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Application of a new synthesized organic ligand as an ionophore in new nano-composite carbon paste electrode and investigation its electrochemical interaction with Cd^{2+} and determination of nano level of this ion

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Abstract: In this article a new synthesized organic macrocycl compound “2,2-thio-bis [4-methyl (2-amino phenoxy) phenyl ether]” (TBMAPPE) was used in a new chemically modified carbon paste electrode for determination of Cd^{2+} ions, as an ionophore. This potentiometric sensor had been fabricated for the rapid determination of Cd^{2+} based on carbon paste electrode consisting of room temperature ionic liquid (RTIL) 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF_6), multi-walled carbon nanotubes (MWCNTs), TBMAPPE and graphite powder. The electrode exhibits a Nernstian response for Cd^{2+} ions over a wide concentration range (5×10^{-8}- 1×10^{-1} mol L-1) with a slope of 29.50±0.10 mV per decade. It has a response time of about 10 s and can be used for a period of 3 months with good reproducibility. Detection limit obtained in the optimal conditions was 7.9×10^{-9} mol L-1. The electrode was successfully used for potentiometric determination of Cd^{2+} in well water. The pH influence and interference of some cations were also studied.

Keywords: Carbon paste electrode; Cd^{2+}; Multi-walled carbon nanotubes; Ionic liquid.

Introduction

An ionic liquid is a liquid that contains essentially only ions. Nowadays, the term ionic liquid is commonly used for salts whose melting point is relatively low (below 100 ^{0}C). In particular, the salts that are liquid at room temperature are called room-temperature ionic liquids (RTILs). Recently RTILs have been used in carbon paste electrodes (CPEs), in which, called carbon ionic liquid electrodes (CILEs) [1 – 3]. RTILs are a good choice as binder in carbon paste electrodes due to their interesting properties, such as stability, low vapor pressure, low toxicity, low melting temperature, high ionic conductivity and good electrochemical and thermal stability [4].

Carbon paste electrodes (CPEs) have attracted attention as ion selective electrodes mainly due to their advantages over membrane electrodes such as renewability, stable response, low ohmic resistance, no need for internal solution [5 –10]. Most of CPEs based potentiometric sensors which have been reported up to now are mainly based on incorporation of a selective agent into the carbon paste. The carbon paste usually consists of graphite powder dispersed in a nonconductive mineral oil. Incorporation of mineral oil gives CPEs some disadvantages. Mineral oil is not component-fixed since it is involved in various refining of petroleum and processing of crude oil, and some unaccounted ingredients may engender unpredictable influences on detection and analysis [11]. In addition they have mechanical problem, their mechanical stability is something between membrane electrodes and solid electrodes. Recently, carbon nanotubes (CNTs) due to their special physicochemical properties such as ordered structure with high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity,

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metallic or semi-metallic behavior and high surface area have been used [13-28]. The combination of these characteristics makes CNTs unique materials with the potential for diverse applications.

The transition metals including cadmium pose a significant risk for human and animals [29, 30]. Because the main source of heavy metals for humans and animals is water [31, 32], reliable and sensitive analytical methods and procedures have an important role to evaluate the impacts of metal pollutants. Wastewater from metal plating industries, nickel–cadmium batteries, phosphate fertilizers, mining, pigment stabilizers and alloys [33] contain high concentration levels of cadmium and contaminate the fresh water bodies. The permissible concentration limits of cadmium discharge in wastewater and drinking water are 0.1 and 0.05 mg L^{-1}, respectively. The effect of acute cadmium poisoning in humans are high blood pressure, kidney damage and destruction of testicular tissues and red blood cells. Thus, it is very important to detect cadmium ions at lower levels in our environments.

The present work describes the construction, potentiometric characterization, and analytical application of a new carbon paste composition based on a TBMAPPE, Fig.**1**, RTIL and multi-walled carbon nanotubes (MWCNTs) as a potentiometric sensor in cadmium detection in waste water samples.

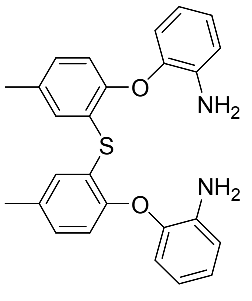

Fig 1. Chemical structure of 2, 2′-thio-bis [4-methyl (2-amino phenoxy) phenyl ether) (TBMAPPE).

Results and discussion

The obtained results from some experimental works revealed that the performance of Cd^{2+} carbon paste potentiometric sensor can be highly improved by using RTIL instead of mineral oil and MWCNTs. For this purpose, the potentiometric responses of the unmodified CPE and modified CPE towards target metal ions were studied in terms of selectivity coefficients, response time, Nernstian slope, linear range, and response stability which are important characterization of every ion selective electrodes.

Electrode composition and modification

It is well known that selectivity of any ion-selective sensor is closely related to the ionophore used as sensing material. Based on the results from the solution studies, TBMAPPE was used to fabricate both modified and unmodified CPEs with a variety of compositions. Results for these CPEs are given in Table **1**. The typical CPE with optimized composition (No. 5) shows a sub-Nernstian slope of ~22.34 mV per decade. However, the electrode composed of 20% BMIM-PF_6, 18% TBMAPPE, 52% graphite powder, 10% MWCNT (No. 10) was found to be optimal for the Cd^{2+}electrode.

This new nano-composition was selected for further examination. As it can be seen from Table **1**, using RTILs instead of paraffin oil in the carbon paste yields more efficient extraction of Cd^{2+} into the CPE. This is probably due to the much higher dielectric constant, low vapor pressure, low toxicity, low melting temperature, high ionic conductivity and good electrochemical and thermal stability of RTIL, they may be a better binder compare to paraffin oil.

Using MWCNTs in the carbon paste improves the conductivity and, therefore, conversion of the chemical signal to an electrical one. Carbon nanotubes have many properties that make them ideal as components in electrical circuits, including their unique dimensions and their unusual current conduction mechanism. 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.

Response of the electrode to various cations

In preliminary experiments, the optimal modified Cd^{2+} carbon paste sensor (No. 10) was tested for wide variety of metal ions, including alkali, alkaline earth, transition and heavy metal ions. The potential obtained for the most sensitive ion-selective electrodes based on TBMAPPE are shown in Fig. **2**. The Cadmium selective electrode exhibited linear response to the logarithm of the activity of Cd^{2+} ions within the concentration range of 5×10^{-8}- 1×10^{-1} M of Cadmium nitrate with Nernstian slope of 29.50±0.10 (mV) per decade at 25 ± 1^0C.

Measuring range and detection limit

Linear curve fitting using IUPAC method has used for the determination of ISE characteristics. The electrode shows a linear response ($y = 29.50x+634.3$, $R^2 = 0.997$) to the activity of Cd^{2+} ion in the range of 5.0×10^{-8} $1.0\times10^{-1}molL^{-1}$(Fig. **3**). By extrapolating based on the linear portion of the electrode's calibration curve, the detection limit of an ion selective electrode can be calculated. In this work, the detection limit of the proposed method was 7.9×10^{-9} mol L^{-1}.

Table 1. The optimization of the carbon paste ingredients.

Electrode No	Binder	ionophore	Graphite Powder	MWCNTs	Slope mv/decade	R^2
1	20%-paraffin	0.0%	80%	0.0%	2.40±0.20	0.990
2	20%-paraffin	5.0%	75%	0.0%	7.500±0.10	0.995
3	20%-paraffin	10%	70%	0.0%	15.35±0.30	0.997
4	20%-paraffin	15%	65%	0.0%	19.20±0.20	0.993
5	20%-paraffin	18%	62%	0.0%	22.34±0.30	0.991
6	20%-paraffin	20%	60%	0.0%	21.80±0. 20	0.996
7	20%-[BMIM] PF_6	18%	62%	0.0%	25.50±0. 30	0.989
8	25%-[BMIM] PF_6	18%	57%	0.0%	25.10±0. 20	.0993
9	20%-[BMIM] PF_6	18%	57%	5.0%	27.25±0.20	0.995
10	**20%-[BMIM]** $\mathbf{PF_6}$	**18%**	**52%**	**10%**	**29.50±0.10**	**0.997**
11	20%-[BMIM] PF_6	18%	47%	15%	28.66±0. 50	0.991

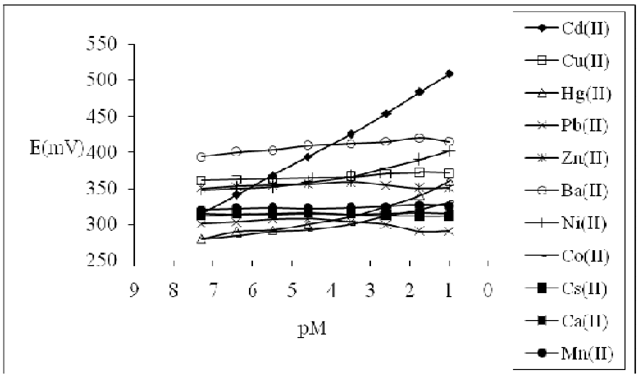

Fig. 2. Schematic diagram of electrode response to various cations.

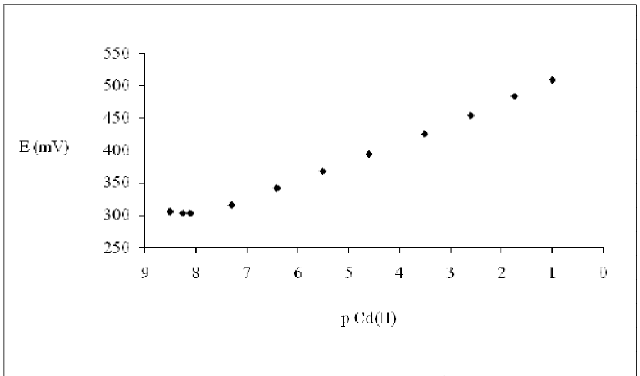

Fig. 3. The calibration curve of the Cd^{2+} nano-composite carbon paste electrode (No. 10).

Effect of pH on the electrode response

The influence of pH on the potential response of the Cd^{2+}-selective electrode was tested at 3×10^{-4} mol L^{-1} Cd^{2+}concentration over the pH range 2–9, and the results are shown in Fig. **4**. As seen, the potential remained constant from pH 4.5–6.5 and the carbon paste electrode can be suitably used in this range of pH. However, the observed potential decrease at higher pH (≥ 6.5) values could be due to the formation of some hydroxy complexes of Cd^{2+}ion in the solution. On the other hand, at pH values lower than 4.5, the electrode potential rises sharply.

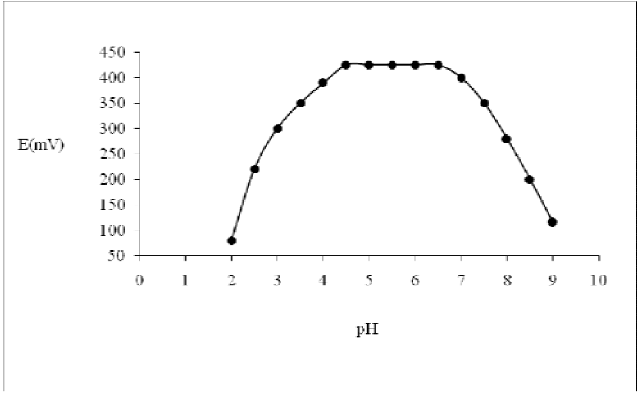

Fig. 4 Influence of pH on the potential response of the cadmium-selective electrode 1.0 x 10^{-3} mol L^{-1} Cd^{2+}.

This is probably due to the simultaneous response of the electrode to H_3O^+ and Cd^{2+}ions [35]. The contribution of H_3O^+ to the potential adds that of Cd^{2+}ion.

Response time of the electrode

The average response time is defined [36] as the time required for the electrode to reach a stable potential within ±1 mV of the final equilibrium value, after successive immersion of the electrode in different cadmium solutions each having a 10-fold difference in concentration or after rapid 10-fold increase in concentration by addition of cadmium nitrate. In this work, the response time in the variation of concentration from 1.0×10^{-7} to 1.0×10^{-3} mol L^{-1} Cd(II) is measured. The measured response time was ~ 10(s).

Lifetime of the electrode

The average lifetime for most ion selective sensors ranges from 4 – 9 weeks. After this time the slope of the sensor decreases, and the detection limit increases. The lifetime of the proposed nano-composite Cd^{2+} sensor was evaluated for a period of 13 weeks, during which the sensor was used two hours per day. The obtained results showed that the proposed sensors can be used for at least 11 weeks. After this time, a slight gradual decrease in the slope from 29.50 to 28.25 mV decade^{-1} is observed.

Selectivity and interference

The selectivity coefficients of the modified carbon paste electrode were evaluated by the fixed interference concentration method [37]. According this method, the potentiometric selectivity coefficient, $K^{pot}_{Cd,M}$, can be evaluated from the potential measerments of solutions containing a fix concentration of interfering ion, M^{n+} (10^{-3} mol L^{-1} for all) and titration with Cd^{2+} solution. The potential values obtained were then plotted against the activity of the cadmium ion. The intersecation of the extrapolated linear portions of this curve will indicate the activity of Cd^{2+}, which is to be used to calculate $K^{pot}_{Cd,M}$ values from the equation:

$$K^{pot}_{Cd,M} = \frac{a_{Cd}}{a_M^{2/n}}\ (DL)$$

The selectivity coefficients and analytical properties of the present electrode are compared with some recently reported cadmium electrodes in Table **2**. This table shows that all 24 cations would not affect the selectivity of the present cadmium electrode, and have a very small value of selectivity coefficient in most cases compared with the previously reported cadmium electrodes.

Table 2. Selectivity coefficient for various interfering cations for Cadmium selective electrode.

Interference (j)	$K_{Cd,j}$		
	[38]	[39]	This work (FIM)
Zn^{+2}	1.65×10^{-4}	-	4.15×10^{-4}
Sr^{+2}	4.50×10^{-3}	1.20×10^{-4}	3.44×10^{-4}
Ba^{+2}	5.50×10^{-3}	7.10×10^{-3}	4.30×10^{-4}
Ni^{+2}	3.50×10^{-5}	3.50×10^{-4}	4.85×10^{-3}
Cr^{+3}	5.50×10^{-5}	1.00×10^{-3}	6.50×10^{-4}
Mg^{+2}	-	1.50×10^{-2}	2.90×10^{-3}
Al^{+3}	9.50×10^{-5}	-	8.40×10^{-3}
Co^{+2}	6.00×10^{-5}	1.00×10^{-4}	5.53×10^{-4}
Mn^{+2}	4.35×10^{-3}	2.40×10^{-3}	1.85×10^{-3}
Pb^{+2}	6.50×10^{-4}	2.50×10^{-3}	7.20×10^{-4}
Fe^{+3}	-	-	4.15×10^{-5}
Tl^{+}	6.50×10^{-5}	-	2.50×10^{-4}
K^{+}	4.00×10^{-5}	5.50×10^{-7}	1.10×10^{-4}
Ag^{+}	3.50×10^{-4}	1.10×10^{-2}	1.20×10^{-5}
Na^{+}	-	3.50×10^{-6}	7.10×10^{-3}
Ca^{+2}	-	1.50×10^{-3}	4.30×10^{-5}
La^{+3}	-	-	4.50×10^{-4}
Eu^{+3}	-	-	9.50×10^{-4}
Cu^{+2}	4.50×10^{-3}	-	5.54×10^{-4}
Gd^{+3}	-	-	2.10×10^{-5}
Nd^{+3}	-	-	6.20×10^{-5}
Dy^{+3}	-	-	3.56×10^{-5}
Sm^{+3}	-	-	4.20×10^{-5}
Ho^{+3}	-	-	1.65×10^{-4}

Response characteristics

The response characteristics of the present electrode are compared with some recently reported cadmium electrodes in Table 3. As it shows, the proposed electrode represents wider dynamic range compare to most of the sensors and near-Nernestian slope compare to sensors referred as; also it has a very short response time in comparison to some of them.

Precision and accuracy of the method

The precision of the method was checked by the analysis of four replicates of the sample, expressed by R.S.D. % at the limit of quantification range, which was < 1%. Also, the accuracy was expressed in terms of percentage deviation of the measured concentration from the actual concentration. The obtained results are within the acceptance range of < 1%.

Table 3. Response characteristics and analytical properties for modified carbon paste cadmium selective electrodes.

DL (mol L^{-1})	Linear range (mol L^{-1})	Slope (mVdecade^{-1})	Response time (s)	Ref.
7.9×10^{-9}	5×10^{-8}- 1×10^{-1}	29.50	10	Proposed electrode
1.82×10^{-7}	2.16×10^{-7}-1.0×10^{-1}	30.00	50	[38]
8.40×10^{-7}	1.00×10^{-6}-1.0×10^{-1}	30.10	20	[39]

Analytical application

The new cadmium selective sensor was successfully applied to obtain recoveries of lead in tap water and waste water samples of Bushehr industrial zone. The analysis was performed by the standard addition technique. The results are given in Table **4**. According to this table, the obtained results are comparable with those obtained by ICP. Thus the sensor provides a good alternative for the determination of Cd^{2+} in real samples.

Table 4. Determination of Cd^{2+}recovery by the proposed electrode in the real samples.

Samples	Cd(II) added (mol.L^{-1})	Cd(II) found[a] (mol.L^{-1})	Recovery (%)	Found cadmium by ICP (mol.L^{-1})
Tap water	2.50×10^{-7}	2.47×10^{-7}(±0. 02)	98.8	2.48×10^{-7}
	4.50×10^{-7}	4.44×10^{-7}(±0.03)	98.7	4.47×10^{-7}
	7.00×10^{-7}	7.10×10^{-7}(±0.01)	101.4	7.13×10^{-7}
	8.50×10^{-7}	8.48×10^{-7}(±0.03)	99.8	8.49×10^{-7}
Waste water	-	1.50×10^{-7}(±0.03)	-	1.47×10^{-7}
	2.50×10^{-7}	3.94×10^{-7}(±0.15)	97.6	3.96×10^{-7}
	4.50×10^{-7}	5.85×10^{-7}(±0.02)	96.7	5.80×10^{-7}
	7.00×10^{-7}	8.46×10^{-7}(±0.01)	99.4	8.52×10^{-7}

[a] Average of four replicate measurements

Conclusion

This work demonstrates that new nano-composite carbon paste electrode fabricated from TBMAPPE, as ionophores, MWCNTs and room temperature ionic liquid, BMIM-PF_6, was used for detection of cadmium ions. The proposed sensor exhibits excellent potentiometric performance. It shows wider working activity range (5.0×10^{-8} - 1.0×10^{-1} mol L^{-1}), Nernstian slope (29.50 mV decade^{-1} of activity), low detection limit (7.9×10^{-9} mol L^{-1}), low response time (~6s) and better selectivity. These values are better or very similar than those previously published ones in the bibliography for other cadmium potentiometric sensors. The sensor could be successfully applied for the determination of Cd^{2+} in diverse samples.

Experimental

Apparatus

The melting points (uncorrected) were measured by an Electrothermal engineering LTD9100 apparatus. Elemental analysis was performed by a CHN-O-Rapid Heraeus elemental analyzer (Wellesley, MA). IR spectra were measured on a Perkin-Elmer model 543, ^1H NMR and ^{13}C NMR spectra were obtained using a Bruker Avance DRX 500 apparatus. The glass cell in which Cd^{2+} carbon paste electrode was placed contained a double junction saturated Ag/AgCl reference electrode (Azar electrode, Iran) as a reference electrode. The Cd^{2+} CPE was used as the working electrode. Both electrodes were connected to adigital mili-voltmeter (HIOKI 3256.50). A Metrohm pH meter (CRISON GLP 22) was used for pH controlling, and a Heidolph type of MR 2,000 stirrer was used for stirring the solutions.

Reagents and materials

The graphite powder with a <50μm particle size (Merck), 2.2 g/cm^3 density and about 20–30 g/100 mL bulk density, V_{total} 0.35cm^3/g and SBET 4.5m^2/g and high-purity paraffin oil (Aldrich) were used for preparation of the carbon pastes. The ionic liquid 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF_6) and chloride and nitrate salts of the cations were purchased from Merck. The multi-walled carbon nanotubes (MWCNTs) with 10–40nm diameters, 1–25µm length, core diameter: 5–10 nm, SBET: 40–600m^2/g, V_{total}: 0.9cm^3/g, bulk density 0.1 g/cm^3, true density 2.1 g/cm^3 and with 95% purity were purchased from Research Institute of the Petroleum Industry (Iran). Distilled deionized water was used throughout all experiments. TBMAPPE as an ionophore was synthesized and purified according to the literature [34].

The Synthesis of TBMAPPE

The TBMAPPE was synthesized according to the literature [34]**.** A suspension of the intermediate 2,2 _-Thio-bis [4-methyl (2-nitro phenoxy) phenyl ether] (1 mmol, 0.488 g) in 100 mL of methanol containing Zn (20 mmol, 1.3 g) and ammonium chloride (excess) was heated to a reflux temperature for 18–20 h. The reaction mixture was cooled to r.t. and filtered through celite to remove the catalyst, and the filtrate was concentrated under reduced pressure. The product was recrystallized from ethanol and water to afford a white crystalline diamine compound (85% yield) (see Scheme 2); m.p. 116 – 118◦C; IR (KBr) 3462, 3370, 3034, 2924, 1620, 1597, 1584, 1510, 1500, 1476, 1459, 1302, 1266, 1226, 1137, 1058, 897, 819, 745 cm−1; ^{1}H NMR (500 MHz, CDCl3); δ2.27 (s, 6H), 3.14 (b, 4H), 6.63–6.69 (m, 2H), 6.75 – 6.80 (m, 6H), 6.91–7.0 (m, 4H), 7.15–7.16 (d, 2H, J = 3Hz) ppm; ^{13}C NMR(500 MHz, CDCl3); δ 153.5, 143.4, 137.9, 133.2, 133.0, 129.3, 124.7, 124.4, 119.6, 118.8, 117.0, 116.6, 20.6 ppm; Elemental analysis: (found values) C (72.84), H (5.63), N (6.57); (calculated values) C (72.87), H (5.64), N (6.54).

Carbon paste electrode preparation

The general procedure to prepare the carbon paste electrode was as follows: Different amounts of the ionophore along with an appropriate amount of graphite powder, ionic liquid and MWCNTs were thoroughly mixed. The resulting mixture was transferred into a insulin Syringe with internal diameter of 2.5 mm and a height of 3 cm as a electrode body. After homogenization of the mixture, the paste was carefully packed into the tube tip to avoid possible air gaps, which often enhance the electrode resistance. A copper wire was inserted into the opposite end of the CPE to establish electrical contact. The external surface of the carbon paste was smoothed with soft paper. A new surface was produced by scraping out the old surface and replacing the new carbon paste. The electrode was finally conditioned for 24 h by soaking it in a 1.0 × 10^{-3} mol L^{-1} cadmium nitrate solution.

Emf measurements

The electrochemical cell can be represented as follows: Ag, AgCl(s), KCl (3 mol L^{-1}) | sample solution | carbon paste electrode Calibration graph was drawn by plotting the potential, E, versus the logarithm of the cadmium ion concentration.

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