (CP) as ion-to-electron transducers (Konopka et al. 2004; Michalska 2006) and also eliminate main drawback of solid-state ISEs with instable potential response which take place due to the formation of aqueous layer in between solid contact (metal, carbon) and the ionic conductor (ion-selective membrane). Recently, polyethylenedioxythiophene (PEDOT) and polyoctylthiophene (POT) have been used as the ion-to-electron transducer for the construction of various SC-ISEs (Bobacka et al. 2004; Vazquez et al. 2004; Paciorek et al. 2003; Sutter et al. 2004; Ochoa and Cordero 2010). In the present work, poly (3,4-ethylenedioxythiophene) (PEDOT) doped with poly (styrene sulfonate) (PSS), i.e., PEDOT/PSS as active ion-to-electron transducer with plasticized PVC sensing membrane, has been used to avoid the aqueous layer at the interface of Pb(II) SC-ISEs.

In this paper, we present Pb(II) SC-ISEs based on conducting polymer PEDOT/PSS as an ion-to-electron transducer and novel naphthalene-sulfonamide (NS) derivative acting as ionophore. The proposed Pb(II) SC-electrode based on NS derivative further applied in the *analysis of Pb(II) ions in various environmental and ayurvedic medicines sample matrices* by direct potentiometry, and the results obtained were compared with atomic absorption spectroscopy (AAS) and volumetric methods.

Materials and methods

All reagents used were of analytical grade, and doubly distilled deionized water was used to prepare solutions. The ionophore naphthalene-sulfonamide (NS) derivative was synthesized as reported in the literature (Bhalla et al. 2012), and structure is shown in Figure (online resource 1). The plasticizers 2-nitrophenyl octyl ether (2-NPOE), bis(2-ethylhexyl) sebacate (DOS), bis(2-ethylhexyl) phthalate (DOP), bis(2-ethylhexyl) adipate (DOA), dibutylphthalate (DBP), tributylphosphate (TBP), and high molecular weight poly(vinyl chloride)(PVC) were used as received from Fluka. Anion excluder potassium tetrakis(4-chlorophenyl)borate (KTpClB) was obtained from Sigma-Aldrich, while lead (II) nitrate and other metal nitrates received from Merck were used without any further purification. Aqueous dispersion of poly(3,4-ethylenedioxythiophene) doped with poly(4-styrene sulfonate) anions (Baytron P) was obtained from Sigma-Aldrich and used as obtained.

Preparation of PEDOT/PSS modified solid-contact ion-selective electrodes

Spectroscopic grade graphite rods 20.0 mm in length and 3.0 mm in diameter were used for the preparation of coated graphite electrodes. At one end of the graphite electrode, a shielded copper wire was glued and the electrodes were sealed into other end of a glass tube having the same diameter with epoxy resin (Araldite). The working surface of the electrodes was polished with fine alumina slurry on the polishing cloth, washed with double-distilled water, and then dried in air. About 100 µL of aqueous suspension of PEDOT/PSS (Baytron P) was pipette and deposited on the bare surface of polished graphite rod (Bobacka 2006; Vazquez et al. 2004). On the other hand, membrane solution was prepared by thoroughly dissolving PVC, plasticizer, ionophore, and additive in 3.0 mL THF (composition given in Table 2). The resulting clear solution was evaporated slowly at room temperature until an oily concentrate mixture was obtained. Then, dry PEDOT/PSS modified graphite electrode was coated with the prepared membrane solution and solvent allowed to evaporate at room temperature. A membrane was formed on the graphite surface, and electrode was allowed to stabilize overnight. The solid-contact polymer modified coated graphite electrodes (SC-PEDOT/PSS-CGEs) was finally conditioned by soaking in 1.0 × 10^{-2} M lead nitrate solution for 72 h until it produced stable and reproducible potential. The potentiometric measurements were carried out using following electrochemical cell assembly:

Graphite Surface	PEDOT/PSS Film	PVC Membrane	Test Solution	3.0 M KCl	Ag-AgCl

All the measurements of electrode potential were made with an Equip-tronics model EQ-602 potentiometer. The pH and conductometric measurements were made using Elico LI model-120 pH meter and Equip-tronics model EQ-664A, respectively. The determinations of lead in different samples by using the reference method were made by employing atomic absorption spectrophotometer (AAS 4129, Electronic Corporation India Limited). For the scanning electron microscopy (SEM) study, the sample holders were cleaned and then dried with acetone solvent. The samples membranes were then fixed onto the holders and coated with gold in the vacuum chamber to increase the conductance of their surfaces. These samples were used to study the morphology of the membrane surfaces by using Carl Zeiss Supra$^{\mathrm{TM}}$ 55, Germany model SEM.

Results and discussion

Preliminary complexation study of naphthalene-sulfonamide (NS) derivative

In order to obtain a knowledge about the stability and stoichiometry of NS derivative with the number of alkali, alkaline earth, and transition metal ions, the NS derivative complexation studies were investigated conductometrically in acetonitrile solutions at 298 K (Singh and Singh 2010; Shamsipur and Ganjali 1997). The 25 mL 1.0 × 10^{-4} M metal ion solution was titrated with NS derivative of (L = liganad) 1.0 × 10^{-3} M and the conductance of the mixture, after each addition of titrate was measured. The Fig. 1 showed the conductance variation plots with various metal ions (M^{n+}= Hg^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Fe^{3+}, Ca^{2+} and Zn^{2+}) in addition to Pb(II) ions. The conductance decreases in the beginning on the addition of ionophore that shows that the metal ions interaction with the ionophore forming a large complex, so decreasing in conductance. At a point, the addition of ionophore does not significantly decreases and conductance become nearly constant. *Break in the plot represent the stoichiometry of complex and found to be 1:1.*

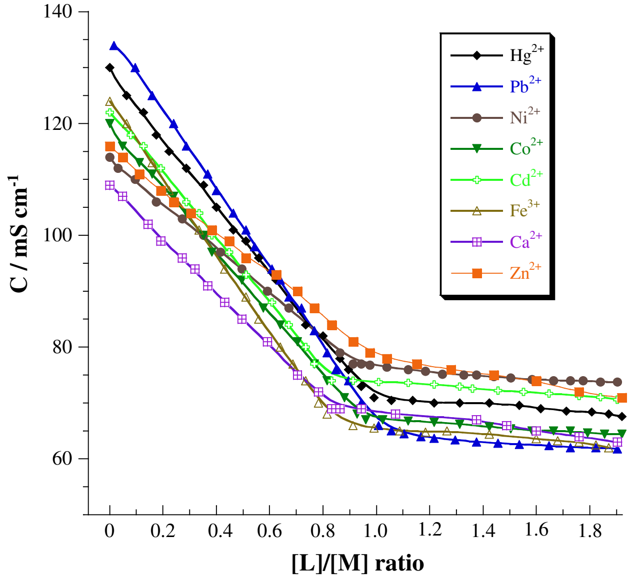

Fig. 1 Plot of conductivity versus ligand/metal ratio with different metal ions

Determination of stability constants

The formation constant of the ion-ionophore complex within the membrane phase is an important parameter that indicates the selectivity of the sensor. The ion-ionophore complex formation constants were evaluated by potentiometric method (Mi and Bakker 1999; Qin et al. 2000). In this method, a sandwich membrane is prepared by fusing two membranes, with only one containing the ionophore. This membrane electrode was brought in contact with the aqueous solution, having identical concentration on both sides, and cell potential was measured. On the other hand, the cell potential of another membrane having no ionophore was measured. The membrane potential (E_M) is determined by subtracting the cell potential of membrane without ionophore from the sandwich membrane. The formation constant is then calculated from the following equation:

$$\beta_{\mathrm{IL}_n} = \left(L_T - \frac{nR_T}{Z_I}\right)^{-n} \exp\left(\frac{E_M Z_I F}{RT}\right)$$

where L_T is the total concentration of ionophore in the membrane segment, R_T is the concentration of lipophilic ionic sites additive, n is the ion-ionophore complex stoichiometry, and R, T, and F are gas constants, the absolute temperature, and Faraday constant, respectively, Z_1 is the charge on ion.

Table 1 The formation constant of NS derivative-M^{n+} complexes using sandwich method

Metal ions	Formation constant $(\log \beta_{IL_n} \pm SD)^a$	Metal ions	Formation constant $(\log \beta_{IL_n} \pm SD)^a$
Pb^{2+}	5.75 ± 0.05	Mg^{2+}	2.65 ± 0.04
Cd^{2+}	3.43 ± 0.03	Hg^{2+}	4.20 ± 0.08
Co^{2+}	3.89 ± 0.05	Li^{+}	2.43 ± 0.07
Cu^{2+}	4.01 ± 0.08	Ca^{2+}	3.30 ± 0.04
Zn^{2+}	3.22 ± 0.02	K^{+}	3.05 ± 0.03
Fe^{3+}	2.89 ± 0.01	Na^{+}	2.95 ± 0.05
NH_4^{+}	1.76 ± 0.06	Ni^{2+}	3.68 ± 0.02

[a] Mean value ± standard deviation (three measurement)

The stability constants of different complexes calculated by the sandwich method are given in Table 1 in which the formation constant $(\log \beta_{IL_n})$ for *Pb(II)-NS complex is maximum (5.75)*, so ionophore shows maximum affinity toward Pb(II) ions. On the other hand, the stability constants for other metal ions are less than Pb(II) ions, which indicate the less affinity of ionophore toward these metal ions. Because of this affinity difference, it is expected that the presented NS derivative ionophore will facilitate the transport of Pb(II) ions in preference to other metal ions. Therefore, the NS derivative ionophore can be used as potential ionophore for preparing solid-contact Pb(II) ion-selective electrode.

Surface characterization

One of the important aspects of ion-selective electrode is the microstructure of the membrane material, which

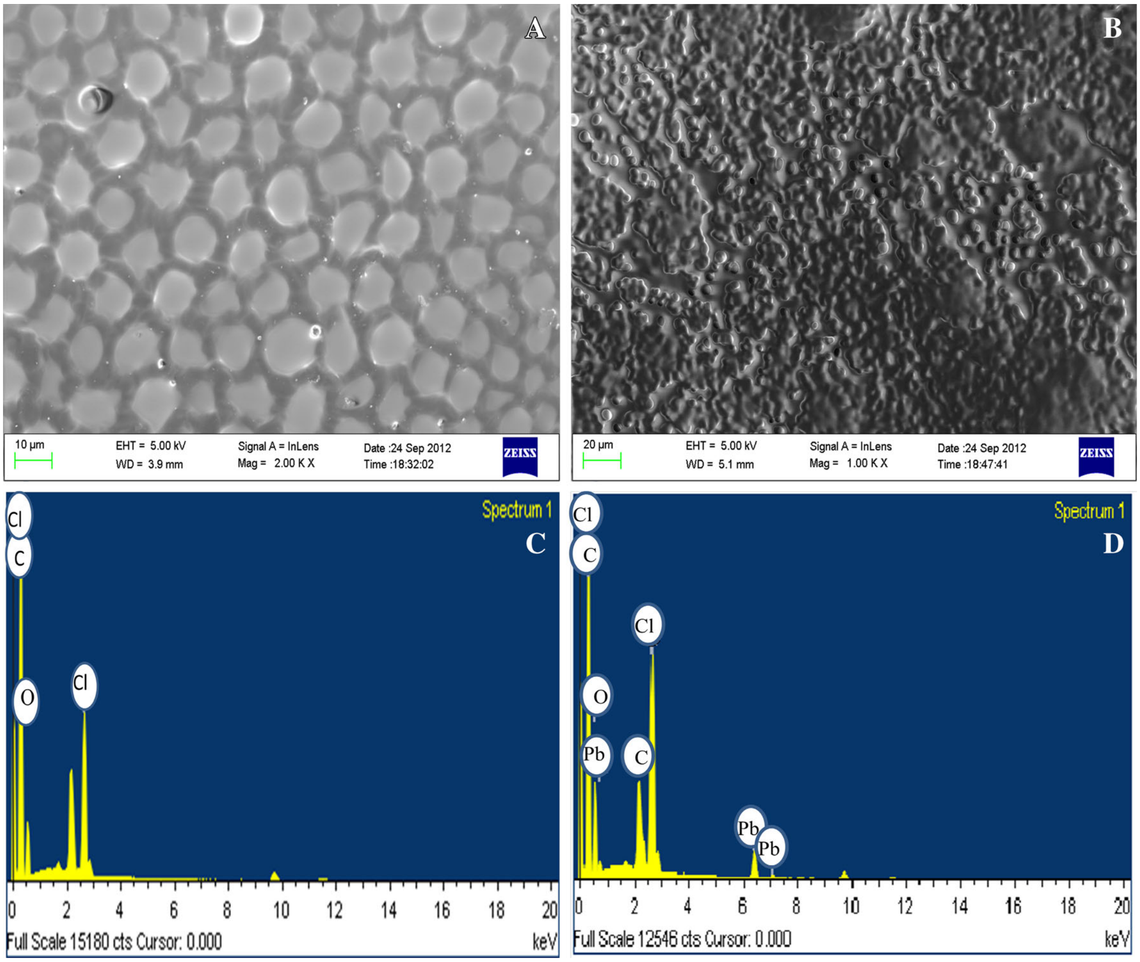

Fig. 2 SEM images of the membrane at different stages (×1,000) (**a**) PVC membrane (**b**) PVC/2-NPOE/ionophore membrane and EDX spectra of (**c**) PVC/2-NPOE membrane without ionophore (**d**) PVC/2-NPOE membrane with ionophore conditioned in 10^{-2} M Pb(II) ions for 24 h

determines the distribution of carrier as well as metal ion in the polymer matrix that further affect the response characteristics of proposed sensor. With the development of the new surface analysis technique such as scanning electron microscopy (SEM), it is possible to image the surfaces of some non-conducting sample like PVC membrane to distinguish their surface characteristics in order to investigate the surface morphology of Pb(II) ion-selective membrane. SEM studies were carried out at different magnification. In Fig. 2, image (a) shows the pure PVC membrane exhibited high porous polymer matrix with a relatively uniform pore size in the sub-micrometer range and physically tight structure in the polymer matrix. The image (b) shows that after the addition of 2-NPOE and NS derivative as ionophore, the pores of pure PVC membrane vanishes and a new layer has been formed that has tiny channel to diffuse the Pb(II) ions. In order to check the selectivity of the NS derivative toward the Pb(II) ions, the EDX spectra of the conditioned membranes 2-NPOE-PVC membrane without ionophore (image c) and 2-NPOE-PVC membrane with ionophore (image d) in 1.0×10^{-2} M Pb(II) solution have been taken. Its clear from image (c) that no Pb(II) content has been detected in the PVC/2-NPOE membrane without ionophore. It shows only PVC membrane constituents such as C, O, and Cl. But on the other hand, the PVC/2-NPOE membrane with ionophore (image d) shows PVC membrane constituents C, O, Cl as well as Pb(II) content. *These results reveal that the ionophore is efficient and selective to form the complex with Pb(II).*

Potentiometric response for multiple ions using SC-PEDOT/PSS-CGEs

In the preliminary experiments, PVC-based SC-PEDOT/PSS-CGEs for a wide variety of mono-, di-, and trivalent metal ions were prepared by incorporating 40.0 mg PVC, 80.0 mg 2-NPOE as plasticizer, 2.0 mg KTpClB as additive, and 3.0 mg of NS derivative as ionophore. These SC-PEDOT/PSS-CGEs were conditioned in respective metal ion solution at 1.0×10^{-2} M concentration for 72 h, and its potential response was noted over the concentration range of 1.0×10^{-1} –1.0×10^{-9} M for different metal ions. It can be seen from Figure (online resource 2) that except Pb(II) ions, the slopes for the linear part of the response of different SC-PEDOT/PSS-CGEs for most of tested cations are much lower than as expected by Nernstian equation. *Results obtained from conductivity, SEM and potentiometry techniques indicate that NS derivative has preferential affinity towards Pb(II) ions* and can be employed as an ionophore for the development of Pb(II) solid-contact ion-selective electrodes.

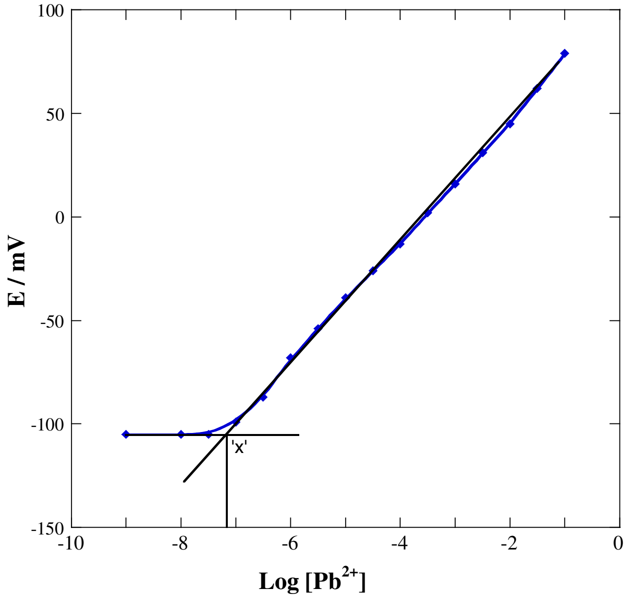

Fig. 3 Potential response curves of NS derivative based SC-PEDOT/PSS-CGE-1 for Pb(II) ions

Potentiometric response for Pb(II) ions using SC-PEDOT/PSS-CGEs

On the basis of results obtained from preliminary investigations on NS derivative, it was decided to employ NS derivative as an ion carrier for the development of Pb(II) solid-contact electrodes. Potentiometric response curve and composition for the SC-PEDOT/PSS-CGE-1 have been shown in Fig. 3 and Table 2, respectively. *Polymeric based SC-PEDOT/PSS-CGE-1 for Pb(II) containing NS derivative as ionophore exhibited Nernstian slope of 29.21 mV/decade over wide concentration range of* 1.0×10^{-1}–1.0×10^{-7}*M with lower detection limit (LOD) of* 5.62×10^{-8}*M (56.2 nm) ('x' in* Fig. 3*).*

Effect of additive content

The properties of ion-selective electrodes (ISEs) based on neutral ionophores are strongly influenced by the ionic sites in their membranes. Although neutral carrier-based ISEs membranes may work properly even when they contain only a small amount of ionic sites, the addition of a salt of lipophilic ion is advisable and beneficial for various other reasons as well. Their main function is to render the ion-selectivity and to reduce the bulk membrane impedence (Diaz and Bakker 2001). In our study, potassium tetrakis(4-chlorophenyl)borate (KTpClB) was incorporated as an additional membrane component. It is clear from Table 2 that as we reduce the amount of KTpClB from SC-PEDOT/

Table 2 Composition and response characteristics of NS derivative based SC-PEDOT/PSS-CGEs for Pb(II) ions

S. no SC-PEDOT /PSS-	PVC (mg)	Plasticizer (mg)	KTpClB (mg)	Ionophore (mg)	Linear range (M)	Detection limit (M)	Slope (mV/dec.) ±0.01
CGE-1	40.0	80.0 (2-NPOE)	2.0	3.0	1.0×10^{-1}–1.0×10^{-7}	5.62×10^{-8}	29.21
CGE-2	40.0	80.1 (2-NPOE)	1.0	3.1	1.0×10^{-1}–5.0×10^{-7}	2.09×10^{-7}	24.14
CGE-3	40.6	80.2 (2-NPOE)	0.0	3.0	5.0×10^{-2}–5.0×10^{-6}	9.20×10^{-5}	11.61
CGE-4	41.0	80.0 (2-NPOE)	2.1	5.0	1.0×10^{-1}–5.0×10^{-7}	1.07×10^{-7}	35.39
CGE-5	40.6	81.0 (2-NPOE)	2.2	1.0	1.0×10^{-1}–1.0×10^{-6}	7.92×10^{-6}	17.12
CGE-6	40.5	81.0 (2-NPOE)	1.9	0.0	1.0×10^{-1}–1.0×10^{-4}	6.95×10^{-4}	8.21
CGE-7	39.8	80.2 (2-NPOE)	2.0	7.0	1.0×10^{-1}–1.0×10^{-5}	2.81×10^{-6}	46.39
CGE-8	40.8	79.7 (DOS)	2.2	5.1	1.0×10^{-2}– 1.0×10^{-6}	5.33×10^{-5}	19.26
CGE-9	40.2	79.9 (TBP)	2.1	5.1	1.0×10^{-2}–1.0×10^{-6}	9.0×10^{-6}	22.91
CGE-10	41.0	80.4 (DOP)	1.9	4.8	5.0×10^{-2}–5.0×10^{-7}	7.79×10^{-7}	15.78
CGE-11	40.0	80.8 (DOA)	1.8	4.9	1.0×10^{-1}–5.0×10^{-6}	1.11×10^{-6}	20.50
CGE-12	40.8	80.3 (DBP)	2.0	5.2	1.0×10^{-2}–5.0×10^{-6}	4.29×10^{-6}	12.36

PSS-CGE-1 (2.0 mg) to SC-PEDOT/PSS-CGE-3 (0.0 mg), the Nernstian slopes and linear range decrease where detection limits change from 5.62×10^{-8} to 9.20×10^{-5} M. *So, it revealed that 2.0 mg amount of KTpClB was found to be optimum for the smooth functioning of SC-PEDOT/PSS-CGE-1 for Pb(II) ions.*

Effect of ionophore

Effect of ionophore content on the response characteristics of Pb(II) solid-contact ISEs incorporating NS derivative as an ion carrier was studied by preparing membrane electrodes SC-PEDOT/PSS-CGE-1 (3.0 mg), SC-PEDOT/PSS-CGE-4 (5.0 mg), SC-PEDOT/PSS-CGE-5 (1.0 mg), and SC-PEDOT/PSS-CGE-7 (7.0 mg) were prepared by using different amount of NS derivative as ionophore. Composition and response characteristics for these electrodes have been given in Table 2. The SC-PEDOT/PSS-CGE-1 containing 3.0 mg of ionophore exhibited Nernstian slope of 29.21 mV/decade over wide concentration range of 1.0×10^{-1}–1.0×10^{-7} M for Pb(II) ions with lower detection limit of 5.62×10^{-8} M (56.2 nM). SC-PEDOT/PSS-CGE-5 containing ionophore 1.0 mg of ionophore exhibited sub-Nernstian slope of 17.12 mV/decade for Pb(II) ions over concentration range of 1.0×10^{-1}–1.0×10^{-6} M with the detection limit of 7.92×10^{-6} M. On the other hand, SC-PEDOT/PSS-CGE-4 and PSS-CGE-7 containing 5.0 and 7.0 mg of ionophore shows super-Nernstian slopes of 35.39 and 46.39 mV/decade for Pb(II) ions over concentration ranges of 1.0×10^{-1}–5.0×10^{-7} M and 1.0×10^{-1}–1.0×10^{-5} M with the detection limits of 1.07×10^{-7} and 2.81×10^{-6} M, respectively. The performance of membrane without ionophore (dummy membrane) was also investigated, and sub-Nernstian slope (8.21 mV/decade) was observed (SC-PEDOT/PSS-CGE-6) with narrow concentration range (1.0×10^{-1}–1.0×10^{-4} M) and high detection limit (6.95×10^{-4} M). This clearly demonstrated the need of carrier in the fabrication of Pb(II) ISEs. *So, the best result was obtained with SC-PEDOT/PSS-CGE-1 containing 3.0 mg content of ionophore.*

Effect of plasticizer

Choosing an appropriate plasticizer is essential for the construction of an ion-selective electrode with high analytical performances, such as Nernstian slope, selectivity, fast response, long life, and lower detection limit (Zhang et al. 2000). Compatibility with polymer and electrodic component (ionophore), low solubility in aqueous solution, low viscosity, low cost, and low toxicity are the desirable properties of the plasticizers (O'Rourke et al. 2011). Plasticizers embedded itself between chains of the polymer and spaces them apart, so free volume increases which is responsible for the flexibility and durability of the membrane. In the present work, six plasticizers of different dielectric constants (ε) and chemical structures such as 2-NPOE, DOS, TBP, DOP, DOA, and DBP were studied on Pb(II) ISEs based upon ionophore NS derivative. From the data in Table 2, it is clear that 2-NPOE is proved to be most suitable plasticizer, which shows Nernstian slope of 29.21 mV/decade with detection limit of 5.62×10^{-8} M

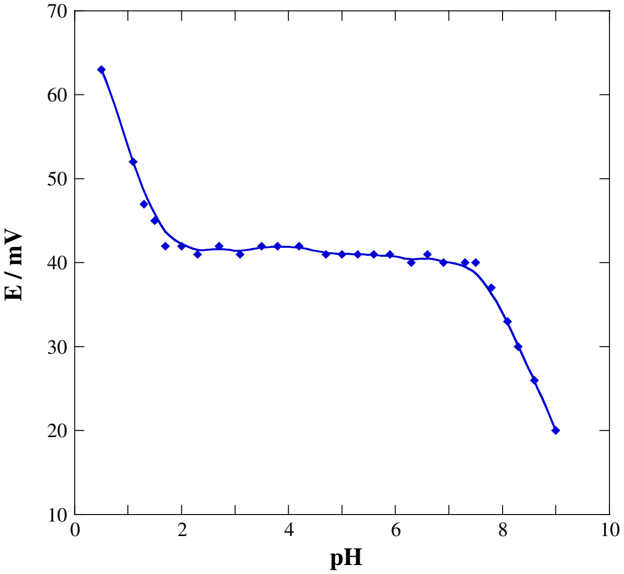

Fig. 4 Effect of pH on potential response of NS derivative based SC-PEDOT/PSS-CGE-1 for Pb(II) ions

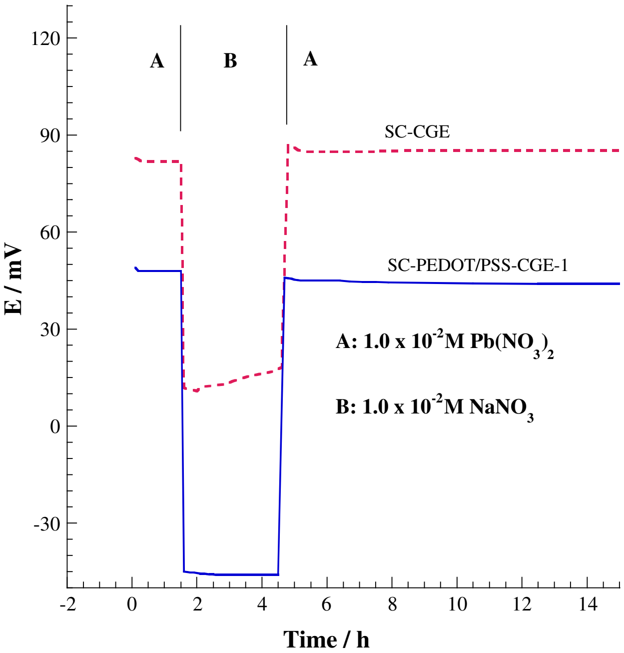

Fig. 5 Water layer test of Pb(II)-selective electrodes with SC-PEDOT/PSS-CGE-1 and SC-CGE recorded in (*A*) 1.0 × 10^{-2} M of Pb $(NO_3)_2$ (*B*) 1.0 × 10^{-2} M $NaNO_3$

(SC-PEDOT/PSS-CGE-1). The plasticizers such as DOS (4.6), TBP (3.5), DOP (5.1), DOA (4.0), and DBP (6.4) {SC-PEDOT/PSS-CGEs 8–12} exhibited sub-Nernstian slopes of 19.26, 22.91, 15.78, 20.50, and 12.36 mV/decade, respectively. All of these imply that the *plasticizer 2-NPOE with high dielectric constant (ε = 24)) showed best response characteristics seem to be favorable environments for the complexation between Pb(II) and NS derivative*, whereas the plasticizers with moderate or lower dielectric constants were not considered so appropriate for construction of Pb(II) SC-PEDOT/PSS-CGE-1. So, 2-NPOE was selected as the plasticizer for further investigation.

Influence of pH on response characteristics of SC-PEDOT/PSS-CGE-1

The potential response of ISEs is affected by the pH of analyte ion solution employed. The pH dependent of SC-PEDOT/PSS-CGE-1 has been tested over the pH range of 1.0–9.0 with 1.0 × 10^{-2} M Pb(II) ions solution. The pH values were adjusted using con. nitric acid or hexamine and potential was measured after each addition. *The potential response remains constant over pH range of 2.0–7.0* as shown in Fig. 4. The noticeable decrease in potential response observed at lower pH can be due to interference of hydrogen ions, and potential response decreasing sharply at higher pH may be due to the formation of some hydroxyl complexes of Pb(II) ions in solution from hydrolysis of Pb(II) nitrate salt.

Aqueous layer test: potential stability of Pb(II) SC-PEDOT/PSS-CGE-1

It has been realized that the thin water layer can form between the PVC membrane and its solid contact. The stability of the proposed electrode was tested using the protocol developed by Fibbioli et al. (2000). The studied electrode modified with PEDOT/PSS was initially immersed in 1.0 × 10^{-2} M $Pb(NO_3)_2$ solution. After 1.5 h, the solution was changed to 1.0 × 10^{-2} M $NaNO_3$ solution (diverse ion). After 3-h diverse, ion solution was replaced by again 1.0 × 10^{-2} M $Pb(NO_3)_2$ solution. Its clear from Fig. 5 that no potential drift was observed for Pb(II) SC-PEDOT/PSS-CGE-1 upon changing the analyte in sample solution from primary ions to the diverse ions and again to primary ions. On the other hand, at similar conditions, the electrode (SC-CGE) without PEDOT/PSS polymer exhibits significant potential drift as shown in Fig. 5. So, these results revealed that *no aqueous layer was formed in between membrane and solid contact, when the solid contact was modified with PEDOT/PSS polymer*.

Table 3 Selectivity coefficients of various diverse ions (B) for NS derivative based SC-PEDOT/PSS-CGE-1

Diverse ions (B)	$\left(\log K^{\mathrm{Pot.}}_{\mathrm{Pb^{2+},B}} \pm \mathrm{SD}\right)^{\mathrm{b}}$	Diverse ions (B)	$\left(\log K^{\mathrm{Pot.}}_{\mathrm{Pb^{2+},B}} \pm \mathrm{SD}\right)^{\mathrm{b}}$
Co^{2+}	−3.05 ± 0.06	Mg^{2+}	−4.20 ± 0.03
Hg^{2+}	−2.53 ± 0.02	Ag^{+}	−3.39 ± 0.08
Cd^{2+}	−3.94 ± 0.07	Li^{+}	−3.49 ± 0.09
Cu^{2+}	−2.98 ± 0.07	Ca^{2+}	−4.10 ± 0.08
Zn^{2+}	−4.25 ± 0.05	K^{+}	−4.20 ± 0.03
Fe^{3+}	−3.15 ± 0.04	Na^{+}	−4.36 ± 0.06
NH_4^{+}	−3.00 ± 0.05		

[b] Mean value ± standard deviation (three measurement)

Response, life time, reproducibility of proposed Pb(II) SC-PEDOT/PSS-CGE-1

The response time of an ISE is the average time required for attaining the equilibrium value of the potential when dipped in successive Pb(II) ion solution, each having the ten-fold difference in concentration. To measure the dynamic response time of proposed SC-PEDOT/PSS-CGE-1, the Pb(II) ions concentration of the test solution was successively changed from lower (1.0×10^{-5} M) to higher (1.0×10^{-1} M). A potential *versus* time trace plot for SC-PEDOT/PSS-CGE-1 is shown in Figure (online resource 3). It is evident from Figure that potential response reached the equilibrium in very short time of <10 s. The potential generated by the *developed sensor remain stable for more than 4 min after which divergence was recorded.* Short response time of SC-PEDOT/PSS-CGE-1 may be due to high electric conductivity of the conducting polymer casted on the graphite rod. SC-PEDOT/PSS-CGE-1 can be used over the period of 4 months without any significant change in Nernstian slope, lower detection limit, linear range, and response time. During this period, slope of electrodes shows only slight change from 29.21 to 27.96 mV/decade for SC-PEDOT/PSS-CGE-1 (online resource 4) and that after more than 4 months time, the selectivity and sensitivity of SC-PEDOT/PSS-CGE-1 get degrading. It may be due to leaching out of the ionophore from the membrane.

Selectivity of proposed Pb(II) SC-PEDOT/PSS-CGE-1

The selectivity coefficient (K) is the very important source of information concerning interference on the electrode response. In the present work, fixed interference method (FIM) based on semi-empirical Nikolsky-Eiseman equation was employed to determine logarithmic selectivity coefficient $\left(\log K^{\mathrm{Pot.}}_{\mathrm{A,B}}\right)$ of proposed Pb(II) SC-PEDOT/PSS-CGE-1.

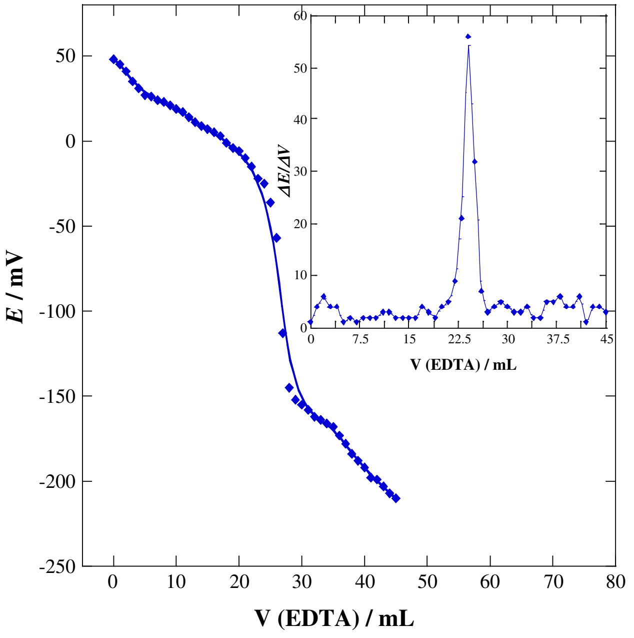

Fig. 6 Potentiometric titration of 1.0×10^{-2} M Pb(II) solution with 1.0×10^{-2} M EDTA using SC-PEDOT/PSS-CGE-1 based on NS derivative

$$K^{\mathrm{Pot.}}_{\mathrm{A,B}} = \left(\frac{a_{\mathrm{A}}}{a_{\mathrm{B}}}\right)^{\frac{z_{\mathrm{A}}}{z_{\mathrm{B}}}}$$

Emf of the cell is measured for solution containing constant activity (a_{B}) of diverse ions with charge Z_{B} and varying activity (a_{A}) of the primary ions with charge Z_{A}.

The values of logarithmic selectivity coefficients $\left(\log K^{\mathrm{Pot.}}_{\mathrm{Pb^{2+},B}}\right)$ obtained by FIM for proposed electrode are shown in Table 3. As it is evident from Table 3, *the SC-PEDOT/PSS-CGE-1 is very selective to Pb(II) ions over all diverse ions*, but among all of them, Hg(II) ions have high selectivity coefficient $\left(\log K^{\mathrm{Pot.}}_{\mathrm{Pb^{2+},Hg^{2+}}} = -2.53\right)$ which indicate the tolerance level of the proposed SC-PEDOT/PSS-CGE-1 toward Hg(II) is low as compared to other diverse metal ions. Taking account the lower detection limit and response time, the observed tolerable Hg(II) concentration was up to 1.0×10^{-2} M. Below this concentration, the Hg(II) ions show no interference in the normal functioning of SC-PEDOT/PSS-CGE-1.

Analytical applications

Due to the high selectivity toward Pb(II) ion, Pb(II)-PEDOT/PSS-CGE-1 was employed to monitor Pb(II) ion concentration in various samples, while AAS and volumetric methods were used as reference methods.

Table 4 Estimation of Pb(II) ions in various sample matrices by SC-PEDOT/PSS-CGE-1

Sample	(Pb(II) content in samples ± SD)^c M				
	Pb(II) added	Ion-selective electrode (SC-PEDOT/PSS-CGE-1)	Atomic absorption spectrophotometry (AAS)	Volumetric method	Percentage compatibility (SC-PEDOT/PSS-CGE-1 with AAS)
Tap water	3.50×10^{-2}	$3.45 \pm 0.04 \times 10^{-2}$	$3.70 \pm 0.04 \times 10^{-2}$	$3.20 \pm 0.07 \times 10^{-2}$	93.24 ± 0.04
Well water	1.50×10^{-4}	$1.61 \pm 0.01 \times 10^{-4}$	$1.55 \pm 0.06 \times 10^{-4}$	$1.11 \pm 0.08 \times 10^{-4}$	103.24 ± 0.03
River water	4.50×10^{-6}	$4.55 \pm 0.07 \times 10^{-6}$	$4.69 \pm 0.08 \times 10^{-6}$	–	97.0 ± 0.07
Industrial waste water	–	$9.22 \pm 0.02 \times 10^{-5}$	$8.90 \pm 0.03 \times 10^{-5}$	–	103.59 ± 0.08
Lead acid batteries	–	$4.98 \pm 0.05 \times 10^{-4}$	$4.98 \pm 0.01 \times 10^{-4}$	$4.70 \pm 0.07 \times 10^{-4}$	100.00 ± 0.08
Naga bhasma	–	$5.00 \pm 0.07 \times 10^{-2}$	$5.25 \pm 0.02 \times 10^{-2}$	$4.35 \pm 0.08 \times 10^{-2}$	95.24 ± 0.07
Basant kasumkar ras	–	$5.06 \pm 0.06 \times 10^{-4}$	$4.68 \pm 0.01 \times 10^{-4}$	$5.20 \pm 0.08 \times 10^{-4}$	108.12 ± 0.04
Ekangveer ras	–	$7.96 \pm 0.03 \times 10^{-6}$	$7.23 \pm 0.04 \times 10^{-6}$	–	110.10 ± 0.03

[c] Mean value ± standard deviation (three measurement)

Potentiometric titration

Proposed Pb(II)-PEDOT/PSS-CGE-1 was found to work well under laboratories conditions. Practical utility of the this electrode was tested by using them as indicator electrode for potentiometric titration of Pb(II) ion solution (1.0×10^{-2} M) with EDTA solution (1.0×10^{-2} M), and corresponding titration curve is shown in Fig. 6. The plot is sigmoid in shape, and the inflexion point of the plot corresponds to 1:1 stoichiometry of EDTA complex, while the potential response after the end point remains almost constant, due to low concentration of free Pb(II) ions in solution. Therefore, the end point and the amount of Pb(II) ions in the solution can be accurately determined by extrapolation of the three linear portion of titration plot.

Estimation of Pb(II) in various sample matrices by SC-PEDOT/PSS-CGE-1

SC-PEDOT/PSS-CGE-1 has been used to determine the Pb(II) content in different water samples such as *tap, well, river, industrial waste water, lead acid batteries and Indian manufactured ayurvedic medicines*. Tap, well, and river water samples were analyzed by SC-PEDOT/PSS-CGE-1 to detect Pb(II) concentration by using its spiked samples; otherwise, it is very difficult to determine Pb(II) in these samples. All others samples have been prepared in same way as already used in our laboratory (Mahajan et al. 2013; Kamal et al. 2014). From the Table 4, it is clear that estimation of Pb(II) in various sample matrices by using SC-PEDOT/PSS-CGE-1 gives compatible result with the AAS and also with volumetric method using EDTA as titrant except those samples where Pb(II) concentration is lower than 1.0×10^{-5} M.

Statistical treatment of SC-PEDOT/PSS-CGE-1 results

To check the reliability of proposed electrode, the results obtained by SC-PEDOT/PSS-CGE-1 and AAS are statistically compared and it is observed that very satisfactory results have been obtained. Linear regression line of SC-PEDOT/PSS-CGE-1 versus AAS yields a correlation of $R = 0.999$ (approx. equal to 1) and 7 degree of freedom with comparison line $y = 1.05x + 0.012$. It is clear from the value of R (R = correlation coefficient) that regression line was undistinguishable from the theoretical $y = x$ comparison line. Similarly, if the paired Student's t test is performed for SC-PEDOT/PSS-CGE-1 versus AAS, the calculated value of t we get is 1.37, whereas the tabular t value is 2.365 (7 degree of freedom with 95 % confidence level). The calculated t value is less than tabular t value, which demonstrated that there are no significant difference between results obtained with both methods SC-PEDOT/PSS-CGE-1 and AAS. So, *we can say that results obtained from SC-PEDOT/PSS-CGE-1 are reliable, reproducible, and acceptable.*

Conclusion

New graphite contact modified with PEDOT/PSS conducting polymer coated with PVC membrane electrode (SC-PEDOT/PSS-CGE-1), which is highly selective to Pb(II) ions, has been developed using naphthalene-sulfonamide (NS) derivative as electro-active material. It shows Nernstian slope of 29.21 mV/decade and wide concentration range 1.0×10^{-1}–1.0×10^{-7} M with lower detection limit of 5.62×10^{-8} M (56.2 nm). Its response time is <10 s and has ability to work within pH range of 2.0–7.0. Developed electrode exhibited excellent selectivity, sensitivity, and large concentration range with no interference observed from diverse ions. It is successfully applied as an indicator electrode in potentiometric titration of Pb(II) ion solution with EDTA. Its high selectivity permits the direct measurement of Pb(II) ions in different environmental and ayurvedic medicine samples. The reliability of proposed electrode has been checked statistically by using paired Student's *t* test.

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