Bis(trans-cinnamaldehyde)-1,3-propanediimine) mercury(II)chloride, [Hg(BPPPB)Cl₂] as Carrier for Construction of Iodide Selective Electrode

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Abstract: Highly selective poly(vinyl chloride) (PVC) membrane of iodide ion selective electrode based on the application of bis(trans-cinnamaldehyde)-1,3-propanediimine)mercury(II)chloride [Hg(BPPPB)Cl₂] as new carrier by coating the membrane ingredient on the surface of graphite electrodes has been reported. The effect of various parameters including membrane composition, pH and possible interfering anions on the response properties of the electrode were examined. At optimum conditions, the proposed sensor exhibited Nernstian responses toward iodide ion in a wide concentration range of 1×10^{-6} to 0.1 M with slopes of 58.0 ± 0.8 mV per decade of iodide concentration over a wide pH range of 3-11 with detection limit of detection of $\sim 8 \times 10^{-7}$ M. The sensors have stable responses times of ≤ 5 s and give stable response after conditioning in 0.05 M KI for 24 h with its response is stable at least 2 months without any considerable divergence in its potential response characteristics. The electrodes were successfully applied for the direct determination of iodide ion in water sample and as indicator electrodes in precipitation titrations.

Keywords: Iodide-selective electrode; Potentiometry; PVC membrane; bis(trans-cinnamaldehyde)-1,3-propanediimine) mercury(II)chloride, [Hg(BPPPB)Cl₂].

Introduction

Iodine and iodide compounds as essential micronutrient have important roles in biological activities such as brain function, cell growth, neurological activities and thyroid function [1-3]. Therefore, diverse analytical methods have been developed for its determination at low concentration levels in a wide dynamic linear range [2-13]. Most of these methods require expensive instrumentation, rather complicated techniques, and/or sample pretreatments. Among these different methods, ISEs with unique advantages such as simplicity, rapid analysis, low cost, wide linear range, reasonable selectivity and non-destructive analysis, have emerged as one of the most promising tools for direct and easy determination of

various species [4-10]. In this pathway, a strong interaction is necessary between the ionophore and the anion for its selective binding. Several iodide-selective electrodes based on the application of selective interaction of transition metal ions with iodide ions and selective coordination of iodide anion to the metal center of the carrier molecules [14-32] has been reported. Most of the iodide potentiometric sensors have high detection limit and narrow working concentration range or have serious interfering affect of other anions such as I^- , ClO_4^- , Cl^- , Br^- and IO_4^- . The wide use of ISEs in routine chemical analysis have accompanied by a search for ionophores that offer improved potentiometric response characteristics. Purpose of this work was the development of iodide-selective electrodes based on plasticized PVC membranes, containing $[Hg(BPPPB)Cl_2]$ as the membrane active ingredients coated on the surface of graphite disk electrodes. Coated type electrodes are very easy to construct and handle, and offer much higher mechanical resistance, compared to their liquid membrane counterparts.

Experimental

Reagents

PVC of high relative molecular weight, dibutyl phthalate (DBP), dioctyl phthalate (DOP), dioctylphenyl phosphonate (DOPP), 4-nitrophenylphenyl ether (NPPE) and bis(2-ethylhexyl) sebacate (BEHS) were used as received from Aldrich. Reagent grade tetrahydrofuran (THF), sodium tetraphenylborate (NaTPB), methyltriocetylammmonium chloride (MTOACl) and all other chemicals were of highest purity available from Merck, and were used without further purification. All aqueous solutions were prepared with deionized water. The pH adjustments were made with dilute nitric acid or sodium hydroxide solutions.

Synthesis of Bis(trans-cinnamaldehyde)-1,3-propanediimine mercury(II)chloride, $[Hg(BPPPB)Cl_2]$

To an ethanolic solution containing 1 mmol of trans-cinnamaldehyde and 0.5 mmol 1, 3-propanediamine after stirring for 4 hours, 1mmol of mercury (II) chloride dissolved in methanol, was gradually added. The reaction mixture was stirred for 2 hours and then the grayish white precipitate was filtrated, washed with ethanol twice and recrystallized form dichloromethane and chloroform to give the complex with 75% yields. $[Hg(BPPPD)Cl_2]$; % $C_{21}H_{22}Cl_2N_2Hg$: Calculated: C, 43.95; H, 3.86; N, 4.88; Found: C, 43.6; H, 3.8; N, 5.1. IR spectrum (KBr, cm^{-1}): 3447(m), 3037(w), 2909(w), 2852(w), 1626(vs), 1594(s), 1443(m), 1381(w), 1340(m), 1272(w), 1172(m), 998(w), 857(w), 749(m), 688(m), 537(w), 478(w), 447(w). UV-Vis spectrum $[(CHCl_3), \lambda(nm)]$: 303 and 231. 1H -NMR spectrum ($CDCl_3$): 7.97(bd, 2H, $J = 6.80Hz$), 7.58(dd, 2H, $J = 15.6Hz$ and $J = 8.80Hz$), 7.42(d, 4H, $J = 5.93Hz$), 7.21(bd, 6H, $J = 7.20Hz$), 6.91(d, 2H, $J = 16.00Hz$), 3.88(t, 4H, $J = 5.00Hz$), 1.81(q, 2H, $J = 4.80Hz$) ppm. Schematic structure of the complexes is presented in Scheme 1.

Scheme 1 Structure of applied ionophore.

Preparation of Electrodes

The coated-graphite electrodes were prepared according to a previously reported method [1-4]. Graphite rods (3 mm diameter and 10 mm long) were prepared from spectroscopic grade graphite. A shielded copper wire was glued to one end of the graphite rod with silver loaded epoxy resin, and the rod was inserted into the end of a PVC tube. The working surface of the electrode was polished with a polishing cloth. The electrode was rinsed with water and methanol and allowed to dry. A mixture of PVC, plasticizer and the membrane additive (MTOACI) to give a total mass of 100 mg, was dissolved in about 4 ml of THF. To this mixture was added the electroactive Hg complex ($\text{Hg}(\text{BPPPB})\text{Cl}_2$) and the solution was mixed well. The polished graphite electrode was then coated, by repeated dipping (several times, a few minutes between dips), into the membrane solution. A membrane was formed on the graphite surface, and was allowed to set overnight. The electrode was rinsed with water and conditioned for ~24 h in 0.05 M potassium iodide solution. The coating solutions are stable for several weeks if keep in refrigerator and can be used for the construction of new membranes.

Potential Measurement

The response characteristics of the prepared coated-graphite electrodes was determined by recording potential across the membrane as a function of I^- concentration at a constant temperature of 25 °C. All the potential measurements were carried out with a digital pH/ion meter, model 692 Metrohm. The potential build up across the membrane electrodes were measured using the galvanic cell of the following type: $\text{Ag}/\text{AgCl}/\text{KCl}(\text{sat'd.}) \parallel \text{test solution} \mid \text{PVC membrane} \mid \text{graphite electrode}$. Potentials were measured relative to a saturated Ag/AgCl reference electrode. The pH of the sample solutions was monitored simultaneously with a conventional glass pH electrode. The performance of each electrode was investigated by measuring its potential in potassium iodide solutions prepared in the concentration range 1×10^{-1} - 1×10^{-7} M by serial dilution of the 0.1 M stock solution at constant pH. The solutions were stirred and the potentials were recorded, until they reached steady state values. The data were plotted as observed potential versus the logarithm of I^- concentration.

Results and discussion

The plasticized PVC-based membrane electrode containing the $\text{Hg}(\text{BPPPB})\text{Cl}_2$ carriers, respond to iodide ion according to Nernstian response while show poor response toward other ions. Therefore, in detail the characteristic performance of the membrane electrode based on the application of this carrier has been reported.

In preliminary experiment, membranes in the presence and absence of carriers were constructed and it was seen that blank membrane show insignificant selectivity toward iodide and its response is not reliable, while addition of proposed carrier to the membrane lead to generation of Nernstian response and remarkable selectivity for iodide over several common inorganic and organic anions. The preferential response toward iodide is believed to be associated with its selective coordination as a carrier to the mercury ion center in the complexes. Soft anions such as iodide are expected to interact with the soft mercury sites in $\text{Hg}(\text{BPPPB})\text{Cl}_2$ complex.

Influence of the membrane composition

The effect of the membrane composition on the response properties of proposed electrode was studied by changing the nature and amount of plasticizer, membrane additives and the amount of carriers.

The influence of the plasticizer type and concentration on the characteristics of the iodide ion-selective electrodes was investigated using plasticizers with different polarities including DBP, DOP, NPE, and DMS at plasticizer/PVC mole of about 2. The electrodes

containing DOP generally showed better potentiometric responses. i.e., sensitivity and linearity of the calibration plots). It seems that DOP, as a low polarity compound among the investigated plasticizers, provides more appropriate conditions for incorporation of the highly lipophile iodide ion into the membrane prior to its coordination with the soft mercury ion in the complexes which this plasticizer has been selected for subsequent work. (Table 1).

The response of the electrodes prepared with different amounts of $\text{Hg}(\text{BPPPB})\text{Cl}_2$ was studied and it was observed that working range and sensitivity of the electrode response were improved by increasing the amount of $\text{Hg}(\text{BPPPB})\text{Cl}_2$ up to 7%. At higher amount of ionophore amount the electrode response, worsened most probably due to saturation or some non-uniformity of the membrane. (Table 1).

The influence of the type and concentration of the membrane additives were also investigated by incorporating MTOACl/ or NaTPB into the membranes and it was observed that membranes response was greatly improved in the presence of the lipophilic cationic additive, MTOACl/, compared to the membranes with no additive at all. On the other hand, no response was observed by addition of anionic, into the membranes. The effect of MTOACl/ concentration in the membranes was investigated at several additive/carrier mole ratios, at MTOACl/carrier mole ratios of ca. 0.56 showed near-Nernstian responses in a wide range of iodide concentration. The optimized membrane compositions and their potentiometric response characteristics are given in Table 1.

Response characteristics and selectivity of the electrodes

The optimum equilibration time and concentration of the conditioning solution for the electrodes were ~ 24 h in 0.05 M KI solution, after which the electrodes generated stable potential responses. The full detail of electrode performance is presented in Table 2.

The influence of pH of the test solution on the response of the coated membrane electrodes based on $\text{Hg}(\text{BPPPB})\text{Cl}_2$ was investigated for 1.0×10^{-3} and 1.0×10^{-2} M iodide solutions, where the pH was adjusted with dilute nitric acid and sodium hydroxide solutions as required. As can be seen from the results shown in Fig. 1, the potential response of the electrodes is independent of pH over the range 3-11, indicating that hydroxide ions are not considerably coordinated to the mercury center in the complexes.

Figure 1. Effect of pH on response of iodide selective electrode at 1×10^{-3} M iodide and 1×10^{-2} M iodide. Membrane compositions and measurement conditions are given in Table 1.

Table 1. Response Performance of the iodide ion-selective electrode, conditions: various membrane composition, conditioned 24 h in 0.05 M KI.

No	Plasticizer	PVC	Ligand	NaTPB	MTOACl	L. R. ^a	Slope c	R. T (S) ^d	L. T (day) ^e
1	59.6(DOP)	29.4	6.5	---	4.5	1.0-0.1	57.3	<10	60
2	64.4 (DOP)	31.9	2.5		1.2	1.0-0.1	52.6	<25	55
3	64.1 (DOP)	31.2	3.3		1.4	1.0-0.1	58.0	<20	
4	61.5 (DOP)	30.8	5.5		2.2	1-0.01	55.71	<18	
5	60.0 (DOP)	29.0	7.6		3.4	1.0-0.001	54.9	<10	
6	61.5(DOP)	30.5	7.0		1.0	6.8-0.001	57.8		
7	60.5(DOP)	29.57			2.8	10-0.1	57.6		
8	59.5 (DOP)	29.5			4.0	1.0-0.1	58.3		
9	58.6 (DOP)	28.7			5.7	2.5-0.1	58.0		
10	60.7(DMS)	29.5			2.8	5.7-0.1	55.1	<25	50
11	60.7 (DBP)					1.0-0.1	58.3	<25	44
12	60.7 (NPOE)					1.9-0.1	65.67	<30	38
13	59.3 (DOP)	29.7	7.0	4.0	---	5.0-0.001	12.8	<60	10

a) linear range (μM -M) b) Detection limit c) Slope (mV per decade concentration) d) response time (s) e) life times (day) all value for membrane composition are (W/W %).

The potentiometric response of the electrodes was examined in the concentration range of 1.0×10^{-7} - 1.0×10^{-1} M and the calibration plot show linearity over the concentration range of 1.0×10^{-6} - 1.0×10^{-1} M with a detection limit of $\sim 8 \times 10^{-7}$ M and sensitivities of 58.5 ± 0.8 mV/decade of iodide concentration ($n=5$). The response time of the electrodes was tested by measuring the time required to achieve a steady state potential (within ± 1 mV) after successive immersion of the electrodes in a series of iodide solutions (each having a 10-fold increase in concentration) from 1.0×10^{-5} to 1.0×10^{-2} M. The electrodes yielded steady potentials within 2 to 5 s and the potential readings stay constant (to within ± 1 mV) for at least 5 min. Typical potential-time plot for the response of the electrodes based on Hg(BPPPB)Cl₂ carriers to successive additions of iodide are shown in Fig. 2.

Table 2. Specifications of the iodide ion-selective electrode.

Properties	Values / Range
Optimized membrane composition	PVC (29.5%), DOP (59.5%), Hg(BPPPB)Cl ₂ (7.0%), MTOACl (4%) MTOACl/ Hg(BPPPB)Cl ₂ mole ratio = 0.56
Electrode type	Coated--graphite electrode
pH range	3–11
Conditioning time	At least 24 h in 0.05 M KI
Linear range (I ⁻ , M)	1×10^{-6} - 1×10^{-1}
Slope (mV/decade)	58.5
Detection limit (M)	$\sim 8 \times 10^{-7}$
Standard deviation of slope (mV/decade)	± 0.8
Standard deviation of measurement	± 0.8 at 1×10^{-2} M ± 1.2 at 1×10^{-3} M
Response time (s)	≤ 10
Life time of the electrode	At least two months

Figure 2. Typical potential-time recorder trace of the electrode based on Hg(BPPPB)Cl_2 . Membrane compositions and measurement conditions are given in Table 1.

The reproducibility and stability of the coated graphite electrodes were evaluated by repeated calibration of the proposed electrode in potassium iodide solutions. Repeated monitoring of potentials and calibration (performance of proposed electrode) using the same electrode gave good slope reproducibility with the standard deviation of slope ≤ 1.2 mV/decade. The standard deviation of 10 replicate measurements at 1.0×10^{-2} and 1.0×10^{-4} M iodide concentrations were between ± 0.8 to ± 1.0 mV (Table 1). Life time study was based on monitoring the change in electrode slope and linear response range with time. The electrodes could be used for at least two months without a considerable change in their response (Table 2).

The potentiometric selectivity coefficients of the coated graphite electrodes were determined by the mixed solution method using a fixed (0.01 M) of the interferences and varying concentrations of iodide (Table 3). The potentiometric selectivity coefficients presented in Table 3 indicate its selective response toward iodide ion over a number of other inorganic and organic anions, do not show tendency toward the highly lipophilic anions such as ClO_4^- , salicylate, N_3^- , Br^- , NO_3^- and NO_2^- . This is due to strong interaction of iodide with mercury center in the complexes, and as such the carriers seem to be promising for construction of iodide-selective electrodes.

Applications

The high degree of iodide selectivity exhibited by the proposed electrode based on Hg(BPPPB)Cl_2 carrier, makes it potentially useful for monitoring concentration levels of iodide in various real samples. The results (Table 4) indicate good agreement between the potentiometric procedures. In addition, the sensors were used as indicator electrodes for potentiometric titration of iodide with silver nitrate and vice versa. The titration curves showed sharp break (about 250 mV) at the equivalence point. Typical results for the titration of silver nitrate with potassium iodide using this proposed electrode good inflection point and accurate estimation of equivalent volume show the suitability of proposed electrode for evaluation of iodide content in various real samples is shown in Fig.3.

Figure 3. Application of the electrode based on Hg(BPPPBB)Cl₂ for potentiometric titration of (A) 100 mL 1×10^{-3} M Ag⁺ with 0.1 M I⁻ and (B) 100 mL 1×10^{-3} M I⁻ with 0.1 M of Ag⁺.

Table 3. Selectivity coefficients of the proposed coated-graphite electrode.

Ion	SSM	FIM
Perchlorate	-2.91	-3.25
Salicylate	-3.41	-3.56
Phosphate	-4.32	-4.45
Azide	-3.80	-3.79
Oxalate	-4.35	-4.45
Bromide	-2.07	-2.54
Chloride	-3.04	-3.24
Carbonate	-4.52	-4.68
Nitrate	-4.76	-4.84
Nitrite	-4.63	-4.78
Sulfate	-4.69	-4.75
Thiocyanate	-1.07	-1.27
Acetate	-4.68	-5.0
Fluoride	-4.01	-4.08
Cyanide	-0.57	-0.87

Table 4. Determination of iodide in tap water and drugs.

Sample	Iodide added	Iodide found
(Tap Water)	-	ND
	3.0×10^{-5}	$3.05 \pm 0.09) \times 10^{-5}$
	9.0×10^{-5}	$9.08 \pm 0.28 \times 10^{-5}$
	6.54×10^{-4}	$6.60 \pm 0.10 \times 10^{-3}$
2. (Meglumine ompound)	$(2.78 \pm 0.14) \times 10^{-3}$ *	$(2.66 \pm 0.15) \times 10^{-3}$
Iodoquinol	210	206.13 ± 0.14

* Iodide concentration in the sample was obtained by titration with AgNO₃ solution.

Table 5. Characteristic Performance of Some Iodide Selective Electrodes.

Ref.	L. T (day) ^a	I. ^b	R. T. (s) ^c	D.L. ^d	pH ^e	L. R. (μM - M) ^f	Central Atom
21	-	-	30-720	4-6 μM	-	10-0.001	Silver (I) and Mercury (II)
22	-	SCN^- , ClO_4^- , Br^-	10	7.5 nM	Low	1-0.003	Silver (I)
23	-	SCN^-	20	-	-	1-0.001 or 10-0.01	Silver (I)
24,25	-	----	Average	-	Low	Low	Mercury (II)
26, 27	-	NO_2^- , SCN^- , ClO_4^- , Br^-	40	0.48 μM	4-8	0.48-0.023	Cobalt (II)
28	-	Average	<10	5 μM	3-4	8-0.1	Nickel (II)
29	-	---	Average	16 μM <	-	40-0.1	Nickel (II) and Cobalt (II)
30	--	---	60	1 μM	Low	Low	Vitamin B12
31	Average	---	7	6 μM	3-11	8-0.05	Cerium (III)
32	90	---	---	5 μM	3.5- 8.5	34-0.1	Manganese (II)
33	---	---	Average	0.45 μM	3.5-10	1-0.5	Iron (III)
34	---	Average	---	High	--	1-0.001 or 10-0.01	Palladyte Amine
35	high	ClO_4^- , Salicylate	Few	10 μM	-	10-0.1	Cobalt
36	28	ClO_3^- , Cl^- , SCN^- , ClO_4^- , Br^-	---	16 μM	5.5- 13.0	40-0.1	Ethyle Violet
37	60	---	60	---	2-9	10-0.001	Manganèse
38	--	----	15	0.2 μM	5.5- 8.0	0.8-0.1	Thiopyrilium Ion Derivative
39	60	OH^-	40 s	0.47	4-8	0.84-0.023	Co (II)
40	90	---	10	1.0	3-9	5.0-0.2	Cu (II)
41		---	15	5.0	2-8	7.5-0.01	Mn (III)
42	---	---	15	0.3	3.1- 9.8	0.5-0.1	Co (II),
43	42	medium selectivity	20	7.0	2.5- 8.0	10-0.01	Miconazole

a) Life Time b) Interference c) Response Time d) Detection Limit e) Applicable pH Range f) Linear Range g) slope (mV/ decade).

Conclusions

New iodide-selective solid-contact membrane electrodes have been prepared using the new carrier. The comparison of result presented in this manuscript with those previously reported in literature show (Table 5) [21-43] electrodes have been shown to have good operating characteristics (Nernstian response; reasonable detection limit; relatively high selectivity, especially with respect to the highly lipophilic anions; wide dynamic range; fast response; applicability over a wide pH range). These characteristics and the typical applications presented in this paper, make the electrode suitable for measuring the iodide content in a

wide variety of samples, without a significant interaction from concomitant anionic species. The results show that there was a coordination interaction between iodide and the proposed carriers, which played an important role in the response characteristics and selectivity of the electrodes.

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