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Iodide–Selective Electrodes Based on Bis(Trans-Cinnamaldehyde)1,3-Propanediimine Mercury (II) Chloride [$BCPHgCl_2$] and Bis(Trans-Cinnamaldehyde)-1,3-Propandiimine Cadmium(II) Chloride [$BCPCdCl_2$] Carriers: Influence of Multiwalled Carbon Nanotubes on the Response Performance

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In this research, new iodide-selective electrode based on incorporating of new Hg and Cd complexes to carbon paste matrices has been reported. To obtain good charestristic performance vis. linear range and detection limit, the influence of amount of multiwalled carbon nanotube (MWCNT), lipophilic cationic and anionic additives and amount of ionophores and Nujol on response properties was investigated and their values was set as carbon powder, MWCNT, Nujol, Carrier: MTOACl, (0.15 g, 5 mg, 36 mg, 26.0 mg, 15.6 mg) and (0.15 g, 10 mg, 45 mg, 25 mg, 17.7 mg) for $BCPHgCl_2$ and $BCPCdCl_2$, respectively. The potentiometric responses of the proposed electrodes are independent of pH of the test solution over the range of 3.0–11.0 for $BCPHgCl_2$ and 3-11.5 for $BCPCdCl_2$ The selectivity sequence of proposed iodide selective electrodes evaluated by different methods such as separate solution method (SSM) and fixed interference method (FIM) show their iodide preference over other ions. Due to high selectivity's proposed electrodes successfully has been applied for accurate evaluation of iodide ion content in various real samples and as indicator electrode in precipitation titration. The electrodes exhibited near-Nernstian slopes of −58.5 ± 1.0 and −58.0 ± 0.7 mV/decade of iodide concentration over the range $1 \times 10^{-6} - 1 \times 10^{-1}$ and $5 \times 10^{-6} - 1 \times 10^{-1}$ $molL^{-1}$ with detection limits of $\sim 0.6 \times 10^{-6}$ and 2.4×10^{-6} M for the electrodes based on $BCPHgCl_2$, and $BCPCdCl_2$ respectively. They have relatively fast response times ≈ 10 s and ≈ 8 s for $BCPHgCl_2$ and $BCPCdCl_2$ and life times of at least two months.

Keywords: Carbon paste electrode, Potentiometry, iodide ion, Multiwalled carbon nanotubes (MWCNTs).

1. INTRODUCTION

Potentiometric determination based on ion selective electrodes (ISEs) of minute quantities of ion species offers great advantages such as adaptable to small sample volume, speed and ease of preparation and procedures, relatively fast response, non-destructive analysis, reasonable selectivity through judicious choice of the membrane active material, low cost, wide linear dynamic range. The design of anion-sensitive membrane electrodes has been of great importance in the filed of ion-selective electrodes (ISEs) [1-3].

Iodine is an indispensable microelement to human, while its vapors irritate the eyes and lungs which are toxic. The maximum iodide allowable concentration in air (when working) is just 1.0 mg m^{-3}. Iodine plays a key role in many biological activities such as, brain functions, cell growth, neurological activities, and metabolism and thyroid functions in addition to is present in the composition of various drugs. Due to vital importance of iodide in environment, medicines and industry, its determination is very important in clinical and chemical analysis [3,4]. Various analytical procedures have been reported for iodide determination.

Some of these methods suffer from draw back such as requiring expensive instrumentation rather complicated techniques and/or sample pretreatments. Selection of an ideal analytical method can be accomplished with considering necessity such as simplicity, speed of analysis, low cost, wide linear range, reasonable selectivity and non-destructive analysis that are unique advantages of ISEs. On the other hand, selectivity of ISE significantly can be improved by incorporation of selective ionophore in the carbon paste or liquid membrane ion selective electrodes. To achieve this requirement, impregnation of transition or heavy metal complexes to the matrices of ISE improves the response properties of ISEs. The anion selectivity's of the ion selective electrodes controlled by the structure of the ligands and the properties of the central metal ions [5].

Therefore, there is a search for ionophores to improve the figures of merit of proposed electrodes. Several iodide- selective electrodes based on the application of complexes of transition metal ions such as $Ag^{+,}$ Hg^{2+}, Co^{2+}, Co^{3+}, Ni^{2+}, Fe^{3+} and Mn^{2+} with various ligands such as triisobutylphosphine sulfide [5,6], thiocarbamoylimine-dithioether derivatives [7], thiourea [8], mercurated polystyrene containing large number of RC_4H_4HgOAC units [9,10], Schiff bases [11,13], tetraazaannulene macrocyclic [14], cyclam derivatives [15], covalently attached phthalocyanine [16], vitamin B_{12} [17], and Schiff base complex of Fe(III) [18] have been reported. In these electrodes, good response properties emerged from selective coordination and attachment of iodide ion to central metal of complexes. The proposed carbon pastes electrodes (chemically modified carbon paste electrodes (CMCPEs)), fabricated in simple way and give a stable electrochemical response. These electrodes can be renewed by removing an outer layer of the paste and re-smoothing the electrode surface. They have lower ohmic resistance than ion-selective electrodes based on polymeric membranes [13-15].

Due to difference in the softness of the central metal ions and total strict, hinder of complexes, their response properties differ with each other. Therefore, application of ionophore of soft transition metal ions such as mercury and cadmium seems to improve the response properties of iodide CPE. The design of selective receptors for anions has been of great interest in the field of molecular recognition. A number of molecules which are capable of displaying selective coordination and recognition with anions have been synthesized [19,20]. One of the most appealing potential applications of these anion receptors is the development of chemical sensors.

Ion selective electrodes have found vast applications in diverse fields of analysis, being of low cost, selective, sensitive and applicable over a wide range of experimental conditions [21,22]

It was pointed out that impregnation of carbon nanotubes (CNTs) with high surface area, high mechanical chemical and thermal stability cause unique improvement in potentiometric response of ISEs [10-16]. Ionophores impregnated in the carbon paste matrices control the selectivity of electrode by selective binding of target ions via strong interaction. Therefore, there is a strong requirement to search new lipophilic character ionophores with low bleeding to sample solution [17]. To cope with limitations of previously reported iodide ISE, the purpose of this work was development of new MWCNT carbon paste iodide selective electrodes based on application of $BCPHgCl_2$ and $BCPCdCl_2$. In order to improve the response of proposed electrodes the influence of effective variables was optimized and at optimum value of all variables the performance of electrodes such as slope characteristics, detection limit, response time, selectivity and dependence of the electrode potential to solution pH was investigated.

2. EXPERIMENTAL

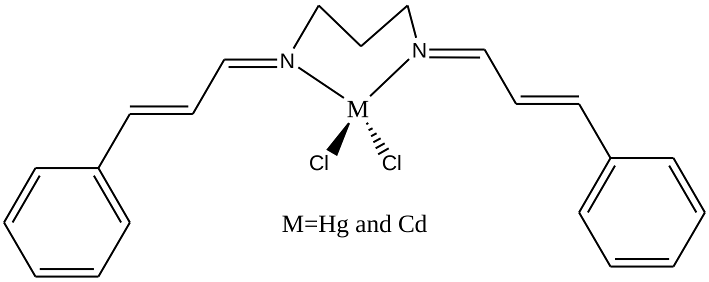
2.1. Reagents

All chemicals such as sodium tetraphenylborate (NaTPB), methyltrioctylammonium chloride (MTOACl), powder with the purity of analytical reagent grade and/or spectroscopic grade was purchased from Fluka and Aldrich and doubly distilled water were used throughout. Graphite powder and high purity Nujol oil from Fluka (Buchs, Switzerland) were used for the preparation of the unmodified and modified carbon paste electrode. Stock solution of 0.5 M iodide solutions were prepared daily from accurate weighting and dissolving required amount of potassium iodide in de-ionized water solution. The pH adjustments were made with dilute nitric acid or potassium hydroxide solutions as required.

2.3. Synthesis of bis(trans-cinnamaldehyde)-1,3-propanediimine M(II) chloride, [$MLCl_2$] (M=Hg and Cd)

To 1 mmol of trans-cinnamaldehyde in ethanol 0.5 mmol 1, 3- propanediamine was added stirred for 4 hours. Then, 1mmol of mercury (II) or cadmium (II) chloride was added gradually. The reaction mixture was stirred for 2 hours till a yellowish white precipitate was obtained and then the precipitate was filtrated and twice washed with ethanol following recrystallization of compounds in dichloromethane and chloroform that respective complexes was obtained with yield 75 and 79%, respectively. Their physical and spectral properties are presented as following: [$BCPHgCl_2$]; % $C_{21}H_{22}Cl_2N_2Hg$: 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 [($CHCl_3$), λ(nm)]: 303 and 231. ^{1}H-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.

[$BCPCdCl_2$]; % $C_{21}H_{22}Cl_2N_2Cd$: Calculated: C, 51.93; H, 4.57; N, 5.77; Found: C, 52.9; H, 4.8; N, 5.9. IR(KBr, cm^{-1}): 3037(m), 2918(w), 1630(s), 1593(m), 1448(m), 1172(m), 1062(w), 988(w), 860(w), 754(m), 692(m), 452(w). Uv-Vis (CH_2Cl_2): 297, 230 nm 1H NMR ($CDCl_3$): 7.91(bd, 2H), 7.63(dd, 2H), 7.44(dd, 4H), 7.21(m, 6H), 6.69(d, 2H), 3.86(bs, 4H), 1.84(m, 2H) ppm. A schematic structure of the complexes is presented in Scheme 1.



Scheme 1. Schematic Structures of applied ionophores

2.3. Electrode preparation and potential measurements

Unmodified carbon paste electrode (CPE) was prepared by thoroughly mixing of 150 mg of reagent-grade graphite powder and 36 mg of Nujol oil with a mortar and pestle based on $BCPHgCl_2$ and 45 mg of Nujol oil with a mortar and pestle based on $BCPCdCl_2$. Modified carbon paste (MWCNT-CPE) was prepared by mixing 150 mg of graphite powder, 36 mg based on $BCPHgCl_2$ and 45 mg based on $BCPCdCl_2$ of Nujol with different weight of ionophore and additive to get different compositions. All carbon paste compositions were packed into 5.0 mL polyethylene syringes with diameter of 2.5 mm. Copper wire was glued (imbedded into carbon paste matrices) on the end of carbon paste for electrical contact.

2.4. Apparatus and potential measurement

The electromotive force (emf) measurements were carried out with the following cell assemblies: CPE│Sample solution│Reference electrode that a double junction Ag/AgCl was used as reference electrode with a pH/mV meter. 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 I^- ion concentration in the range of $1 \times 10^{-7}– 1 \times 10^{-1}$ M by serial dilution of the 0.5 M stock solution at constant pH. The solutions were stirred and potential readings recorded when they reached steady state values. The data were plotted as observed potential versus the logarithm of I^- concentration.

3. RESULTS AND DISCUSSION

The carbon paste iodide selective electrodes based on $BCPHgCl_2$ and $BCPCdCl_2$ complexes in the present of MTOACl (ionic additive) were highly selective to iodide ion with respect to several anions. The electrodes behave reversibly in iodide solutions of different concentrations and have fast exchange kinetic and reach equilibrium response about 10 s. The CPE based on mercury and cadmium complexes based on specific type of interaction lead to generation of potential across carbon paste electrode relative to the iodide ion concentration.

3.1. Influence of the membrane composition

The amount of carrier was changed while the ratios of MTOACl/carrier concentrations were the same for the entire carbon paste electrode. The working range and sensitivity of the electrode response were improved by increasing the concentration of $BCPHgCl_2$ and $BCPCdCl_2$ up to 26 and 25 mg. Further addition of the carrier concentration worsened the electrode response, most probably due to saturation or non-uniformity of the electrodes.

The effect of the type and concentration of the ionic additives were also investigated by impregnating MTOACl or NaTPB into the carbon paste matrices that the potentiometric response properties of the CPEs based on both carriers was greatly improved in the presence of MTOACl as a lipophilic cationic additive. In comparison, carbon paste electrode without additive or in the presence of NaTPB no nernstian response was achieved for iodide ion. The effect of MTOACl amount in the CPE at several additive/carrier mole ratios was examined and it was found that electrodes with MTOACl/carrier mole ratios of ~0.6 and ~0.71 for $BCPHgCl_2$ and $BCPCdCl_2$ exhibited maximum sensitivity over a wide range of iodide concentration. Among the different carbon paste compositions studied, electrode composition with 26 mg carrier (Table 1), 100% mol ratio MTOACl, 36 mg Nujol and 150 mg graphite powder based on $BCPHgCl_2$ and 25 mg carrier, 100% MTOACl, 45 mg Nujol and 150 mg graphite powder based on $BCPCdCl_2$, show highest sensitivity and widest linear range, that were selected as the optimum composition for further studies (Table 2).

3.2. Influence of carbon nanotubes on performance of iodide ion selective electrode

MWCNTs powder surface was activated via stirring with 10% (v/v) hydrochloric acid solution for 2 h. Treated MWCNTs after filtering and washing with distilled deionized water dried at 80 °C for 5 h. 1 g of treated MWCNT was suspended in 250 mL of 32.5% (W/W) nitric acid solution and stirred for 36 hours at room temperature. The mixture was filtered and thoroughly rinsed with distilled de-ionized water until neutral pH and dried at 80 °C for 2 hours. The oxidation of MWCNTs and appearance of new functional groups was followed using FT-IR-spectroscopy as powerful and acceptable protocol. IR spectra of MWCNT and oxidized MWCNT are shown in Fig. 1. IR spectrum of chemically modified MWCNT shows some important characteristic vibrational frequencies at 3400-2500(bw), 1627(w), 1155(s), 673(s), 592(s). The FESEM images of the as going and oxidized MWCNTs are shown in Fig. 2(a, b). It can be seen that the surface morphology of the modified MWCNTs are homogeneous and relatively smooth, while the morphologies of the oxidized MWCNTs is highly disperse in the surface without any aggregation and approximately uniform in size distribution.

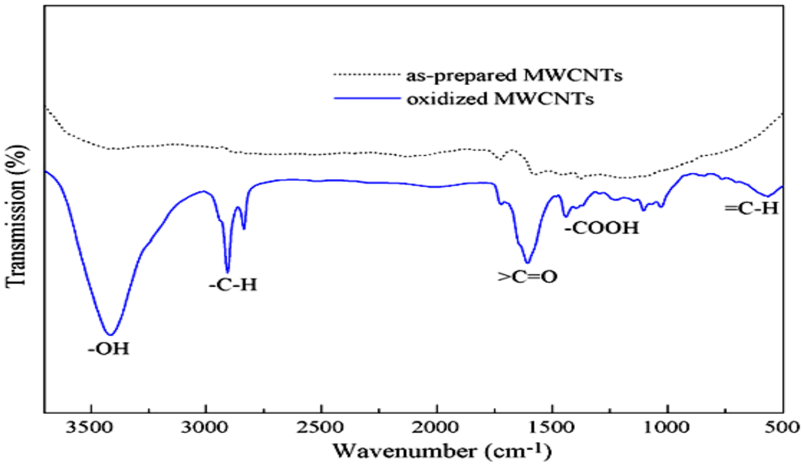


Figure 1. FT-IR spectra of as-prepared and oxidized MWCNT

Previously it has been reported that addition of carbon nanotube to the carbon paste composition improves the conductivity and transduction of the chemical signal to electrical signal. In this regard, similar CPE at optimum values of all variables and different amount of oxidized MWCNT has been prepared

As it can be seen from typical presented results for $BCPHgCl_2$ (Table 1) one can notice that the response properties of proposed electrodes vis. Linear range, detection limit and correlation coefficient of proposed electrode response was improved significantly by addition of oxidized MWCNTs till 30 mg.

3.3. Effect of pH

Oxygen can oxidize iodide to iodine in low pH . On the other hand the reaction of metal–Schiff base complex with iodine is possible, accompanied by electron transfer between the central metal, and iodine is possible. The behavior of the proposed CPE based on $BCPHgCl_2$ and $BCPCdCl_2$ ionospheres in the pH range of 3.0-11.0 and 3.0- 12 at two iodide concentration of 1.0×10^{-3} and 1.0×10^{-2} M was investigated and typical results are given in Fig. 3. The results show OH^- cannot compete with iodide ion even at high pH values. The iodide solution over liner concentration experimental working range without pH change can be applied for potentiometric evaluation of iodide

Table 1. Influence of carbon paste composition based on $BCPHgCl_2$ response of iodide selective electrode.

N	Carbon powder (mg)	Hg based Carrier (mg)	NaTPB (mg)	Nujol (mg)	MWCNT(mg)	L. R. (μM-M)	D.L (μM)	Slope(mV/decade)
1	150	4	2.4	36	……	5.0-0.01	3.5	22.6
2	150	8	4.8	36	……	5.0-0.1	3.4	23.3
3	150	14	8.4	36	……	50-0.1	10.0	36.7
4	150	18	10.8	36	……	50-0.1	10.0	40.9
5	150	20	12.0	36	……	50-0.1	14.05	47.9
6	150	22	13.2	36	……	50-0.1	30.7	51.8
7	150	24	14.4	36	……	5.0-0.1	2.06	46.4
8	150	26	15.6	36	……	5.0-0.1	1.92	54.6
9	150	28	16.8	36	……	5.0-0.1	0.05	33.9
10	150	30	18.0	36	……	5.0-0.1	0.1	33.5
11	150	26	3.1	36	……	50-0.1	11.0	20.1
12	150	26	6.2	36	……	5.0-0.1	13.34	22.7
13	150	26	9.4	36	……	1.0-0.1	0.08	28.0
14	150	26	12.5	36	……	1.0-0.1	0.5	44.7
15	150	26	18.7	36	……	5.0-0.1	2.5	40.9
16	150	26	15.6	18	……	5.0-0.1	2.5	29.9
17	150	26	15.6	54	……	1.0-0.1	3.6	43.0
18	145	26	15.6	36	5	1.0-0.1	0.6	58.5
19	140	26	15.6	36	10	5.0-0.1	3.1	47.3
20	130	26	15.6	36	20	5.0-0.1	3.9	35.5
21	120	26	15.6	36	30	1.0-0.1	0.05	17.0
22	150	26	……	36	…...	50-0.01	40.0	29.9
23	150	……	15.6	36	…...	50-0.1	32.0	38.7
24	150	……	……	36	…...	5.0-0.1	1.83	41.5

ion. This observation may be due to this fact that the OH^- as hard anion has low tendency for coordination to the soft Hg^{+2} and Cd^{+2} ions center in the proposed ionophores.

The dynamic response time of the proposed electrode at optimum value of all variables at various concentrations (1.0×10^{-7} to 1.0×10^{-1} mol L^{-1}) of I^- ion was evaluated. Results illustrate that electrodes based on Hg and Cd complexes at optimum values of all other in the whole concentration range the electrode give liner response of $1 \times 10^{-6} - 1 \times 10^{-1}$ M and $3 \times 10^{-6} - 1 \times 10^{-1}$ M for electrode based on $BCPHgCl_2$, $BCPCdCl_2$ and reach equilibrium responses about 10 s and 8 s. The response characteristics of both electrode is presented in Table 3.

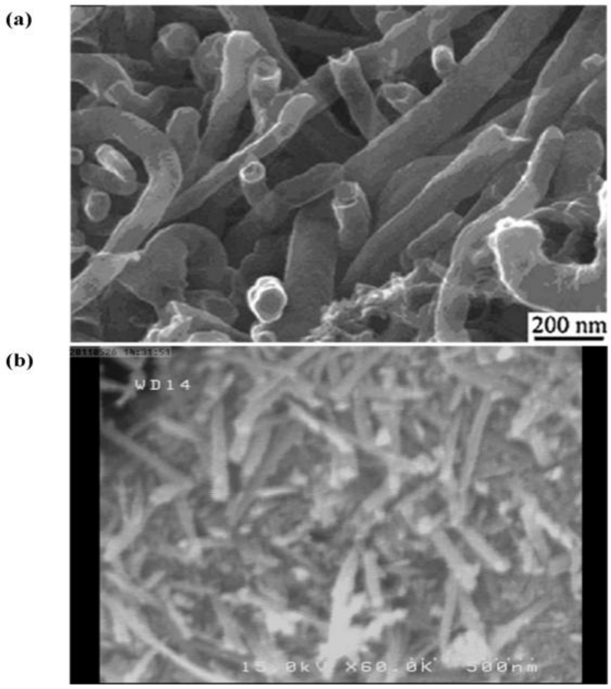


Figure 2. The FESEM images of the as-preparing and oxidized MWCNTs

Table 2. Influence of carbon paste composition based on BCPCdCl$_2$ response of iodide selective electrode.

N	Carbon powder (mg)	Carrier (mg)	NaTPB (mg)	Nujol (mg)	MWCNT(mg)	L. R. (µM-M)	D.L (µM)	Slope(mV/decade)
1	150	5	3.54	45	……	5.0-0.01	3.07	20.65
2	150	10	7.1	45	……	5.0-0.1	4.1	25.4
3	150	15	10.6	45	……	50-0.1	13.3	33.0
4	150	18	12.8	45	……	50-0.1	11.7	39.1
5	150	20	14.2	45	……	50-0.1	40.0	40.8
6	150	22	15.6	45	……	50-0.1	30.3	47.7
7	150	24	17.0	45	……	5.0-0.1	2.06	49.4
8	150	25	17.7	45	……	0.5-0.1	0.1	54.9
9	150	26	18.4	45	……	0.5-0.1	0.05	48.9
10	150	28	19.8	45	……	5.0-0.1	4.3	41.7
11	150	30	21.3	45	……	50-0.1	11.0	39.1
12	150	25	3.5	45	……	5.0-0.1	0.05	19.7
13	150	25	7.1	45	……	5.0-0.1	0.1	28.1
14	150	25	10.6	45	……	5.0-0.1	0.9	37.3
15	150	25	14.2	45	……	5.0-0.1	2.8	47.3
16	150	25	21.3	45	……	1.0-0.1	0.05	36.2
17	150	25	17.7	18		1.0-0.1	0.4	33.0
18	145	25	17.7	36		1.0-0.1	0.8	40.5
19	140	25	17.7	54		50-0.1	30.3	47.3
20	130	25	17.7	45	5	5.0-0.1	3.9	44.8
21	120	25	17.7	45	10	5.0-0.1	2.4	58.0
22	120	25	17.7	45	20	5.0-0.1	0.1	29.0
23	120	25	17.7	45	30	5.0-0.1	1.0	34.1
24	150	25	……	45	…...	50-0.01	40.8	40.9
25	150	……	17.7	45	…...	50-0.1	5.0	36.9
26	150	……	……	45	…...	5.0-0.1	1.5	48.5

Table 3. Response characteristics of the proposed iodide ion selective electrodes.

Properties	Values/range	
Optimized electrode composition	Carbon powder: MWCNT, Nujol, Hg carrier: MTOACl (0.15g : 5 mg, 36 mg : 26 mg,	Carbon powder, MWCNT: Nujol, Cd Carrier MTOACl, (0.15g, 10 mg, : 45 mg, 25 mg : 17.71 mg)
Electrode type	Carbon paste electrode	
pH range	3.0-11.0	
Linear range I^- (M)	1.0×10^{-6} - 1.0×10^{-1}	5.0×10^{-6} - 1.0×10^{-1}
Slope (mV/decade)	-58.5	-58.0
Detection limit (M)	0.6×10^{-6}	2.4×10^{-6}
S.D of slope (mV/decade)	± 1.0	± 0.7
Response time (s)	≈ 10 s	≈ 8 s

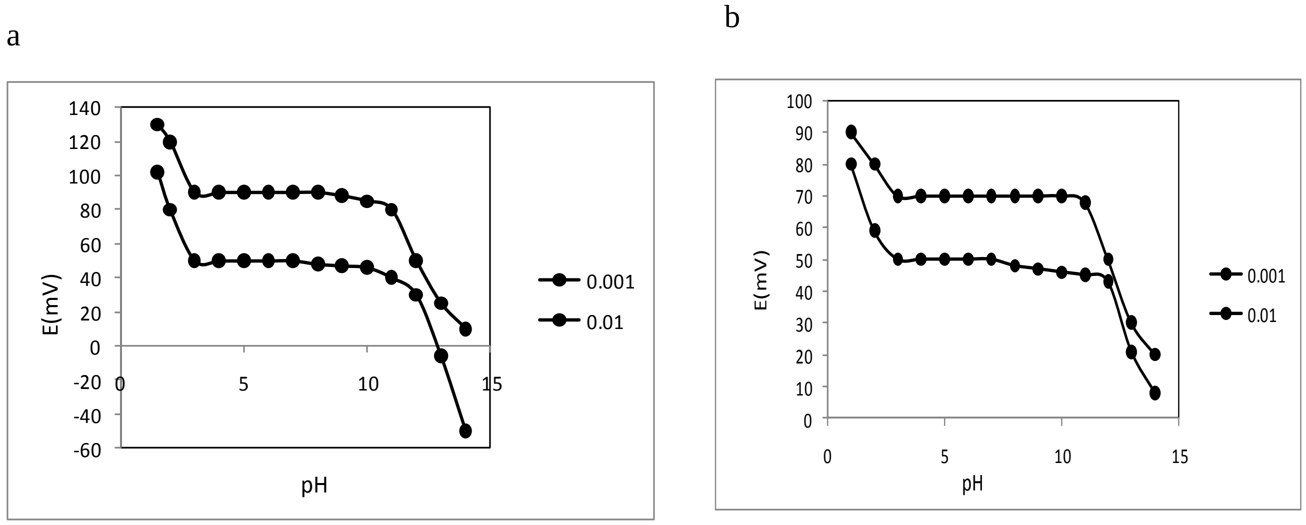


Figure 3. Effect of pH test solution on the potential response of the iodide selective electrode based on MWCNT-IPC in the presence of 1.0×10^{-2} and 1.0×10^{-3} M iodide ion

3.4. Response characteristics and selectivity of the electrodes

The potentiometric response of the electrodes was examined in the concentration range of 1×10^{-7} to 0.1 M iodide. The electrodes exhibited near-Nernstian slopes of -58.51 ± 1.00 and -58.01 ± 0.73 mV/decade of iodide concentration over the range $1\times10^{-6}-1\times10^{-1}$ M and $5\times10^{-6}-1\times10^{-1}$ M , with detection limits of $\sim0.6\times10^{-6}$ and 2.4×10^{-6} M for the electrodes based on $BCPHgCl_2$ and $BCPCdCl_2$ respectively. The dynamic response time of the electrodes was ≈ 10 s and ≈ 8 s under stirred conditions when the electrodes were inserted in 1×10^{-5} to 1×10^{-1} M iodide solutions (Fig.4).

Repeated monitoring of potentials and plotting calibration curve over a period of 2 months over linear range of proposed electrode show a very slight gradual decrease in the calibration slopes of the electrode. On the other hand, the relative standard deviation (RSD) of the slope of calibration curve for the same electrode (between electrode variation) stored in air potassium iodide solution over periods of 50 days and 2 month were 2.1 and 3.3 %, respectively.

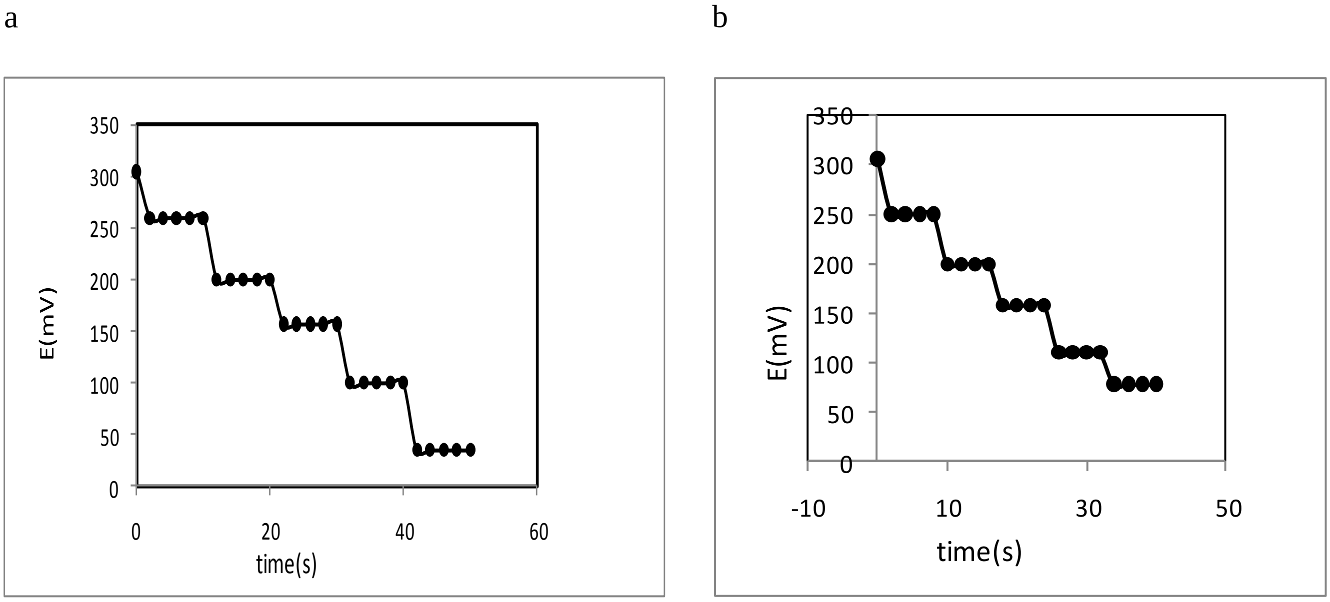


Figure 4. Response time of proposed of the iodide selective electrodes based on MWCNT-IPC in the presence of different concentrations (1.0×10^{-5} – 1.0×10^{-1}) of iodide ions based on $BCPHgCl_2$ and BCPCd Cl_2..

Higher RSD values were observed when the electrodes were stored in ambient air or in distilled water (Table 2). The standard deviation of slope for several electrodes (within electrode variation), constructed by using the same membrane solution for $BCPHgCl_2$ and $BCPCdCl_2$ ionophores, were −58.51 ± 1.00 and −58.01 ± 0.73 mV/decade of iodide concentration, respectively.

The selectivity for a certain anion in ISEs is a combination of two contributions: (i) the free energy of the transfer of the anion from the aqueous solution to the membrane phase and (ii) the free energy related to the specific interaction of the anion with the ionophore (receptor). It has been proven difficult to control selectivity among anions, due to low charge to radii ratios, sensitivities to pH and high solvation energies [22, 23].

The potentiometric selectivity coefficients of the proposed carbon paste electrodes were determined by the separate solution method (SSM), using 0.01 M solutions of iodide and interfering ions, and by the fixed interference method (FIM) using 0.01 M interfering ions and varying concentrations of iodide ion. Table 4 lists the potentiometric selectivity coefficients of the optimized electrodes (according to Tables 1 and 2) based on $BCPHgCl_2$ and $BCPCdCl_2$ ionophores. It was found that the electrodes based on both ionophores are highly selective towards iodide with respect to a variety of anions. There is a satisfactory agreement between the two sets of results obtained for several anions by the FIM and SSM methods.

Table 4. Selectivity coefficients of the proposed carbon paste iodide selective electrodes

	-Log*K*			
Ion	Hg carrier		Cd carrier	
	FIM	SSM	FIM	SSM
Permanganate	2.28	2.3	3.1	3.36
Perchlorate	3. 8	4.39	3.74	3.3
Salicylate	3.8	3.3	4.54	4.1
Bromide	4.2	4	3.2	2.93
Chloride	3.24	2.3	2.64	2.86
Carbonate	2	1.3	3.82	3.2
Nitrate	4.18	4.3	1.98	2.3
Nitrite	3.1	3.3	2.1	3.91
Sulfate	4.23	4.3	3.78	3.65
Thiocyanate	1.54	1.5	1.56	1.66
Histamine	3.76	3.60	4.85	4.78

3.5. Analytical applications

The resulting electrodes were applied to the determination of iodide in a drug preparation (Meglumine Compound Injection, from Darou Pakhsh Pharmaceutical Co., Iran, is an iodide-containing drug used for protection from light and secondary X-rays). The sample was prepared by refluxing 1.0 mL of the drug preparation in concentrated sodium hydroxide solution in the presence of zinc powder for 30 min. After cooling, the reaction mixture was filtered and washed with water three times. The filtrate was acidified with H_2SO_4 and diluted to 1 L with water. The iodide content of the resulting solution was determined potentiometrically by the standard addition method. The results obtained by the electrode method are in agreement with those obtained by titration with standard $AgNO_3$ solution as given in Table 5.

The electrodes were also applied for the determination of iodide added to tap water samples and as indicator electrodes for potentiometric titration of silver and iodide ions. The direct potentiometric measurement was carried out using the standard addition technique. The results for the determination of iodide ion at several concentrations are in agreement with the known iodide content as given in Table 5. The electrodes were also found useful for the potentiometric titration of Ag^+ with iodide and vice versa. Typical titration plots are shown in Figure 5.

Table 5. Application of the Electrodes Based on $BCPHgCl_2$ and $BCPCdCl_2$ Carriers for Determination of Iodide Added to Tap Water and a Drug Preparation samples (All Concentrations are in M).

Sample	Iodide added	Iodide found $BCPHgCl_2$	Iodide found $BCPCdCl_2$
1. (Tap Water)	-	ND	ND
	8.0×10^{-6}	$(8.35 \pm 0.38)\times10^{-6}$	$(8.41 \pm 0.41)\times10^{-6}$
	1.6×10^{-5}	$(1.49 \pm 0.08)\times10^{-5}$	$(1.52 \pm 0.0.07)\times10^{-5}$
	4.0×10^{-5}	$(4.18 \pm 0.18)\times10^{-5}$	$(4.20 \pm 0.17)\times10^{-5}$
	8.0×10^{-5}	$(8.28 \pm 0.42)\times10^{-5}$	$(8.21 \pm 0.40)\times10^{-5}$
	4.90×10^{-4}	$(5.04 \pm 0.06)\times10^{-4}$	$(5.06 \pm 0.0.06)\times10^{-4}$
	4.76×10^{-3}	$(4.77 \pm 0.04)\times10^{-3}$	$(4.78 \pm 0.0.09)\times10^{-3}$
2. (Meglumine Compound)	$(2.78 \pm 0.14)\times10^{-3}$ *	$(2.89 \pm 0.16)\times10^{-3}$	$(2.66 \pm 0.15)\times10^{-3}$

* Iodide concentration in the sample was obtained by titration with $AgNO_3$ solution.

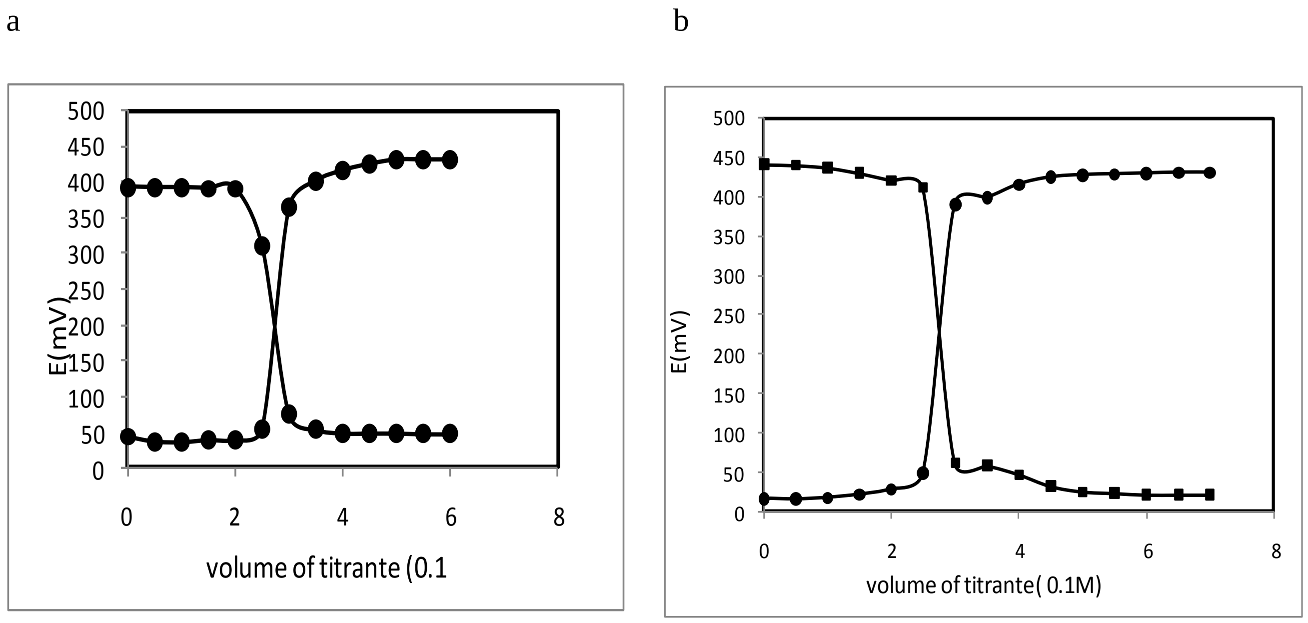


Figure 5. Application of the electrode based on (a) $BCPHgCl_2$ for potentiometric titration of (A) 25 mL of 1×10^{-3} M Ag^+ with 0.1 M I^- and (B) 25 mL of 1×10^{-3} M I^- with 0.1 M Ag^+ and (b) $BCPCdCl_2$ for potentiometric titration of (A) 25 mL of 1×10^{-3} M Ag^+ with 0.1 M I^- and (B) 25 mL of 1×10^{-3} M I^- with 0.1 Ag^+

4. CONCLUSIONS

New iodide-selective carbon paste electrodes have been prepared using two new complexes. The 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. On the results discussed in this paper, these new ionophores can be considered as a suitable ionophore for construction of a carbon paste selective electrode for the direct determination of iodide ions in solution. The proposed sensors exhibit wide working concentration range, shorter response time, greater tolerance to pH variations and high selectivity towards the target ions over other anions.

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