Study of lead Ion Selective Membrane Electrode Formed by Cation Exchanger 2-amino-4 methyl -N-hydroxy-benzene-carboxamide (AMHBCA) for the Selective and Determination of Pb^{2+} Ions

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Abstract

A lead ion selective composite cation exchanger 2,-amino-4 methyl -N-hydroxy-benzene-carboxamide (AMHBCA) was used as electro active component for the construction of a ion selective membrane electrode. The membrane electrode are formed by using plasticizer dibutyl(butyl) phosphonate (DBBP), diisodecyl Phthalate (DIDP), diisononyl Phthalate (DINP) and PVC in different composition. The membrane electrode formed by using diisodecyl Phthalate (DIDP) plasticizer showed a Nernstian response 28.6 mv per decade for Pb^{2+} ions over a wide concentration range. The electrode works satisfactory in the concentration range 6.0×10^{-5} to 1.0×10^{-1} M with near Nernstian slope of 29.6 mv per decade of concentration between pH from 2.6 to 5.8.The electrode also showed better selectivity for Pb^{2+} ion over many interfering ions. Results of the investigation reveal that the membrane electrode prepared by using 4 mg of organic ion exchange (AMHBCA), 80 mg DIDP and 150 mg PVC is the best. The performance of the electrodes is comparable with existing electrode in term of working concentration range, slope, pH, response time and selectivity over a number of cations.

Key Words: - Plasticizer, Ion selective membrane electrode, Pb^{2+}, pH, Nernstian response, selectivity, solvent effect.

Introduction

Many organic, inorganic, chelating, intercalating, and composite materials were studied as electroactive materials for the preparation of ion-selective membrane electrodes. Furthermore, the electrochemical detection used by ISE electrodes has a short analytical time, low power cost, high sensitivity, and easy adaptability for in-situ and online measurement. Electrochemical detection has become one of the most developed methods for continuous

online monitoring of heavy metals. Modern electrochemical detection principles, coupled with recent advances in microelectronics and microfabrication, has led to powerful and compact analytical devices that can potentially be readily adopted for continuous and real-time monitoring of heavy metals (1,2). In particular, applications of lab-on-a-chip (LOC) and microfluidics technologies have allowed for great improvements in compactness, reduction in fluid volume, and lower fabrication costs, among other advantages (3-5). Furthermore, wireless communication technologies have allowed the development of a sensor network that enables more efficient online continuous monitoring of heavy metal based on electrochemical technologies (6). The research activity of ISEs was very much boosted with the development of homogeneous crystal membrane fluoride electrode in 1966 by Frant and Ross (7), followed a year later by a liquid membrane electrode for calcium by same coworkers (8). Ion-selective electrodes (ISEs) are electro analytical sensors whose signals depend on the activities of ions in solution and exhibit a certain degree of selectivity for particular ionic species. The operation of classical ISEs is based on direct measurement of a single membrane potential at zero net current.

At present, efforts are primarily directed toward gathering of highly scattered information and unification and standardization of experimental approaches and routine analytical procedures, as reflected, e.g., in the activities of the International Union of Pure and Applied Chemistry. A common type of conductive sensing membrane is made of a plasticized polymeric phase, typically with poly(vinyl chloride) as a polymeric matrix, lipophilic ion-exchanger sites, and a lipophilic or covalently immobilized ionophore. The ionophore providing selectivity to a certain ion is embedded in the polymeric matrix. There are a variety of ISEs for lead detection that have been developed with different materials as ionophores. Heavy metal-selective electrodes have been prepared using different types of electro active materials. The mixture of tetraphenyl borate salt of lead and polyalkoxylate could be successfully used as electro active components of heterogeneous membranes for the preparation of Pb^{2+} sensors (9). Ren (10) has described a Pb^{2+}-selective electrode. Using naphthalene-1-dithicarboxylate Pb^{2+} complex whereas, Jain and Tyagi (11) used araldite based membranes of bismuth tungstata. In this direction, a number of crown ethers (12-15) been used as electro active phase in the heterogeneous membranes to prepare Pb^{2+}-selective electrodes. These electrode generally show overall better performance compared to electrode prepared by using electro active materials (16,17). Much attention has been paid to use of ionophore (ligands or complexes) as sensing materials for neutral carrier type ion selective electrodes due to the unique properties of the compounds. Schiff base with nitrogen and oxygen donor atoms are well known to form strong complexes with transition metal ions. Some of the Schiff bases are reported to form strong complexes with a specific ion due to geometric factor (18,19). Schiff's bases and their metal complexes have proved to be good ion carriers for the construction of ion selective sensors both for cations and anions.

The performance of the ISEs varies in terms of their selectivity, sensitivity, limit of detection (LOD), and durability. As they are a large number of lead-selective ionophores, the primary groups of those chemical compounds include amides, thioamides, crown ethers, and calixarenes (20,21). An oxy-diamides ISE electrode developed in early years showed lead (II) selectivity for many cations (22). Another oxy-diamides group ISE was developed for lead (II) selectivity over sodium, potassium, and magnesium (23). A tertiary amide showed near-Nernstian responses for divalent cations but poor selectivity towards lead (II) over potassium and sodium. In general, amide derivatives exhibit higher stability constants than the thioamide derivatives while thioamides have a superior selectivity.

Meterials and Method:

All chemicals used in these studies were analytical grade reagents. dibutyl(butyl) phosphonate (DBBP), dibutyl(butyl) phosphonate (DBBP), diisodecyl Phthalate (DIDP), diisononyl Phthalate (DINP), PVC and tetra hydro furan (THF),metal solution of their nitrate salts were prepared in doubly distilled water and standardized before use. The compound 2,-amino-4 methyl -N-hydroxy-benzene-carboxamide (AMHBCA) was available in the lab. A digital pH/potentiometer (ECIL, India, Model pH 5678A) was used for determining the potentials; pH of solutions was measured with same digital pH meter.

The homogenous membranes of the 2,-amino-4 methyl -N-hydroxy-benzene-carboxamide (AMHBCA) were found to be very fragile and broke down on usage. Hence, they were not suitable for preparing electrodes.Such heterogeneous membranes of the above using different binders such as epoxy resin, polystyrene and PVC was prepared. The membranes prepared with PVC were found to be the best as they exhibited sufficiently resistance to mechanical and chemical effects and generated reproducible results.

Therefore detailed studies of the electrode using PVC based membranes were only carried out. To prepare PVC based membranes appropriate amount of PBI, PVC and plasticizer were dissolved in 20 ml THF in a beaker. The THF allowed evaporating and volume was considerably reduced. This concentrated mixture was then poured in acrylic rings placed on a smooth glass plate. After few hours, thramporent membranes were obtained. From these membranes a circular piece was cut out and glued on the one and pyrex glass tube with help of araldite. The composition used for the membrane is indicated in Table-1 and 2.

Result and Discussion:

Membranes of AMHBCA as Sensor for Pb^{2+}

The potential of the cell using different membrane electrode was determined as a function of cadmium nitrate concentration taking in the test solution is given in Table 2 and a graph was plotted. The concentration range over which the electrode give almost linear

potential response is taken as their working concentration range. The working concentration range for different electrode as evaluated from the graphs is given in Table 1. It is seen that the electrode No.-1 have membrane without plasticizer exhibits working concentration range of 3.2×10^{-4} to 1.0×10^{-1} M. However, on addition of plasticizer to the membrane electrode number No. 2, 3 and 4, the working concentration over is changed. The plasticizer DIDP, DBBP and DINP (electrode No. 2 ,3, 4) increased the working concentration range. It is further seen from the table that the plasticizer lower the response time and reduce the slope of electrode .The addition of DIDP to the membrane (electrode No.-2) lowers the slope to a near Nernstian value of 28.6 mv/decade of concentration. Out of the four electrodes, the electrode No-2 has the lower response time, near Nernstian slope and maximum working concentration range. Therefore all further detailed studies were carried out with this electrode only. The electrode could be used over a period of one month without showing any significant change in potential .However, electrode were kept in 0.1 M lead nitrate solution when not in use.

pH and Solvent Effect

The effect of pH, which was adjusted by nitric acid /sodium hydroxide, on the performance of the electrode was investigated over range of 0.5 to 4.5 at 1.0×10^{-3} M concentration of Pb^{2+} and graph (Fig.) was plotted. It is seen that the useful pH range for the electrode is 2.6 to 5.8 as the potential remain constant. The change in potential at lower pH values can be attributed to H^+ ion confluxing and at performance of the electrode was also investigated in partially non aqueous media by studying potential response in water-methanol mixture .The values of slope and working concentration of the electrode in presence of 15% and 30% amount of methanol was calculated from the result and gathered in Table 3. Potential vs. concentration plots in 15% and 30% methanol solution show that the electrode works satisfactory in partial non aqueous media containing up to 15% methanol content only.
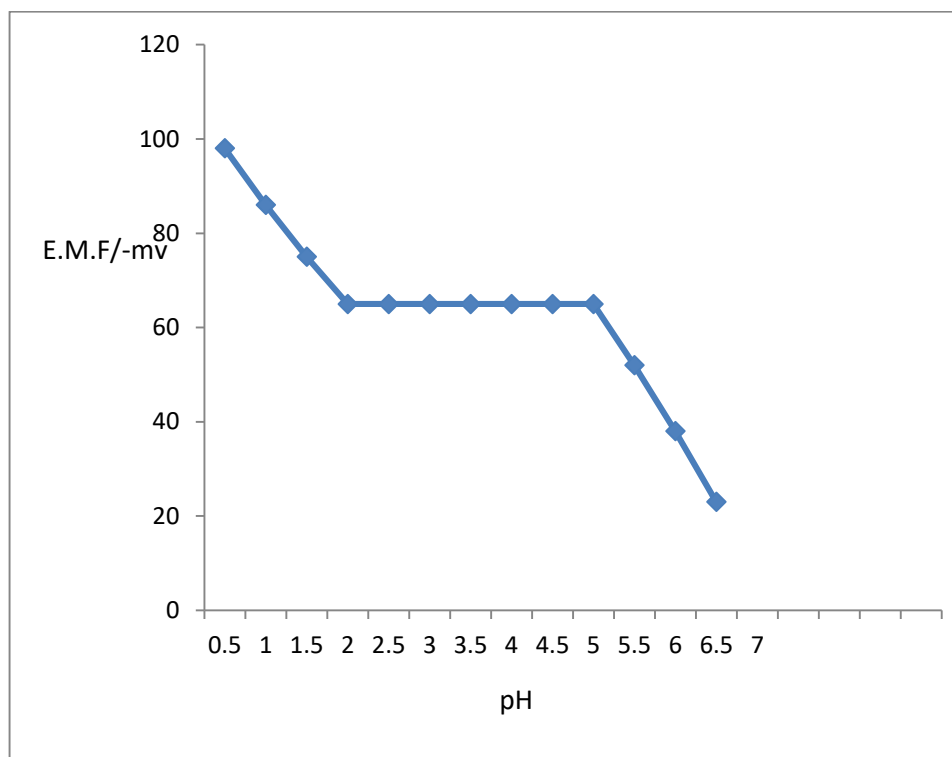
Fig: - Effect of pH on cell potential based electrodes No.2 $[Pb^{2+}] = 1.0 \times 10^{-3}$ M

Selectivity

The selectivity of the electrode was determined by IUPSC fixed interface method at 1.0×10^{-1} M concentration of interfering ions. The values were calculated and given in Table 4. Thus, these ions would not cause any significant interference in the determination of Pb^{2+}.

Table-1

Composition of PVC membranes based on AMHBCA and performance characteristics of Pb^{2+} selective electrode based on them (all in mg).

Sensor No.	components in sensors (%w/w)					working concentration range M	Slope mv/decade
	AMHBCA	PVC	DIDP	DBBP	DINP		
1	4	150	-	-	-	3.2×10^{-4} - 1.0×10^{-1}	27.5
2	4	150	100	-	-	6.0×10^{-5} - 1.0×10^{-1}	29.6
3	4	150	-	100	-	2.4×10^{-5} - 1.0×10^{-1}	26.7
4	4	150	-	-	100	5.3×10^{-5} - 1.0×10^{-1}	37.2

Table-2

Variation in membrane potential of AMHBCA based membrane electrode systems in Pb^{2+} solution of different concentration with an internal reference solution of concentration ($1.0 \times 10^{-1}M$).

Tesr solution M	Potential observed, -mv and sensor No.			
	1	2	3	4
1.0×10^{-6}	74	77	68	82
5.0×10^{-6}	72	81	71	84
1.0×10^{-5}	54	80	72	86
5.0×10^{-5}	55	81	70	85
1.0×10^{-4}	54	76	69	85
5.0×10^{-4}	48	56	65	75
1.0×10^{-3}	42	48	46	62
5.0×10^{-3}	22	37	22	42
1.0×10^{-2}	15	26	19	28
5.0×10^{-2}	5	12	7	14
1.0×10^{-1}	0	0	0	0

Table-3

Performance of Pb^{2+} selective sensor No.2 in 15% and 30% (v/v) non aqueous medium.

Non aqueous content % (v/v)	Slope mv/decade of activity	working concentration range M
Nil	29.6	6.0×10^{-5} - 1.0×10^{-1}
Methanol		
15	31.3	6.2×10^{-5} - 1.0×10^{-1}
30	34.1`	7.7×10^{-5} - 1.0×10^{-1}

Table-4

Selectivity coefficient Values K_{Pb}^{2+}, B observed for Pb^{2+} selective sensor (No-2) for various interfering ion (B) using fixed interference method.

Interfering ion(B)	Selectivity coefficient K_{Pb}^{2+},B	Interfering ion(B)	Selectivity coefficient K_{Pb}^{2+},B
Na^+	3.6	Mg^{2+}	0.25
Ag^+	6.2	Sr^{2+}	0.42
Co^{2+}	0.48	Ca^{2+}	0.52
Pb^{2+}	0.43	Zn^{2+}	0.61
Cu^{2+}	0.452	Fe^{3+}	0.07
Ba^{2+}	0.89	Al^{3+}	0.05

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