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Selective and Sensitive Determination of Pd^{2+} Ions in Various Samples using a Ion Selective Membrane Electrode

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Abstract

A Palladium ion selective composite cation exchanger antipyrano mercapto pyrimidine (APMP) 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),dibutyl phthalate (DBP),1-chloronaphthalelene (CN) and PVC in different composition. The membrane electrode formed by using dibutyl phthalate (DBP) plasticizer showed a Nernstian response 30.2 mv per decade for Pd^{2+} ions over a wide concentration range. The electrode works satisfactory in the concentration range 7.0×10^{-5} to 1.0×10^{-1} M with near Nernstian slope of 30.2 mv per decade of concentration between pH from 2.3 to 3.3.The electrode also showed better selectivity for Pd^{2+} ion over many interfering ions. Results of the investigation reveal that the membrane electrode prepared by using 6 mg of organic ion exchange APMP, 100 mg DBP 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, pH, Nernstian response, selectivity, Ion selective membrane electrode, Palladium, solvent effect.

Introduction

Membrane electrodes specified and selective for a particular ion are not new. The most successful and widely used membranes for hydrogen ion were made from ion exchanging glass which was studied by Cramer. In the last four decades several studied have been conducted to know the preparation, properties and signification of such membrane electrodes. Although some research activity in the field of ISEs started quite early, Systematic investigation in this direction started in 1950.When Punur and coworkers (1,2) studied the

behaviour of silver iodide precipitate as a model substance. The research activity of ISEs was very much boosted with the development of homogeneous crystal membrane fluoride electrode in 1966 by Frant and Ross (3), followed a year later by a liquid membrane electrode for calcium by same coworkers (4). 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.

The theoretical background has been developed gradually (by, e.g., Nicoloisky and Eisenman) and its present state was completed during the 1970s. Nicoloisky initiated a remarkable development with his theory which assumed that electrode response is dependent on the active sites of the glass capable of ion exchange. Equilibrium potentials were derived from electrochemical potentials and the Nicoloisky concept enabled the selectivity coefficient of an electrode to be calculated. 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.

Palladium has increasing importance in today's industries due to increasing applications for the production of dental and medical devices, jewelry, automobile and catalytic converters. It is widely used in the synthesis of many materials because of its catalytic properties (5).

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 (6). Ren (7) has described a Pb^{2+}-selective electrode. Using naphthalene-1-dithicarboxylate Pb^{2+} complex whereas, Jain and Tyagi (8) used araldite based membranes of bismuth tungstata. In this direction, a number of crown ethers (9-12) 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 (13-15)

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 (16, 17). 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.

Detection of palladium contents in samples is usually carried out by using analytical tools such as atomic absorption/emission spectroscopy, solid-phase micro extraction, adsorptive cathodic stripping voltammetry, high performance liquid chromatography, ion-coupled plasma emission-mass spectroscopy, X-ray spectroscopy, electrothermal

vaporization, flow injection and fluorescence spectroscopy (18). Potentiometric measurements with palladium ion selective electrode allow the direct determination of free Pd^{2+}ion concentration in aqueous samples. ISEs ISEs (ion-selective electrodes) based on ionophores are few used (19-22). An important requirement for preparation of an ion selective sensor is that membrane electro active material should have high lipophilicity and strong affinity for a target metal ion and poor affinity to the others (23). It is well known that coordination abilities of legends containing sulfur atom, are very selective to the transition metal ions (24). However, most of these show some limitations in their working activity range, selectivity, response time, pH range and lifetime. Thus, the development of reliable sensing ion selective sensors for palladium ion is considerable importance for environment and human health. To improve the analytical selectivity, it is essential to search novel carrier compounds that would interact with palladium ion with high selectivity. Because of the legend that contain sulphur highly selective for Pd (II), classified as a "soft" Lewis acid (25). The use of PD (phenyl disulfide) as an ionophore is reported in the construction of a Palladium (II)-PVC membrane electrode and their characteristic and properties of selective electrode were studied.

Meterials and Method:

All chemicals used in these studies were analytical grade reagents. dibutyl(butyl) phosphonate (DBBP),dibutyl phthalate (DBP),1-chloronaphthalelene (CN), poly vinyl chloride (PVC),and tetra hydro furan (THF),metal solution of their nitrate salts were prepared in doubly distilled water and standardized before use. The compound antipyrano mercapto pyrimidine (APMP) 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 APMP 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 APMP as Sensor for Pd^{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 3.5×10^{-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 DBP, DBBP and CN (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 DBP to the membrane (electrode No.-2) lowers the slope to a near Nernstian value of 30.2 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 Palladium 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 Pd^{2+} and graph (Fig.) was plotted. It is seen that the useful pH range for the electrode is 2.3 to 3.3 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 10% and 20% amount of methanol was calculated from the result and gathered in Table 3. Potential vs. concentration plots in 10% and 20% methanol solution show that the electrode works satisfactory in partial non aqueous media containing up to 10% methanol content only.

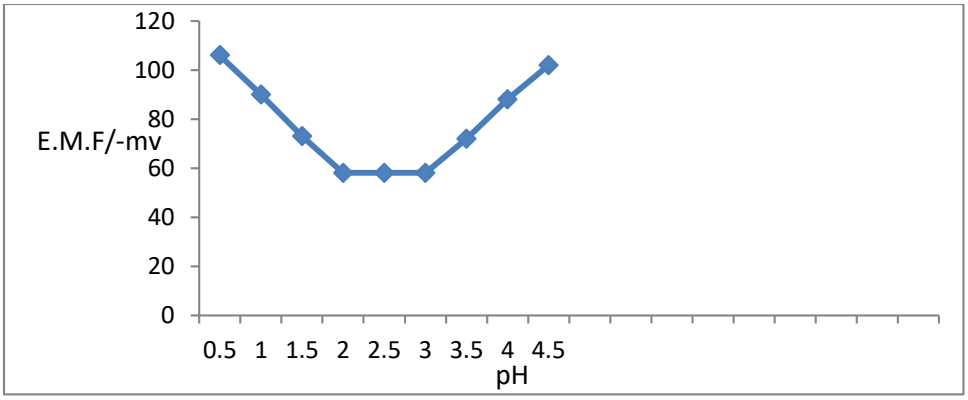

Fig: - Effect of pH on cell potential based electrodes No.2 [Pd^{2+}] =1.0×10^{-3} M

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 Pd^{2+}.

Table-1

Composition of PVC membranes of APMP and performance characteristics of Pd^{2+} selective electrode based on them.

Sensor No.	components in sensors (%w/w)					working concentration range M	Slope mv/decade
	APMP	PVC	DBP	DBBP	CN		
1	6	150	-	-	-	3.5×10^{-4} - 1.0×10^{-1}	27.5
2	6	150	100	-	-	7.0×10^{-5} - 1.0×10^{-1}	30.2
3	6	150	-	100	-	1.4×10^{-5} - 1.0×10^{-1}	28.7
4	6	150	-	-	100	5.3×10^{-5} - 1.0×10^{-1}	38.2

Table-2

Variation in membrane potential of APMP based membrane electrode systems in Pd^{2+} solution of different concentration with an internal reference solution of concentration (1.0×10^{-1}M).

Tesr solution M	Potential observed, -mv and sensor No.			
	1	2	3	4
1.0×10^{-6}	65	87	78	92
5.0×10^{-6}	64	91	81	95
1.0×10^{-5}	63	90	82	96
5.0×10^{-5}	65	91	81	95
1.0×10^{-4}	64	86	80	96
5.0×10^{-4}	58	66	64	85
1.0×10^{-3}	52	59	56	73
5.0×10^{-3}	33	38	34	51
1.0×10^{-2}	20	27	28	39
5.0×10^{-2}	8.0	11	7.0	12
1.0×10^{-1}	0	0	0	0

Table-3

Performance of Pd^{2+} selective sensor No.2 in 10 % and 20% (v/v) non aqueous medium.

Non aqueous content % (v/v)	Slope mv/decade of activity	working concentration range M
Nil	30.0	7.0×10^{-5} - 1.0×10^{-1}
Methanol		
10	31.5	6.2×10^{-5} - 1.0×10^{-1}
20	34.4	7.7×10^{-5} - 1.0×10^{-1}

Table-4

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

Interfering ion(B)	Selectivity coefficient K_{Pd}^{2+},B	Interfering ion(B)	Selectivity coefficientK_{Pd}^{2+},B
Na^{+}	3.8	Mg^{2+}	0.63
Ag^{+}	6.3	Sr^{2+}	0.40
Co^{2+}	0.50	Ca^{2+}	0.56
Pb^{2+}	0.45	Zn^{2+}	0.63
Cu^{2+}	0.45	Fe^{3+}	0.08
Ba^{2+}	0.98	Al^{3+}	0.06

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