

Multi-walled carbon nanotubes-ionic liquid-carbon paste electrode as a super selectivity sensor: Application to potentiometric monitoring of mercury ion(II)

Hadi Khani^{a,*}, Mohammad Kazem Rofouei^a, Pezhman Arab^b, Vinod Kumar Gupta^{c,d}, Zahra Vafaei^a

^a Faculty of Chemistry, Tarbiat Moallem University, Mofateh, Tehran, Iran

^b School of Chemistry, University College of Science, University of Tehran, Tehran, Iran

^c Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247 667, India

^d Chemistry Department, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia

ARTICLE INFO

Article history:

Received 10 May 2010

Received in revised form 28 June 2010

Accepted 9 July 2010

Available online 15 July 2010

Keywords:

Mercury determination

Carbon paste electrode

Carbon nanotubes

Ionic liquid

ABSTRACT

In this article a super selectivity potentiometric methodology, using an ion-selective electrode, for determination of mercury ion(II) in aqueous solution was investigated. For modification of the electrode a room temperature ionic liquid, 1-n-butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF₄), was applied as a super conductive binder, and Multi-walled carbon nanotubes (MWCNTs) was used in the composition of the carbon paste to improve conductivity and transduction of chemical signal to electrical signal. Moreover, incorporation of 1-(2-ethoxyphenyl)-3-(3-nitrophenyl)triazene (ENTZ) as an ionophore to this composition caused to significantly enhanced selectivity toward Hg(II) ions over a wide concentration range of 1.0×10^{-4} to 5.0×10^{-9} M with a lower detection limit of 2.5×10^{-9} M (0.5 ppb) and a Nernstian slope of $29.3 \pm (0.2)$ mV decade⁻¹ of Hg(II) activity. The electrode has a short response time (~5 s) and can be used for at least 55 days without any considerable divergence in potentials, and the working pH range was 2.0–4.3. Finally, the proposed electrode was successfully used as an indicator for potentiometric determination of Hg(II) in dental amalgam and water samples.

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1. Introduction

The determination of trace amounts of heavy metal ions is of interest in several fields including environmental analysis, process control, biology, and medicine. Mercury is an environmentally and toxicologically important element that its neurotoxicity has been reported to result in hearing loss, mental deterioration, speech difficulty, impaired vision, vestibular dysfunction and autism [1]. The growing awareness of environmental mercury pollution and toxicity necessitates the determination of its very low concentrations in a variety of samples, especially water. The allowed mercury level set by World Health Organization (WHO) for drinking water is $1 \mu\text{gL}^{-1}$ [2]. Mercury is also considered by the Environmental Protection Agency (EPA) as a highly dangerous element because of its accumulative and persistent character in the environment and biota. As a result, the quantification of very low mercury level has been of increasing importance in environmental and clinical chemistry since its negative roles in human's life; therefore, various methods, such as inductively coupled plasma (ICP) optical emission spectrometry [3], ICP mass spectrometry [3,4], cold vapor

atomic absorption spectroscopy (CVAAS) [5,6] or neutron activation analysis [7] were applied for determination of low levels of mercury. Most of the mentioned methods are time consuming, too costly, and not capable of on-site mercury in most analytical laboratories; also, their monitoring involves multiple sample manipulations. However, electrochemical detection offers several advantages over these methods, such as ease of use, low cost, direct detection, miniaturization, and fast response times [8]. The development and application of ion-selective electrodes for sensing of metal cations [9–16] and anionic species [17,18] continues to be an interesting area of analytical research as they provide accurate, rapid, non-destructive and low cost methods of analysis.

Nowadays, conventional potentiometric carbon paste ion-selective electrodes are highly selective, highly sensitive, and of low detection limit. Over the past five decades, carbon paste, i.e., a mixture of carbon (graphite) powder and a binder (pasting liquid), has become one of the most popular electrode materials used for the laboratory preparation of various electrodes, sensors, and detectors [19]. The operation mechanism of such chemically modified carbon paste electrodes (CMCPEs) depends on the properties of the modifier materials used to import selectivity and sensitivity towards the target species. Initially, non-conductive reagents, such as mineral oil or paraffin oil were used as binders, but their electrochemical capability was poor due to their low conductiv-

* Corresponding author. Tel.: +98 21 88848949; fax: +98 21 88820993.

E-mail addresses: h.khani@tmu.ac.ir, khani.hadi@yahoo.com (H. Khani).

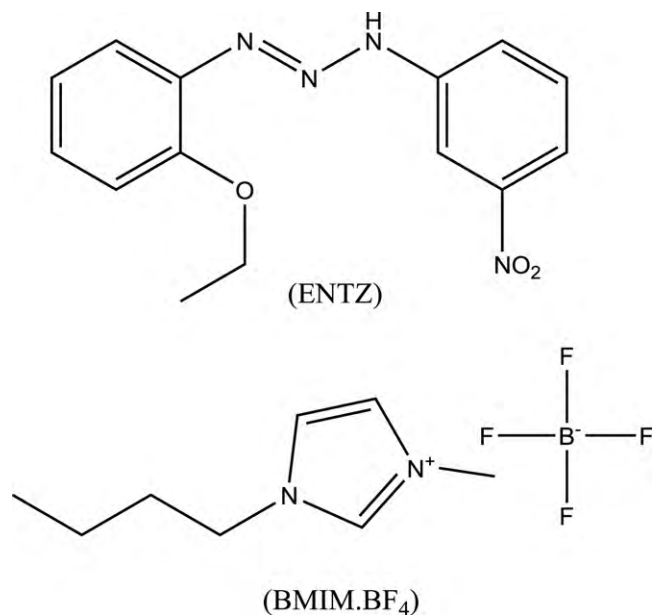


Fig. 1. Structures of ENTZ and BMIM·BF₄ used as modifier in the proposed electrode.

ity. Room temperature ionic liquids (ILs) have a lot of advantages, such as high viscosity, high ionic conductivity, low volatility, wide electrochemical windows, and high chemical and thermal stability, which have been applied to modify the electrodes and have shown excellent electrochemical behaviors [20].

MWCNTs are built from sp² carbon units and contain concentric graphite tubules with multiple layers of graphite sheets [21]. MWCNTs have been one of the most actively studied materials in carbon paste electrodes [22–25] because of their unique structure and extraordinary physical properties, such as an ordered structure with a high aspect ratio, large ratio of surface area to mass, ultra-light weight, high thermal conductivity, metallic or semi-metallic behavior, high electrical conductivity and remarkable mechanical strength [26]. The combination of these characteristics makes MWCNTs unique materials with the potential for diverse applications.

In our previous reports sulfur-containing compounds such as mercapto thiadiazole compounds and silica sol–gel network were used for self-assembled gold nanoparticle modified carbon paste electrodes and were applied for potentiometric determination of sub ppb level of Al(III) and Cu(II) cations [27–29].

In the current study, two chief aspects of work have been highlighted. Firstly, a new type carbon paste electrode composed of MWCNTs, graphite powder, and (1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMIM·BF₄) (Fig. 1), to displace the traditional carbon paste electrode, was investigated. Secondly, 1-(2-ethoxyphenyl)-3-(3-nitrophenyl)triazene (ENTZ) (Fig. 1) was used and incorporated to the prepared matrix as a high selective ionophore for reliable quantification of mercury ion(II). To our surprise, using MWCNTs and displacement of paraffin oil with BMIM·BF₄ have greatly enhanced the potentiometric sensitivity and showed good reproducibility, low response time and long-term stability. Moreover, the new MWCNTs-ionic liquid-carbon paste electrode could be renewed easily by mechanical polishing whenever needed. These results indicated that the combination of MWCNTs with BMIM·BF₄ in the presence of ENTZ provides a promising carbon paste matrix in potentiometric sensing of mercury ion(II).

2. Experimental

2.1. Reagents and solutions

All analytical reagent grade chemicals and distilled water were used for preparing all aqueous solutions. The graphite powder (Merck, Germany) along with the paraffin oil (Aldrich, USA) was of high purity and was used for the preparation of the carbon pastes. Ionic liquid (1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMIM·BF₄), chloride and nitrate salts of the cations used are all purchased from Merck. The multi-walled carbon nanotubes (MWCNTs) with 10–40 nm diameters and 1–25 μm length were purchased from Research Institute of the Petroleum Industry (Iran). A stock solution of 1.0 × 10⁻² M Hg(II) was prepared by dissolving of 0.3426 g Hg(NO₃)₂·H₂O in water. Then 0.5 mL of 1.0 M HNO₃ was added and the solution was diluted to 100 mL in a standard flask. More dilute sample solutions were prepared daily by appropriate dilution of the stock solution with water. All the other metal nitrate solutions were freshly prepared by accurate dilution from their stock standard solution of 0.01 M, with distilled, de-ionized water.

2.2. Apparatus

All potentiometric measurements were made with a pH/mV meter (Metrohm-827, Switzerland) using proposed sensor in conjunction with a double junction Ag/AgCl (Azar electrode, Iran) reference electrode. UV–vis absorption spectra were recorded using the double-beam in-time spectrophotometer (Perkin–Elmer model Lambda 25, U.S.A.) and the temperature of the cell holder was maintained at 25 ± 0.1 °C. Elemental analysis was performed by a CHN-O-Rapid Heraeus elemental analyzer (Hanau, Germany). IR spectra were found on a Perkin–Elmer model 843 (U.S.A.), the ¹H NMR spectra were obtained using BRUKER AVANCE DPX 300 MHz apparatus (Germany).

2.3. Synthesis and characterization of ENTZ

The 1-(2-ethoxyphenyl)-3-(3-nitrophenyl) triazene (ENTZ) used as the ionophore and its structure is shown in Fig. 1. It was synthesized as follows: a 100 ml flask was charged with 10 g of ice and 15 ml of water and then cooled to 0 °C in an ice-bath. After that, 0.69 g (5 mmol) of 3-nitroaniline and 3.61 g (0.1 mol) of hydrochloric acid (*d* = 1.18 g mL⁻¹) were added to the mixture, and then a solution of NaNO₂ containing 0.35 g (5 mmol) in 10 ml of water was added during 15 min under stirring solution. Afterwards, 0.68 ml (5 mmol) of 2-ethoxyaniline (1.06 g mL⁻¹) was added drop wise with vigorous stirring for a period of 30 min to this mixture. Finally, a solution containing 14.76 g (0.18 mol) of sodium acetate in 45 ml of water was added and stirred for 45 min. The orange-colored product was filtered and dissolved in diethyl ether. After the evaporation of diethyl ether, a purified sharp pale orange powder, which has a melting point of 101–102 °C, was produced (yield, 72%). Infrared and ¹H NMR spectra and CHN analysis, were confirmed the ENTZ structure. IR (KBr): 3389, 3325, 2984, 1600, 1519, 1468, 1343, 1253, 1209, 1113, 1045, 894, 739 cm⁻¹, ¹H NMR (DMSO): δ 1.37 (CH₃, 3), 4.13 (CH₂, 2), 6.94–8.06 (phenyl protons, 8), 12.89 (NH, 1), CHN: (C₁₄H₁₄N₄O₃)C: 58.66%, H: 4.82%, N: 19.52%.

2.4. Electrode construction

The general procedure to prepare the carbon paste electrode was as follows: different amounts of the ionophore ENTZ along with appropriate amount of graphite powder, ionic liquid and MWCNTs were thoroughly mixed. The resulting mixture was transferred into a glass tube. Electrode bodies were made from 1 mL polypropylene

syringes (3 mm i.d.), the tip of which had been cut off with a cutter. After the mixture homogenization, the paste was packed carefully into the tube tip to avoid possible air gaps, often enhancing the electrode resistance. A copper wire was inserted into the opposite end to establish electrical contact. The external electrode surface was smoothed with soft paper. A new surface was produced by scraping out the old surface and replacing the carbon paste. The electrode was finally conditioned for 2 h by soaking in a 1.0×10^{-7} mol L⁻¹ Hg(NO₃)₂ solution at the pH of 3.0.

2.5. Potentiometric measurements

All electromotive forces (EMF) measurements were carried out with the following cell assembly:

Ag/AgCl|samplesolution|carbonpasteelectrode

The proposed carbon paste electrode was connected to the pH/mV meter as an indicator electrode and the Ag/AgCl reference electrode was connected to the reference terminal of the meter. For all measurements the two electrodes were immersed in a 50 ml beaker containing de-ionized water, and the solution was stirred using a magnetic stirrer. The pHs of the test solutions containing mercury ion were adjusted about 3.0 at the required value by the addition of 1.0 mol L⁻¹ sodium hydroxide and/or 1.0 M nitric acid. The electrode was allowed to equilibrate until a steady state response was achieved (about 30 s). An accurately measured volume of standard Hg(II) solution was added by microsyringe to the stirred solution and the potential was recorded after 10 s. Consecutive amounts of Hg(II) were added so that a final Hg(II) concentration in the range from 1.0×10^{-10} to 1×10^{-3} M was obtained. The potential of the electrode against the Ag/AgCl reference electrode was recorded after each Hg(II) addition, and then plotted as a logarithmic function of Hg(II) activity. All measurements were corrected using the Debye–Hückel approximation.

2.6. Spectrophotometric study

To have a clear picture about the stoichiometry and stability of the ligand for various metal ions, we investigated the interaction of ENTZ with a number of metal ions in an acetonitrile solution by the spectrophotometric method. For this purpose, the spectra of a series of solutions containing a constant concentration of ligand (5.0×10^{-5} M) and varying amounts of the metal ions were obtained. It was found during experiments that the addition of Hg(II) to acetonitrile solution of ENTZ resulted in fast changes in the color of the solution from pale yellow to dark orange, while the addition of alkali, alkaline earth and transition-metals showed no observable color change in the ENTZ solutions. The results showed that the ENTZ, with the most stable complex with Hg(II) ion ($\log K_f = 8.20$), is expected to act as a selective ionophore for preparation of Hg(II)–carbon paste electrodes.

The spectra of Hg(II)–ENTZ are shown in Fig. 2. It is seen that by addition of metal to ENTZ, the absorbance band of ENTZ at wavelength 270 nm increases and at 363 nm decreases by increasing in metal ion concentration; In addition a new absorbance band at 393 nm appears. Such a pronounced effect on the electronic spectra of the complexes could be related to a large change in the conjugation of the ligand. The absorbance versus [Hg(II)]/[ENTZ] mole ratio plots, obtained at wavelength of 363 and 430 nm, for ENTZ are shown in Fig. 2. As can be seen from this figure the absorbance–mole ratio plot revealed one distinct inflection point at [Hg(II)]/[ENTZ] molar ratio of about 1, emphasizing the formation of 1:1 complex in the solution. For the evaluation of the formation constant from absorbance–mole ratio data, again the non-linear least-squares curve-fitting program KINFIT was used

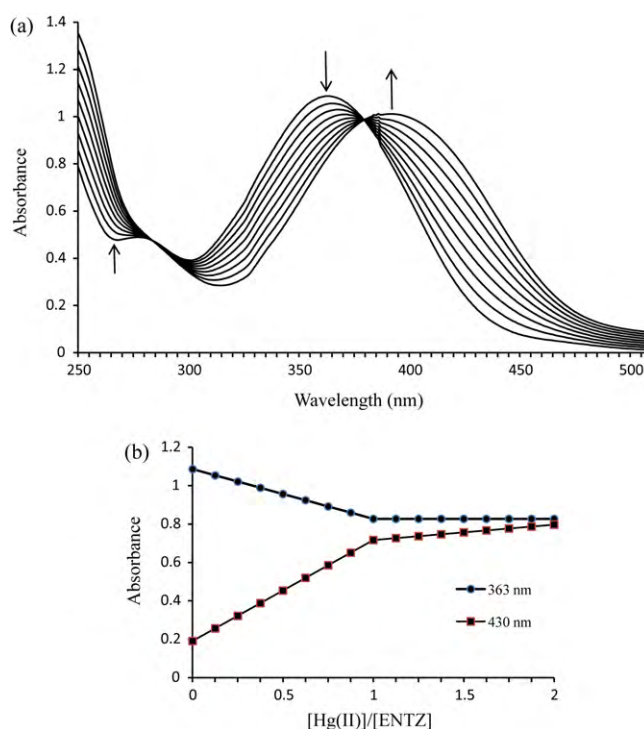


Fig. 2. (a) UV–vis absorption spectra of ligand (ENTZ) in acetonitrile (5.0×10^{-5} M) in the presence of increasing concentration of Hg(II) ion. (b) Absorbance versus [Hg(II)]/[ENTZ] molar ratio plots.

[30]. The formation-constant values (K_f) of the resulting 1:1 complexes are reported in Table 1.

3. Results and discussion

3.1. Carbon paste electrode composition

Some important features of the carbon paste electrode, such as the properties of the binder, the binder/graphite powder ratio, the nature and amount of ionophore, and especially, the nature and amount of the nano-material used, have been reported to significantly influence the sensitivity and selectivity of the ion-selective electrodes [27–29]. Thus, different aspects of the preparation of a MWCNTs-ionic liquid-carbon paste electrode based on ENTZ were optimized and the results are summarized in Table 2. As seen, the electrode without ENTZ modifier shows a poor potentiometric response towards Hg(II) ion (no. 1, 3). This indicates that ENTZ

Table 1
Formation constants of different metal–ENTZ complexes in acetonitrile.^a

Metal	$\log K_f$
Hg ²⁺	8.20 (± 0.02)
Ag ⁺	3.24 (± 0.04)
Cd ²⁺	2.54 (± 0.03)
Zn ²⁺	1.47 (± 0.06)
Pb ²⁺	3.67 (± 0.03)
Fe ³⁺	4.24 (± 0.05)
Cu ²⁺	2.97 (± 0.06)
Co ²⁺	3.46 (± 0.04)
Mn ²⁺	2.82 (± 0.03)
Ni ²⁺	2.84 (± 0.04)
Cr ³⁺	2.23 (± 0.03)
Al ³⁺	3.22 (± 0.04)

^a Values in parentheses are SDs based on three replicate analyses.

Table 2
Optimization of the carbon paste ingredients; optimized values are bold.^a

NO	Composition (wt%)				Electrode characteristics				
	MWCNTs	Binder	GP	ENTZ	Slope (mV decade ⁻¹)	LR (M)	LOD (M)	R ²	RT (s)
1	–	35-PO	65	–	8.2 (±1.2)	6.4 × 10 ⁻⁷ to 1.0 × 10 ⁻⁴	4.0 × 10 ⁻⁷	0.976	15
2	–	30-PO	62	8	27.5 (±0.8)	1.0 × 10 ⁻⁷ to 2.0 × 10 ⁻⁴	6.1 × 10 ⁻⁸	0.978	50
3	–	30-IL	65	–	13.4 (±1.8)	2.5 × 10 ⁻⁷ to 3.0 × 10 ⁻⁴	1.0 × 10 ⁻⁷	0.977	10
4	–	30-IL	62	8	31.3 (±0.5)	8.7 × 10 ⁻⁸ to 5.0 × 10 ⁻⁴	5.8 × 10 ⁻⁸	0.985	15
5	10	30-IL	52	8	26.5 (±0.3)	2.2 × 10 ⁻⁸ to 6.0 × 10 ⁻⁴	9.6 × 10 ⁻⁹	0.989	8
6	15	30-IL	47	8	27.3 (±0.2)	8.8 × 10 ⁻⁹ to 2.0 × 10 ⁻⁴	6.2 × 10 ⁻⁹	0.995	7
7	20	30-IL	42	8	29.3 (±0.2)	5.0 × 10⁻⁹ to 1.0 × 10⁻⁴	2.5 × 10⁻⁹	0.999	5
8	20	30-IL	44	6	28.3 (±0.3)	9.3 × 10 ⁻⁹ to 4.0 × 10 ⁻⁴	6.5 × 10 ⁻⁹	0.998	5
9	20	30-IL	40	10	30.8 (±0.4)	2.5 × 10 ⁻⁸ to 1.0 × 10 ⁻⁴	1.5 × 10 ⁻⁸	0.999	5
10	20	32-IL	40	8	30.6 (±0.3)	6.7 × 10 ⁻⁹ to 1.0 × 10 ⁻⁴	4.2 × 10 ⁻⁹	0.998	5
11	20	28-IL	46	8	28.2 (±0.2)	8.3 × 10 ⁻⁹ to 5.0 × 10 ⁻⁴	5.9 × 10 ⁻⁹	0.997	6
12	25	30-PO	37	8	26.5 (±0.6)	4.0 × 10 ⁻⁷ to 8.0 × 10 ⁻³	1.7 × 10 ⁻⁷	0.988	25

MWCNTs: multi-walled carbon nanotubes; GP: graphite powder; PO: paraffin oil; LOD: lower detection limit; ENTZ: 1-(2-ethoxyphenyl)-3-(3-nitrophenyl)triene; LR: linear range; IL: ionic liquid (BMIM-BF₄).

^a Values in parentheses are SDs based on four replicate analyses.

is the most important component in the proposed carbon paste electrode for sensing of Mercury ion.

It is known that the nature and amount of the lipophilic additive strongly influence the response of the ion-selective sensors, such as reducing the matrix resistance, improving the response behavior and selectivity and in some cases, where the extraction capability is poor, increase the sensitivity of the sensors [31]. BMIM-BF₄ as solvent mediator, in particular, has a dual function: it acts as a liquifying agent, enabling homogenous solubilization and modifying the distribution constant of the ionophore used. For a binder to be adequate for use in sensors, it should gather certain properties and characteristics such as having high lipophilicity and conductivity, low tendency for exudation from the paste matrix, low vapor pressure and high capacity to dissolve the substrate and other additives present in the paste [32]. As mentioned in Section 1 these properties is all collected in ILs which makes the utilization of ILs in carbon pastes, very essential.

From Table 2, it was obvious that in the absence of BMIM-BF₄ and the existence of other components, the response of the recommended electrode was decreased (no. 12). Because, applying BMIM-BF₄, with higher dielectric constant than paraffin oil as a binder, in the composition of the carbon paste improves the polarity of the sensor and increases the mobility of the Hg(II) ions. If the polarity of the sensor increases, Hg(II) ions as a divalent ion, can be extracted from aqueous solution to the sensor easier and the potential response attains to its Nernstian value [24]. In addition, replacement of paraffin oil by BMIM-BF₄ causes an increase in conductivity of the sensor and reduces the response time and improves the dynamic working range. It should also be noted that ENTZ can be dissolved in BMIM-BF₄ and therefore the mobility of ionophore in the carbon paste adjusts by this way, which will lead to fast exchange kinetics of the metal–ligand complexation–decomplexation at the surface of the paste.

In addition, the electrodes without MWCNTs gave a limited working concentration range and relatively high detection limit (no. 2, 4). This is due to properties of MWCNTs which make them ideal as components in electrical circuits, including their unique dimensions and their unusual current conduction mechanism. Using MWCNTs in the composition of the carbon paste not only improves the conductivity of the sensor, but also increases the transduction of the chemical signal to electrical signal. By increasing the conductivity, the dynamic working range and response time of the sensor improve. If the transduction property of the sensor increases, the potential response of the sensor improves to Nernstian values [24,25]. Furthermore, using MWCNTs leads to the expanding of the surface of paste by fabrication of three-

dimensional nanostructures, as well as diminishing the Ohmic resistance of the paste.

Anyway, increasing amount of the MWCNTs higher than 20% in the composition of the carbon paste leads to less Nernstian values than 29.3 mV decade⁻¹ and thus decreases its sensitivity and also causes long response time of the proposed electrode. It is probably due to the high surface area formed on the electrode surface that may offer special opportunities for the capturing ions on the surface of the paste.

As it is seen from Table 2, the MWCNTs-ionic liquid-modified electrode with the graphite powder/BMIM-BF₄/ENTZ/MWCNTs percentage ratio of 42/30/8/20 was selected as the one with the optimal ingredient composition (no. 7). It exhibited a Nernstian slope of 29.3 ± (0.2) mV decade⁻¹ in a wide mercury ion concentration range between 5.0 × 10⁻⁹ and 1.0 × 10⁻⁴ M (Fig. 3). The LOD for the electrode was equal to 2.5 × 10⁻⁹ M (0.5 ppb). This LOD was calculated when the linear regions of the calibration graphs were extrapolated to the baseline potentials. This detection limit value for the electrode no. 7 was at least tow to tree orders below than that of the conventional Hg(II) polymeric membrane electrodes or traditional carbon paste electrodes.

These results show that the ENTZ is an excellent ionophore for Hg(II) ion, also, addition of BMIM-BF₄ and MWCNTs to the paste improves the linear range, the detection limit and the response time of the electrode.

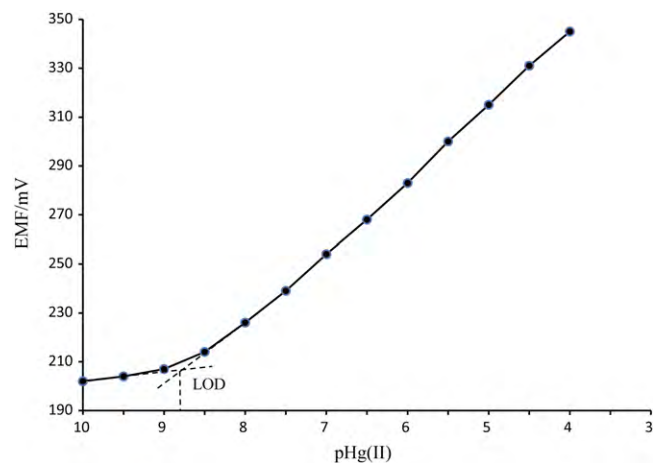


Fig. 3. Calibration curves for Hg(II)-carbon paste electrode based on ENTZ, BMIM-BF₄, and MWCNTs at pH ~ 3.0.

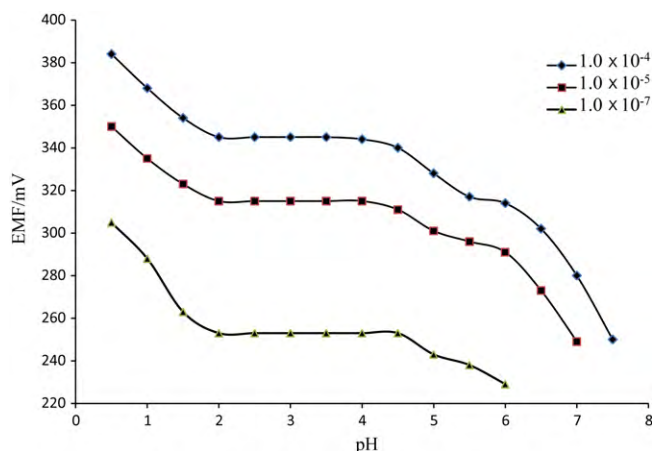
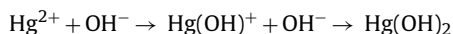


Fig. 4. Effect of pH on cell potential of sensor no. 7 at 1.0×10^{-4} and 1.0×10^{-5} M Hg(II) solutions.

3.2. Effect of pH of the test solution

The influence of pH on the response of the proposed sensor to 1.0×10^{-4} and 1.0×10^{-5} M Hg(NO₃)₃ solutions was studied over a pH range of 0.5–9.0, and the results are shown in Fig. 4. In the pH range of 2.0–4.3, the potential did not change with changing pH, indicating the applicability of this sensor in this pH range. The pH of the solution was adjusted at the required value by the addition of 1.0 M sodium hydroxide or 1.0 M nitric acid. As can be seen in Fig. 4 the potential was constant and quantitative in the pH range of 2.0–4.3. Beyond the range, however, relatively drastic drifts in the potential versus pH behavior were observed. At pH < 2.0, the electrode response increased rather irregularly with increasing analyte acidity. At such high acidic solutions, the observed increase in potential indicates that the protonated ionophore possesses a poor response to the Hg(II) ions and strong response to H₃O⁺ ions in the solution. Between pH 4.0 and 6.0, the potential was found decreased due to the formation of Hg(OH)⁺ ion and diminishing the concentration of Hg(II) in the solution. As can be seen in Fig. 4 the potential decreased sharply at higher pHs (>6) due to the formation of Hg(OH)₂ which not reacts with the ligand. These results can be explained by the following chemical equilibrium:



3.3. Selectivity studies

The selectivity behavior is obviously one of the most essential characteristics of an ion-selective electrode, determining the feasibility of a reliable measurement in the target sample. In

this work selectivity coefficients of the electrode towards different cationic species (Mⁿ⁺) were evaluated by using both of the matched potential method (MPM) and the fixed interference method (FIM) [33]. According to the MPM, the activity of Hg(II) was increased from $a_A = 1.0 \times 10^{-5}$ mol L⁻¹ as reference solution to $a'_A = 6.0 \times 10^{-5}$ mol L⁻¹, and the corresponding changes in potential (ΔE) were measured. Afterwards, a solution of an interfering ion of concentration a_B , in the range 5.0×10^{-4} to 1.0×10^{-5} mol L⁻¹, was added to a new 1.0×10^{-5} mol L⁻¹ (reference solution) until the same potential change (ΔE) was recorded. The selectivity factor, $K_{A,B}^{\text{MPM}}$, for each interference was calculated using the following equation:

$$K_{A,B}^{\text{MPM}} = \frac{\Delta a_A}{a_B} = \frac{a'_A - a_A}{a_B}$$

In addition, the selectivity coefficients of interfering species were evaluated by the fixed interference method (FIM). In this manner, the CPE and the reference electrode was placed in 50.0 mL of 1.0×10^{-3} mol L⁻¹ interference ion solution. Various volumes of 0.0001, 0.001 or 0.01 mol L⁻¹ of mercury nitrate solution were added by microsyringe. The solution was stirred magnetically throughout and after each addition, the cell potential was recorded. In this manner, the mercury ion concentration was varied over a wide range (1.0×10^{-9} to 1.0×10^{-4} mol L⁻¹) while the interference ion (Mⁿ⁺) concentration was kept constant without having to transfer the electrodes to new solutions. The pHs of total test solutions were constant about 3. The values in Table 3 reflect a very high selectivity of this electrode for reliable quantification of mercury ion(II) over a wide variety of other metal ions.

Also, there is a good correspondence between the formation constants and the selectivity coefficients order, because the selectivity of an ion-selective sensor is mainly related to the stability of the complex between ion and ionophore.

The effect of some biological species such as ascorbic acid, dopamine, uric acid, fructose, maltose, glutamine, and vitamin B12 on the response of the proposed electrode has also been studied. For this propose the selectivity behavior of mentioned compound were evaluated by using matched potential method (MPM). Fortunately the obtained result in Table 3 indicated that the proposed electrode has a high performance to determination of Hg(II) in biological samples.

Moreover the performance of the electrode assembly toward Hg(II) ions was observed in solutions contaminated with cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) surfactants. The obtained results shown that small amounts (up to 5.5×10^{-4} mol L⁻¹) of CTAB and SDS do not disturb the functioning of the proposed sensor, but at higher concentration (8.5×10^{-4} mol L⁻¹ and above) they can cause some problems. This is evident because these substances can disturb the measurements because of their molecule adsorption on the electrode

Table 3
Selectivity coefficients of various interfering species for proposed sensor (no. 7), calculated by FIM and MPM methods.^a

Species	K_{FIM}	K_{MPM}	Species	K_{FIM}	K_{MPM}
Ag ⁺	$6.2 (\pm 0.4) \times 10^{-4}$	$1.5 (\pm 0.3) \times 10^{-4}$	Ba ²⁺	$2.3 (\pm 0.2) \times 10^{-5}$	$8.4 (\pm 0.1) \times 10^{-6}$
Tl ⁺	$1.0 (\pm 0.1) \times 10^{-4}$	$7.5 (\pm 0.2) \times 10^{-5}$	Fe ³⁺	$8.0 (\pm 0.4) \times 10^{-4}$	$1.2 (\pm 0.3) \times 10^{-4}$
NH ₄ ⁺	$5.0 (\pm 0.3) \times 10^{-5}$	$3.6 (\pm 0.2) \times 10^{-5}$	Cr ³⁺	$8.6 (\pm 0.2) \times 10^{-5}$	$3.5 (\pm 0.3) \times 10^{-5}$
Na ⁺	$1.5 (\pm 0.3) \times 10^{-5}$	$1.0 (\pm 0.3) \times 10^{-5}$	Al ³⁺	$1.4 (\pm 0.3) \times 10^{-4}$	$8.8 (\pm 0.4) \times 10^{-5}$
K ⁺	$2.4 (\pm 0.2) \times 10^{-5}$	$9.2 (\pm 0.2) \times 10^{-6}$	Ga ³⁺	$1.7 (\pm 0.2) \times 10^{-5}$	$7.9 (\pm 0.2) \times 10^{-6}$
Cd ²⁺	$2.0 (\pm 0.4) \times 10^{-4}$	$6.5 (\pm 0.3) \times 10^{-5}$	Ascorbic acid	–	No response
Zn ²⁺	$1.0 (\pm 0.2) \times 10^{-4}$	$8.0 (\pm 0.2) \times 10^{-5}$	Dopamine	–	No response
Pb ²⁺	$5.4 (\pm 0.5) \times 10^{-4}$	$1.0 (\pm 0.3) \times 10^{-4}$	Uric acid	–	No response
Cu ²⁺	$2.8 (\pm 0.3) \times 10^{-4}$	$9.0 (\pm 0.4) \times 10^{-5}$	Fructose	–	No response
Co ²⁺	$4.7 (\pm 0.4) \times 10^{-4}$	$1.0 (\pm 0.2) \times 10^{-4}$	Vitamin B12	–	No response
Mn ²⁺	$2.5 (\pm 0.3) \times 10^{-4}$	$7.7 (\pm 0.3) \times 10^{-5}$	Maltose	–	No response
Ni ²⁺	$2.0 (\pm 0.2) \times 10^{-4}$	$9.1 (\pm 0.3) \times 10^{-5}$	Glutamine	–	No response

^a Values in parentheses are SDs based on three replicate analyses.

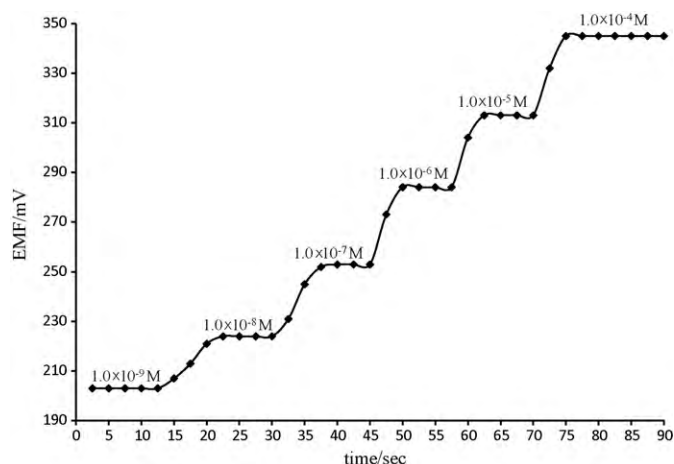


Fig. 5. Dynamic response of the proposed carbon paste electrode (no. 7) obtained by successive increase of Hg(II) ion.

surface, which results in potential instability and prolonged time of electrode response. Correspondingly, this would result in a large measuring error or alter the original selectivity [34].

3.4. Response time of the electrode

Generally, dynamic response time is an important factor for any sensor. The critical emf response of the electrode was assessed according to IUPAC recommendations [33]. The average time required for the mentioned electrode to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of Hg(II) ion solutions, each having a 10-fold difference in concentration, was investigated. The measurements of potential versus time were carried out with the Hg(II) nitrate solutions from lower (1.0×10^{-9} M) to higher (1.0×10^{-4} M) concentrations (Fig. 5). The electrode reaches equilibrium in about 5–10 s. As shown in Fig. 5, the response time increased to 10 s when the concentration was lowered to 1.0×10^{-9} M because of the longer equilibration time. Whereas higher concentrations ($\geq 5.0 \times 10^{-8}$ M) have response times of less than 5 s due to fast exchange kinetics of the metal–ligand complexation–decomplexation at the surface of the paste.

3.5. Lifetime, renewal surface, homogeneity and reproducibility of the electrode

For the lifetime evaluation of the recommended carbon paste electrode five the same electrodes were prepared. They were tested for a period of 8 weeks, during which the electrodes were used extensively (1 h per day). The obtained results showed that only after seventh week a slight gradual decrease in the slopes (from $29.2 \pm (0.3)$ to $27.8 \pm (0.5)$ mV decade $^{-1}$) was observed. Moreover, after this time, detection limit was increased to $7.8 \pm (0.3) \times 10^{-9}$ M.

Table 4

Comparison studies of recently published Hg(II)-ion-selective electrode based on various ionophore.

Ref.	Slope (mV decade $^{-1}$)	pH range	Detection limit (mol L $^{-1}$)	Linear range (mol L $^{-1}$)	Interfering cation ($K_{Hg,M}^{Pot}$) 10^{-3}
[34]	30.0	2.0–4.5	4.4×10^{-8}	7.0×10^{-8} to 1.0×10^{-1}	Ag $^{+}$, Pb $^{2+}$, Cd $^{2+}$, Cu $^{2+}$, K $^{+}$, Ni $^{2+}$
[35]	58.8	3.8–7.8	1.5×10^{-7}	3.2×10^{-7} to 3.2×10^{-4}	Ag $^{+}$, Pb $^{2+}$, Cu $^{2+}$, Na $^{+}$, K $^{+}$, Cr $^{3+}$, NH $_4^{+}$
[36]	32.6	1.0–4.0	8.91×10^{-7}	1.0×10^{-6} to 1.0×10^{-1}	Ag $^{+}$, Pb $^{2+}$, NH $_4^{+}$, Na $^{+}$, K $^{+}$, Li $^{+}$
[37]	30.2	2.6–4.2	5.0×10^{-8}	1.0×10^{-7} to 1.0×10^{-2}	Ag $^{+}$, Zn $^{2+}$, Pb $^{2+}$, Ni $^{2+}$, Cd $^{2+}$, Cu $^{2+}$
[38]	29.6	3	6.5×10^{-7}	1.0×10^{-6} to 1.0×10^{-1}	Ag $^{+}$, Zn $^{2+}$, Pb $^{2+}$, Fe $^{3+}$, Cd $^{2+}$, Cu $^{2+}$
[39]	30.0	3–4	5.0×10^{-8}	1.0×10^{-7} to 1.0×10^{-2}	Ag $^{+}$
[40]	28.1	4–7	1.0×10^{-7}	1.0×10^{-7} to 1.0×10^{-1}	Al $^{3+}$, Zn $^{2+}$, Pb $^{2+}$, Fe $^{3+}$, Cd $^{2+}$, Cu $^{2+}$, Ni $^{2+}$, Ba $^{2+}$, Mg $^{2+}$
[41]	25.0	6.6–9.3	8.9×10^{-6}	1.2×10^{-5} to 1.0×10^{-1}	Al $^{3+}$, Zn $^{2+}$, Pb $^{2+}$, Fe $^{3+}$, Cd $^{2+}$, Cu $^{2+}$, Na $^{+}$, NH $_4^{+}$, Mg $^{2+}$
This work	29.3	2.0–4.3	2.5×10^{-9}	5.0×10^{-9} to 1.0×10^{-4}	–

Decreasing of the electrode response after this time is due to triazine compounds, which here used as an ionophore, are not very stable compounds at the ambient temperature and may be decayed after a long period. Anyway, if the electrode during non-usage store within distilled water at refrigerator, its life-time will increase to several months without any divergence or change in the response of the electrode.

The slope of the calibration graph obtained by this electrode was found to decrease slightly after two times of use starting at 29.2 ± 0.3 mV and reaching 21.8 ± 0.6 mV at the last measurement. For the present electrode the decrease may be attributed to surface contamination and memory effect [35]. Therefore, the electrode surface should be polished to expose a new fresh layer ready for use after each calibration.

To test paste homogeneity, the proposed electrode was applied for mercury measurement in a 1.0×10^{-5} M Hg(II) solution. The measurement was repeated ten times and after each measurement the electrode surface was renewed by squeezing a little carbon paste out of the tube and a fresh surface is smoothed on a piece of weighing paper. The average potential was 315 mV and standard deviation 0.50%, which are reasonable values.

In order to evaluate the reproducibility of this electrode, a series of pastes (five) with optimum composition (no. 7) was prepared and the responses of these electrodes were tested to Hg(II) ion concentration. The results showed the average of slopes, detection limits and linear dynamic ranges were $29.3 \pm (0.2)$ mV decade $^{-1}$, $2.5 \pm (0.3) \times 10^{-9}$ M, and $5.0 \pm (0.3) \times 10^{-9}$ to $1.0 \pm (0.5) \times 10^{-4}$ M, respectively.

3.6. Comparative study

For comparative purposes, Table 4 lists the linear range, detection limit, slope, pH range and selectivity coefficients of recently published Hg(II)-selective electrodes [34–41] against the proposed electrode. As can be seen from this table most of these Hg(II)-selective electrodes suffer interfering effects from Ag $^{+}$, Zn $^{2+}$, Pb $^{2+}$, Ni $^{2+}$, Cd $^{2+}$ and Cd $^{2+}$ ions and as it is evident, most of the interfering ions do not have any effect on the response of proposed electrodes and most of them show low values of selectivity coefficients, indicating no interference in the performance of the carbon paste electrodes assembly. It is noteworthy that the limit of detection, linear range, and slope of the proposed electrode are also considerably improved with respect to those of the recently reported Hg(II)-selective electrodes.

3.7. Assay performance of the proposed electrode

3.7.1. Determination of Hg(II) in dental amalgam and water samples

In order to illustrate this electrode application in practical analysis, the mercury content of different environmental (sea, laboratory and river water) samples was determined by the proposed electrode. The collected water samples were first acidified with HNO $_3$

Table 5
Analytical results for Hg²⁺ ion in water samples and dental amalgam by proposed sensor at pH ~ 3.0.^a

Sample	Hg(II) (mol L ⁻¹)				Recovery (%)	
	Added	Found by ISE (DDM) ^b	Found by ISE (SAM) ^b	% compatibility	By DDM	By SAM
Sea water	5.0 × 10 ⁻⁵	5.16 (±0.26) × 10 ⁻⁵	4.97 (±0.12) × 10 ⁻⁵	96.31	104.2	99.4
	5.0 × 10 ⁻⁸	4.95 (±0.17) × 10 ⁻⁸	5.11 (±0.15) × 10 ⁻⁸	96.86	98.6	102.2
Lab water	5.0 × 10 ⁻⁵	5.08 (±0.20) × 10 ⁻⁵	5.18 (±0.21) × 10 ⁻⁵	98.06	104.6	103.6
	5.0 × 10 ⁻⁸	4.96 (±0.33) × 10 ⁻⁸	4.91 (±0.15) × 10 ⁻⁸	98.99	99.2	98.2
River water	5.0 × 10 ⁻⁵	5.11 (±0.22) × 10 ⁻⁵	5.24 (±0.25) × 10 ⁻⁵	97.51	106.4	104.8
	5.0 × 10 ⁻⁸	5.09 (±0.27) × 10 ⁻⁸	4.92 (±0.17) × 10 ⁻⁸	96.66	102.4	98.4
Dental amalgam (%)	–	57.31 (±0.21)%	58.22 (±0.15)%	98.43	–	–
		58.11 (±0.09)% (ICP)				

^a Values in parentheses are SDs based on four replicate analyses.

^b DDM: direct determination method; SAM: standard addition method.

and then filtered through a packed filter to remove oils and other organic impurities. Each sample was analyzed in quadruplicate and the analysis by sensors was repeated under identical conditions. The mercury concentration of the samples was determined with proposed electrode by using both of the standard addition method and direct potentiometry using calibration curve method. In Table 5 the results of both the methods were compared and have been found to be fairly in agreement with each other. The results of analysis of each water sample showed that the Hg(II) recovery was almost quantitative. Moreover, the Hg(II) content of dental amalgam was determined by proposed electrode and the inductively coupled plasma technique (ICP). The preparation of sample was done according to Ref. [42]. The results obtained by the proposed electrode in combination with that obtained by ICP are depicted in Table 5. As it is derived from this table, the determined Hg(II) concentration in this samples, using simple aqueous standard solutions for calibration, was in good agreement with the certified ICP technique.

3.7.2. Determination of Hg(II) ion concentration in binary and ternary mixtures

The proposed electrode was applied for the monitoring of the Hg(II) ions concentration in various binary and ternary mixtures, because of the high selectivity and the very low detection limit of the constructed Hg(II) sensor. The corresponding results are summarized in Table 6. It can be seen from the table that the Hg(II) ion recovery, in the presence of the added cations with higher concentration than Hg(II) ion, is satisfactory and in the range 98.8–103.3%.

Table 6
Monitoring of Hg(II) ions concentration in various binary and ternary mixture at pH ~ 3.0.^a

Hg ²⁺ (mol L ⁻¹)	Added cation (mol L ⁻¹)	Recovery (%)
1.0 × 10 ⁻⁶	Fe ³⁺ (1.0 × 10 ⁻³)	101.5 (±0.4)
1.0 × 10 ⁻⁶	Ag ⁺ (1.0 × 10 ⁻³)	100.9 (±0.2)
1.0 × 10 ⁻⁶	Pb ²⁺ (1.0 × 10 ⁻³)	101.2 (±0.3)
1.0 × 10 ⁻⁶	Cu ²⁺ (1.0 × 10 ⁻³)	99.6 (±0.1)
1.0 × 10 ⁻⁶	Cd ²⁺ (1.0 × 10 ⁻³)	99.3 (±0.4)
1.0 × 10 ⁻⁶	Mn ²⁺ (1.0 × 10 ⁻³)	99.1 (±0.4)
1.0 × 10 ⁻⁶	Zn ²⁺ (5.0 × 10 ⁻³)	99.6 (±0.4)
1.0 × 10 ⁻⁶	Co ²⁺ (1.0 × 10 ⁻³)	98.9 (±0.3)
1.0 × 10 ⁻⁶	Al ³⁺ (1.0 × 10 ⁻³)	98.8 (±0.6)
1.0 × 10 ⁻⁶	Cr ³⁺ (1.0 × 10 ⁻³)	99.7 (±0.4)
1.0 × 10 ⁻⁶	Ga ³⁺ (5.0 × 10 ⁻³)	99.7 (±0.3)
1.0 × 10 ⁻⁶	Na ⁺ (5.0 × 10 ⁻³)	99.8 (±0.4)
1.0 × 10 ⁻⁶	Fe ³⁺ , Ag ⁺ (1.0 × 10 ⁻³)	103.3 (±0.8)
1.0 × 10 ⁻⁶	Fe ³⁺ , Pb ²⁺ (1.0 × 10 ⁻³)	102.7 (±0.5)
1.0 × 10 ⁻⁶	Ag ⁺ , Pb ²⁺ (1.0 × 10 ⁻³)	102.3 (±0.5)
1.0 × 10 ⁻⁶	Pb ²⁺ , Cu ²⁺ (1.0 × 10 ⁻³)	101.7 (±0.4)
1.0 × 10 ⁻⁶	Pb ²⁺ , Cd ²⁺ (1.0 × 10 ⁻³)	100.9 (±0.4)

^a Values in parentheses are RSDs based on four replicate analyses.

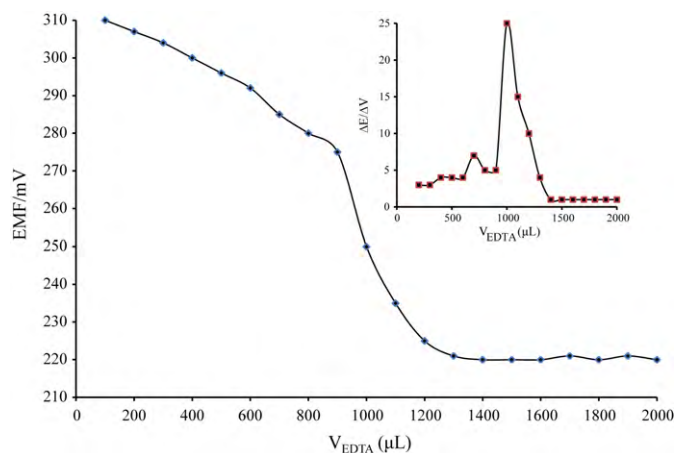


Fig. 6. Potential titration curves of 10.0 mL 1.0 × 10⁻⁴ M Hg(NO₃)₂ solution with 1.0 × 10⁻³ M of EDTA and its first order derivative at pH ~ 3.0.

3.7.3. Titration of Hg(II) solution with EDTA

The potentiometric titration of Hg(II) solutions was carried out with EDTA solution using the proposed electrode as the indicator electrode in conjunction with a Ag/AgCl reference electrode. In this manner, 10.0 mL of 10 × 10⁻⁴ mol L⁻¹ Hg(NO₃)₂ solution was titrated with 10 × 10⁻³ M EDTA solution while the pH of solution was constant about 3. As can be seen from Fig. 6 the titration curves showed good inflection point at the equivalence point. Before the end point, the potential shows usual logarithmic change with the volume of titrant added, while the potential response after the end point remains almost constant, due to the low concentration of free mercury(II) ions in solution.

4. Conclusion

In present study, the non-conductive binder in traditional carbon paste electrode was replaced by an ionic liquid, which is considerably viscous, water immiscible, and chemically inert while being electrochemically conductive. Coupling of MWCNTs with ionic liquid (BMIM-BF₄) enhances the signal transducers, improves the potentiometric characters, and enlarges the active surface area at the present composite electrode. By incorporating ENTZ in composite of this electrode, high selectivity and sensitivity to mercury ion were observed. The modified CPES show better potentiometric response than unmodified CPES in terms of sensitivity, Nernstian slope, linear range, and response stability. Since the electrode shows excellent sensitivity, selectivity and stability, it may find application in the analysis of real samples.

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