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A Novel Ion- Selective Electrode Sensor Based on Crafted Polymer Sugar Thia Crown Ether for the Determination of Cadmium (II)

Fadhil Faez Sead
Department of Chemistry, Faculty of Dentistry, The Islamic University, Najaf, Iraq

Hussein Jasim Mohammed
Department of Chemistry, Faculty of Science, University of Kufa, Iraq

Ahmed Ibrahim Hamzah
Affiliation, City, Country/Territory

Ghadeer Sabah Bustani
Department of Chemistry, Faculty of Dentistry, The Islamic University, Najaf, Iraq | Department of Medical Laboratory Technique, Altoosi University College, Najaf Iraq

***Abstract*---**A Cadmium (II) ion-selective electrode (ISE) based on Thia polymeric crown ether (SPCE-Cd2+) as a membrane carrier in a PVC matrix was successfully built for the determination of Cd2+ ions. Using Dimethyl phthalate (DMP) plasticizer, the electrode showed a Nernstian liner response spanning the range of 1*10-1 to 1*10-7 M with a slope of (28) ±2 mV per decade charge and a detection limit of 1*10-9 M. The sensor has a 10-second response time. The cadmium ion-selective electrode is highly precise in its selectivity for Cd2+ over other cations. Some alkali and transition metal ions have selectivity coefficients in the range of 1 * 10-7 to 1 * 10-1. It worked well as an indicator electrode in the potentiometric measurement of the cadmium ion.

***Keywords*---**cadmium, crown ether, ion-selective electrode, potentiometric sensor, thia polymeric.

Introduction

Supramolecular can be realized as an area of chemistry in which research is focused on the complex multi-molecular kinds formed from molecular

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***Corresponding author**: Sead, F. F.; Email: fadhil.faiz@iunajaf.edu.iq*
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components that have comparatively modest temples. The robust development of supramolecular chemistry has confirmed the expansion of many other disciplines in resumption, and this highlights its powerful animation. More notice has been paid to the development of new species for electrode modulation established on supramolecular confession [1-3]. In recent years, an increase in cadmium ion concentration in water has been observed. Cadmium is one of the heavy metals that have a major role in environmental poisoning, especially water. So it is found in different proportions in the human body, and most organs contain the toxic element cadmium. The reasons for the rise of cadmium are due to its frequent use in industry. In industrial cities, its concentration increases. Cadmium in the human body is dangerous due to its easy absorption and entry into biological processes. Cadmium is a major environmental pollutant, interfering with gene expression through a complex and difficult-to-understand mechanism, causing DNA damage and altered gene expression [4]. Cadmium can be determined by several methods, including the spectroscopic method[5].

Chromatography [6] Colorimetric and dark-field microscopic [7] Inductively coupled plasma mass spectrometry [8]. Differential Pulse Voltammetry [9] .Use ion-selective electrode [10-13]. Most of the crown ether is employed within the preparation of the selective membrane ion that's utilized in most methods of electrochemical analysis to estimate some elements in samples [14-17]. The problem of cadmium ion determination methods requires complex and expensive devices, including spectrophotometers and cyclic voltammetry devices, so during this research, a potentiometric device was used, which is cheaper in terms of cost. Most of the studies focus on the utilization of crown ether within the application of the ion-selective electrode, but during this research, we put high light on the utilization of a polymer graft with crown ether, which is derived from monosaccharide and is adsorbed on the surface of the element cadmium to be measured. Due to the importance of these macrocycles, we have decided to prepare the novel macrocycle thiacrawn ether (SPCE) and its cationic complex (SPCE-Cd2+). According to the reference, new SPCE-Cd2+ were synthesized [18]. In this paper, we report the use of SPCE-Cd2+ as an excellent sensor in the construction of novel ion-selective electrodes. For this study, it was necessary to investigate the prepared polymer by applying the selective electrode ion using the voltaic method and observing the results. The purpose of this investigation is to apply this method to measures.

Experimental methods

Reagents and apparatus

Merck provided all the solvents, which were utilized without additional purification. Nitrophenyl octyl ether (NOPE) (99.0%), dimethyl phthalate (DMP) (99.0%), ethanol, methanol, acetonitrile, tetrahydrofuran (THF), polyvinylchloride (PVC), nitrate salt, and double distilled water were all used in all solution preparations. All pH measurements were taken at the University of Kufa's Faculty of Pharmacy, using a Hanna HI9811-5 with a glass–saturated calomel mixed electrode and a flame atomic absorption spectrometer (Shimadzu AA-6300).

Membrane preparation

The selective sensors were prepared by mixing 1.5mg (4.9%) ionophore SPCE – Cd+2 prepare in the lab university of Kufa [17], 18mg (59.01%) plasticizer as DMP, NOPE, and 11mg (36.06%) PVC in 3ml of THF with stirring. The solution was poured into glass casting and left for 2 days in order to evaporation of solvent[19-23] . The experimental design was utilized to take a Pyrex test tube (length of 10 cm, radius of 10 mm) and add immersed wire (length of 10 cm, radius of 1 mm). Shape wire spring of gold and then cut the ion-selective electrode (ISE) membrane to half radius with binding by cover parafilm.

EMF measurement

An EMF was measured at 25 oC using a saturated-calomel electrode with a single junction and a gold-wire as an internal reference for an ion-selective electrode immersed in 20 ml. Different concentrations of ion solution were studied in order to determine the potential sensor with stirring. Before use, all sensors were immersed in the main solution at 0.1 M for 24 hours before being washed with deionized water. IUPAC cell electrochemistry was used to test the sensor's response [Au wire | Internal solution (0.01M Cd(NO3)2.4H2O] | ion-selective electrode membrane | test solution | KCl. Sat. Hg/Hg2Cl2 (Reference electrode)].The results showed that there is a difference in the use of plasticizers in electrode preparation, response, and concentration.

Results and Discussion

Effects of plasticizer calibration curve

A Cadmium–polymer thia crown ether complex is being prepared and tested as a novel electro active material in poly vinyl chloride (PVC) matrix sensors for determining the Cadmium ion in solutions and environmental samples using direct potentiometry. The response potentials of the offered electrodes at various concentrations of Cd+2 presented liner range from (1 * 10-1 _1* 10-7) M with Nernstian slopes of 28 and 21 mV per decade for DMP and NOPE as plasticizers, respectively. The correlation coefficient values for two electrodes were 0.99, and the live time for all electrodes was around 30 days. The electrode's selectivity and sensitivity are determined not only by the structure of the ionophore utilized, but also by the membrane preparation and the properties of the plasticizer used.

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Table 1
Performance characteristics of Cd(II) ion selective sensor SPCE-Cd2+

Membrane	SPCE-Cd2+	SPCE-Cd2+
Plasticizer DMP	18mg	------
Plasticizer NOPE	-------	18mg
PVC	11mg	11mg
Range	1*10-1 ¬- 1*10-7	1*10-1-1*10-6
Detection limit	1*10-9	1*10-6
pH	3-8	3-8
T/ oC	5-50 OC	------
Time response	< 10 Second	-------
Slope Nernst mV/decade	28	21
R Square	0.99	0.99
Selectivity $log\ K^{Pot}_{Cd^{2+},ion\ interferance}$		
Cu+2	0.03	-----
Al+3	0.004	-----
Ag+1	0.002	-----
K+1	0.001	------
Na+1	0.001	------
Bi+3	0.005	------
Fe+3	0.005	------
Pb+2	0.02	-------
Statistical analysis		
N total	6	----
Mean	765	-----
Standard Deviation	0.6324	-----
Variance	0.4	-----
Sum	4590	------
Coefficient of Variation	8.27*10-4	-----
E real	0.1305	-----
%RE	99.86	-----

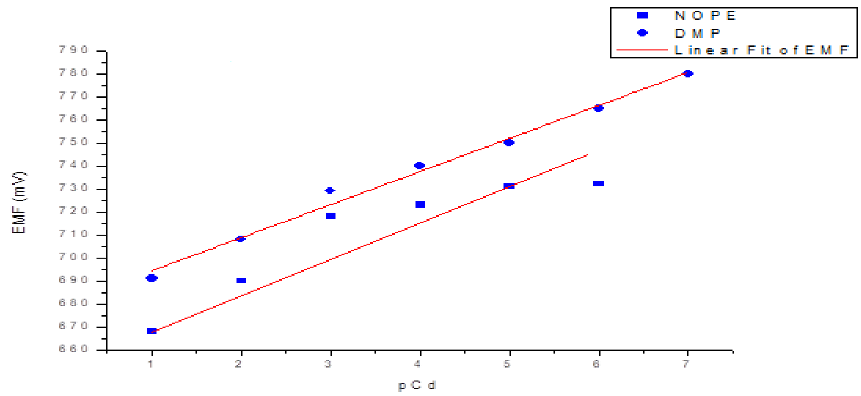

Figure 1. Calibration curves of Cd2+electrodes containing (SPCE-Cd2+) polymer ionophore and (NOPE, DMP) as plasticizers

Influence of pH of membrane sensor

The influence of pH on the response of the electrodes was tested by measuring potential variation in the electromotive force over a pH range of 2.0–10.0 for two different plasticizers with (1*10^{-2}M) Cd^{2+} and the results are listed in table 1. The pH was adjusted by introducing a few drops of HCl 0.01 M and NaOH 0.01 M solutions. As it can be seen, the potential remained nearly constant over a wide range of pH (fig. 2). This reveals that the proposed electrodes can be used to measure a wide range of cadmium ion samples without pH adjustment.

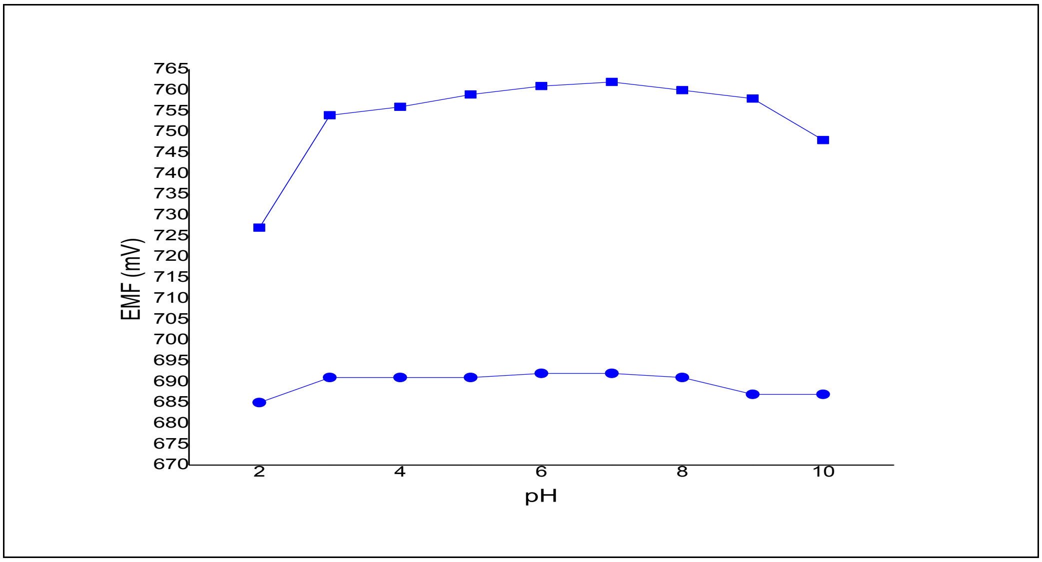

Figure 2. Effect of pH in membrane of Cd $^{2+}$

Response time of membrane sensor SPCE-Cd^{2+} contain DMP plasticizer

In order to reach within 1$\pm$ mV of the final equilibrium rate, the response time for the electrodes setup on DMP, as plasticizer, the response time of new sensors is a very important characteristic. In order that, after the ion selective electrode was taken out of the $1*10^{-2}$ M Cadmium (II) solution, immersed into higher concentration is ($1*10^{-3}$M) and low concentration is ($1*10^{-7}$M). The response time is measured as the time required to reach 98% of the steady potential for the cadmium solution. The response time of the electrode was less than 10 seconds (fig. 3).

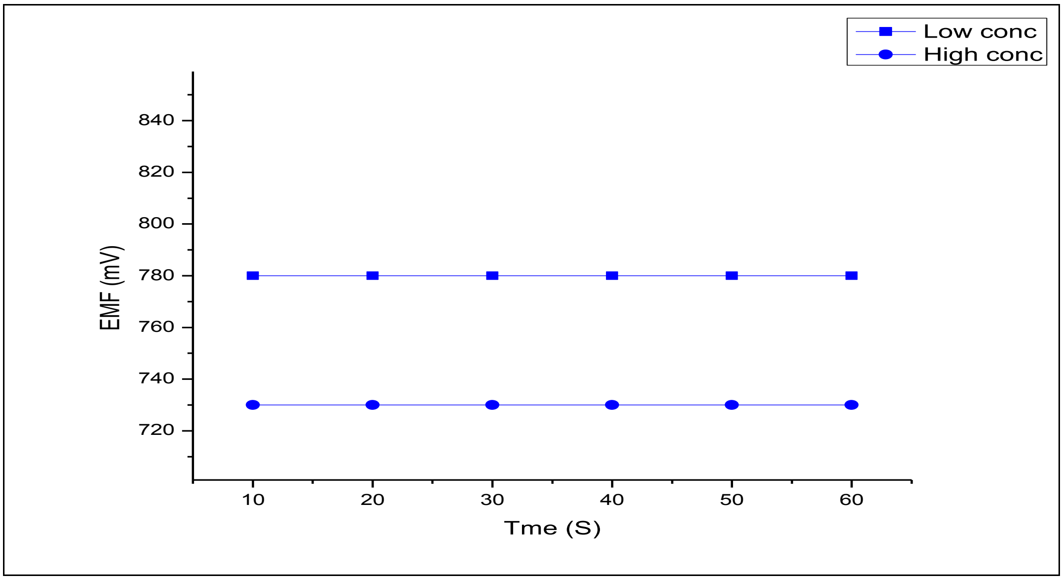

Figure 3. Response time of sensor of the Cd^{2+} ion selective electrode based SPCE-Cd^{2+}

Estimation of the selectivity sensor

The most fundamental parameter of sensors is their selectivity. This factor is expressed by potentiometric selectivity coefficients. Selectivity coefficients for SPCE-Cd2+ towards various inorganic cations were assessed using the matched potential method [27]. For the SPCE-Cd2+, all of the examined ions cause a neglected disturbance .The performance of the proposed sensor was supported at different concentrations of various cations. The results obtained indicated that the selectivity coefficient by the electrodes presented to the tested cation, which indicated the excellent selectivity of Cd2+ against some alkaline metals, alkali ions, and transition ions. The value of the selectivity coefficient of the SPCE-Cd2+ moiety carrier sensors with DMP plasticizers is far smaller than 1.0, a higher number than the cation being studied in (fig. 4). The sensor is selective enough over interference ions and may be used to determine Cd2+ within the presence of those cations by direct potentiometer support of the subsequent equations [28].

$$logK_{A,B}^{Pot} = \frac{FZ_A}{2.303RT}[E_2 - E_1] \qquad \text{……Charge A=B with same } a_A = a_b$$

$$logK_{A,B}^{Pot} = \frac{FZ_A}{2.303RT}[E_2 - E_1] + \left(1 - {Z_A}/{Z_B}\right)\log a_A \qquad \text{……Charge A≠B with same } a_A \neq a_b$$

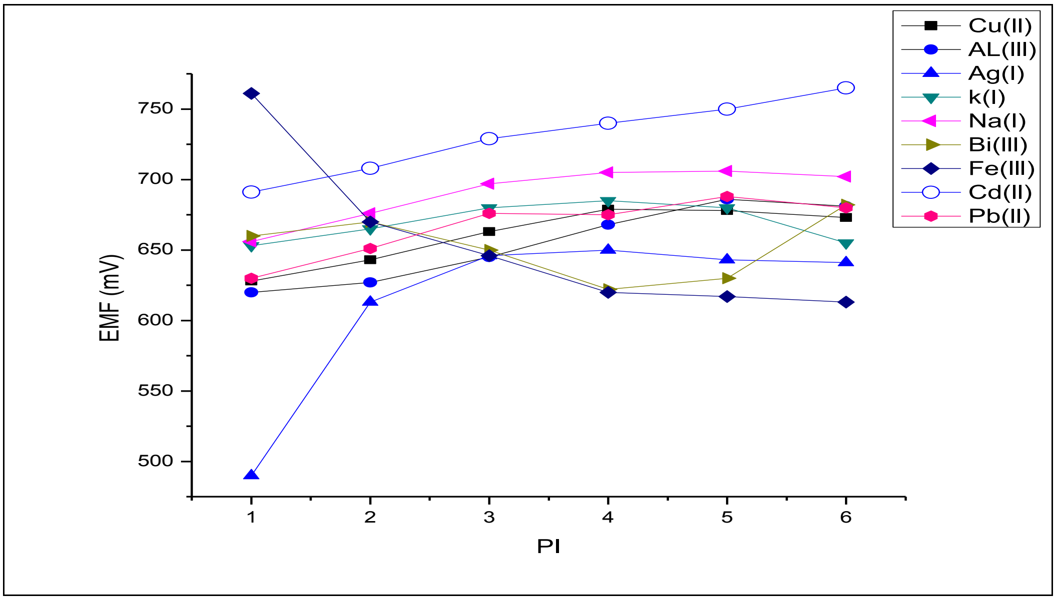

Figure 4. Potential response of various ions on Cd^{2+} selective electrode based on DMP plasticizer

Effect of temperature

One of the important factors contributing to significant measurement errors is temperature. A single degree difference in sample temperature can sometimes result in errors greater than 3% of temperature on the response of heavy metal ions, and the sensor was tested by measuring the variation in the EMF (mV) versus temperature range of (5-50) ^{o}C. The result obtained for the electrode is shown in fig. 5, which is stable at 50 ^{o}C.

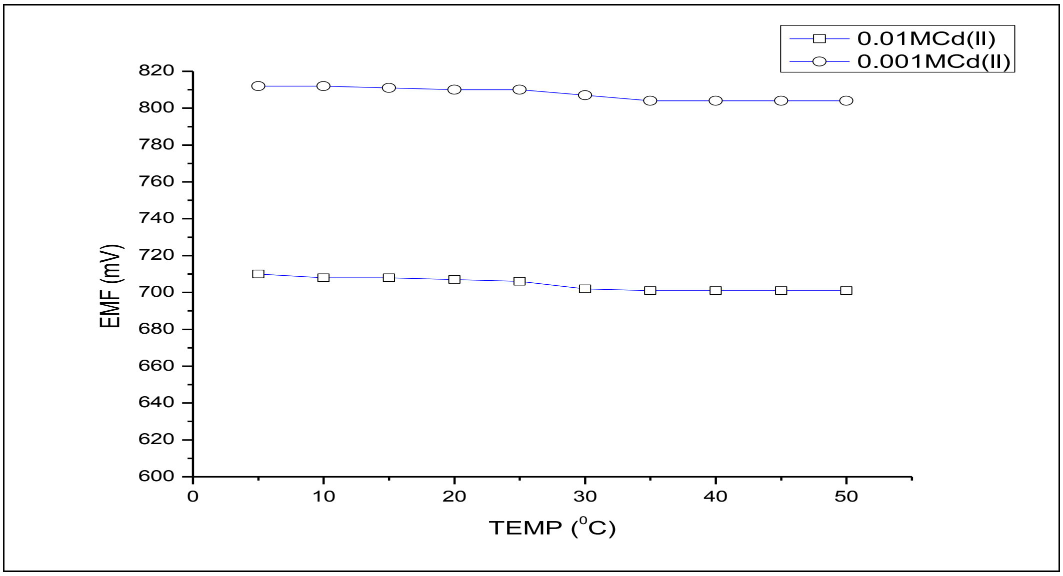

Figure 5. Effect of temperature with sensor with concentration ($1*10^{-2}$ - $1*10^{-3}$)

Statistical treatments and application analysis

The proposed sensor of the SPCE-Cd^{2+} used was analyzed by taking samples of water waste and tap water instrument samples. The result was compared to these given titration methods used ion Cd^{2+} determination in new sensor prepare. While used another method for the determination of samples by atomic flame absorption. Table. 1,2 show there was no significant difference between the determination result of the proposed sensor with another route Atomic Flame Absorption at confidence level 96 % the methodology has great promise for accurate and rapid determination of Cd ion in wastewater. The sensor prepared from the polymer SPCE-Cd^{2+} material was compared with other sensors, the prepared materials Table. 3 shows the difference in characterization response time limit detection and interference.

Table 2

Cd^{2+} levels Molar in Samples by proposing sensor SPCE-Cd^{2+} Method and Flame Atomic Absorption Spectroscopy

Sample	Atomic flame absorption	Ion selective electrode SPCE-Cd^{2+} method
Waste water	$1*10^{-3}$ M	$1*10^{-3}$ M
Tap water	$1*10^{-6}$ M	$1*10^{-6}$ M

Table 3
Comparison of Ion-Selective Electrodes with SPCE –Cd^{2+}

Type ISE	Liner Range	Detection limit	Time response	pH	Ref.
2–Acetylthiophene Semicarbazone	1×10^{-5} - 1×10^{-1} M	-	10 s	3.4-7.6	[19]
bis (2-diphenylphosphorylalkyl) phenyl ethers of ethylene glycols	1×10^{-7}–1×10^{-1} M	-	-	-	[20]
13-bis (8-quinolyl)	1.0 × 10− 5 to 1.0 × 10− 1	8.4 × 10− 6	15s	1.0–6.0	[21]
mono aza crown ether	15 µM to 65 µM	4.5 µM	-	-	[22]
N, N′-bis (salicylaldehyde) phenylenediamine	5.7 × 10−8 to 3.7 × 10−3 M	3.2 × 10−8	14s	2.5–7.5	[23]
SPCE –Cd^{2+}	1×10^{-7}–1×10^{-1} M	1×10^{-9}	<10s	2-8	Present work

Conclusion

The Cadmium ion-selective electrode sensor based on SPCE has excellent selectivity, a short response time of less than 10 seconds, and perfect repeatability. The sensor is relatively simple to construct, and the optimal makeup method resulted in a liner concentration range of 1.0 *10-1 to 1.0 *10-7 M with a slope of Nernistian 28.21 mV/decade and a limit of detection of 1 *10-8 M. The sensor SPCE-Cd2+ was used to determine Cd (II) in a sample of wastewater, and the results were good when compared to the flame atomic absorption technique.

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