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Nano-Composite Clozapine Potentiometric Carbon Paste Sensor Based on Biomimetic Molecular Imprinted Polymer

M.R. Ganjali[1], *T. Alizade*[2], *B. Larijani*[3], *F. Faridbod*[1,3,*], *P. Norouzi*[1]

[1] Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran
[2] Department of Applied Chemistry, Faculty of Science, University of Mohaghegh Ardabili, Ardabil, Iran
[3]Endocrinology and Metabolism Research Center, Tehran University of Medical Sciences, Tehran, Iran
[*]E-mail: faridbodf@gmail.com

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A clozapine selective nano-composite carbon paste sensor based on a biomimetic molecular imprinted polymer (MIP) as a sensing element is introduced. The artificial host for clozapine (CLZ) was imprinted based cross-linked polymer. Methacrylic acid (MAA) was used as a functional monomer and chloroform was used as polymerization solvent. Then, nano-composite paste were composed of MIP as a sensing element, multi-walled carbon nanotube (MWCNT), nanosilica (NS), graphite powder, and room temperature ionic liquid (RTIL). The best results were obtained from the nano-composite sensor with the electrode composition of 5% MWCNT, 1% NS, 20% CLZ-MIP, 20% RTIL, and 54% graphite powder. The proposed sensor shows a Nernstian response (28.8±0.3 mV decade^{-1}) in the range of 1.0×10^{-6}-1.0×10^{-2} mol L^{-1} with detection limit of 1.0×10^{-6} mol L^{-1}. The nano-composite based sensor displayed very good selectivity, response time, and specially, lifetime. It was successfully applied in analysis of Clozapine in pharmaceutical formulation.

Keywords: Molecular Imprinted Polymer (MIP), Clozapine, Sensor, Potentiometry, Ionic Liquids, Multi-walled carbon nanotube (MWCNT), Nanosilica (NS)

1. INTRODUCTION

Clozapine (CLZ), Fig. 1,8-chloro-11-(4-methyl-1-piperazinyl)-5H-dibenzo[b,e]-[1,4]diazepine (CLZ), is a typical antipsychotic drug with a low potential for inducing extra pyramidal side effects, used to treat positive and negative symptoms of schizophrenic patients who do not respond well to traditional neuroleptic drugs [1] and may increase the risk for granulocytopenia and agranulocytosis [2].

Due to the importance of the assay of antipsychotic drugs such as CLZ in pharmaceutical and in biological fluids, there are many methods for its determination which are mainly based on the gas chromatography (GC) [3], GC–mass spectrometry (GC-MS), high-performance liquid chromatography (HPLC) [4], and colorimetric detection [5]. These methods are very accurate and precise for analysis. However, fast, simple and inexpensive measurement of this compound is of great importance in the therapeutic applications, toxicological studies and especially in pharmaceutical factories.

Different electrochemical method have been recently used for drug monitoring [6,7], but potentiometric detection based on selective electrodes, offers several advantages such as speed and ease of preparation and procedures, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity, and low cost [8-15]. These electrodes are widely used for various applications now days [16-28]. The most important part of this kind of sensors is finding or designing a suitable sensing element. One of the best sensing materials is molecular imprinted polymer (MIP).

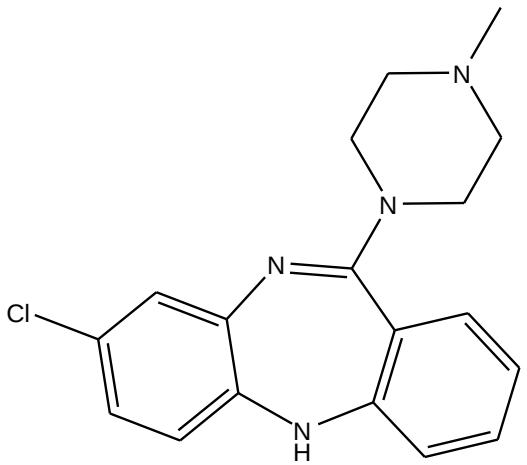

Figure 1. Chemical structure of Clozapine

Molecular imprinting polymer (MIP) is gained by arranging functional monomers around a template compound and then fixing the monomers in this spatial arrangement with a cross-linker [29]. A technique for producing specific recognition sites in synthetic polymers is called molecular imprinting that has achieved wide acceptance [30]. The template molecule (target or print molecule) is then removed to produce a polymer with molecular recognition sites, which are able to selectively rebind the template and analyte with similar structures [31]. They are low-cost to produce, reusable, appropriate to a number of different operating conditions, and display high mechanical and chemical stability [32].

Here, a molecular imprinted polymer (MIP) for CLZ was synthesized and used as a very selective sensing element in construction of CLZ nano-composite carbon paste electrode. Biological recognition elements such as antibodies, enzymes and aptamers have been used as specific receptors to a target molecule in a wide variety of sensors. However, they have many difficulties for their practical uses such as lack of stability, reusability, cost and not easy to obtain. During recent years, a new

approach has been used to synthesis the hosts which possess a structure capable of binding complementary guests to develop specific recognition materials. MIPs can behave specifically, and mimic bio-receptors; so, they are called "biomimetic recognition elements".

Potentiometric sensors based on carbon paste are the best choice when the recognition element is a MIP. Carbon paste electrodes provide a renewable surface, stable response and low ohmic resistance and also can be easily modified by nano-materials [33-38].

2. EXPERIMENTAL PART

2.1. Apparatus

The glass cell in which the potentiometry was carried out into contained an Ag/AgCl electrode (Azar electrode, Iran) as a reference electrode and nano-composite carbon paste electrode (NCCPE) as an indicator electrode. Both electrodes were connected to a mili-voltmeter (±0.1).

The following cell was assembled for the conduction of the EMF (electromotive force) measurements:

NCCPE | CLZ sample solution || Ag/AgCl–KCl (satd.)

2.2. Reagents and materials

The multi-walled carbon nanotubes (MWCNTs) (10-40 nm diameters, 1-25 μm length, SBET: 40-600 m^2/g and with 95% purity were purchased from a local company (Research Institute of the Petroleum Industry, Iran). Graphite powder with a 1–2 μm particle size (Merck Co.) and high-purity paraffin oil (Aldrich) were used for preparation of the carbon pastes. The ionic liquid (1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) and chloride and nitrate salts of the cations were all purchased from Merck Co. Nanosilica is Wacker HDK® H20. Clozapin Molecular imprinted polymer was synthesized according to the previously reported procedure [39]. CLZ as the template and methacrylic acid (MAA) as a functional monomer was used. The polymerization solvent was chloroform.

2.3. Preparation of NCCPE

The procedure for NCCPE preparation was as follows: various amounts of CLZ-MIP along with appropriate amount of graphite powder, paraffin oil or IL, nano-silica and MWCNTs were thoroughly mixed. After homogenization of the mixture, the resulting paste was transferred into a plastic tube with 6 mm o.d. and a height of 3 cm. 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. External surface of the carbon paste was smoothed with soft paper [33-38]. The electrode was finally conditioned for about 40 h by soaking it in a 1.0×10^{-3} M of CLZ solution (pH=4.5).

3. RESULTS AND DISCUSSION

3.1. Carbon paste composition

Two types of carbon paste electrode were made; modified and unmodified CPE with a variety of compositions. The results for these CPEs are given in Table 1. The unmodified CPE with optimized composition (electrode no. 3) shows a sub-Nernstian slope of 20.9 mV per decade.

From Table 1, it was obvious that in the absence of CLZ-MIP and presence of other components (no. 12), the response of the CPE was very low (slope of 5.2±0.6 mV per decade).

Using MWCNTs in the carbon paste improves the conductivity of the electrode and, therefore, conversion of the chemical signal to an electrical signal is better occurred. Carbon nano-tubes especially multi-walled ones have many properties that make them ideal as components in electrical circuits, including their unique dimensions and their unusual current conduction mechanism. Using nano-silica in the composition of the carbon paste can also improve the response of the electrode. Nano-silica is a filler compound which has high specific surface area. It has a hydrophobic property that helps extraction of the ions into the surface of the NCCPE. Also, it enhances the mechanical properties of the electrode. Using room temperature ionic liquid in the composition of the carbon paste electrode, instead of paraffin oil, causes more efficient extraction of ions with high charge density into the carbon paste surface. This is due to the much higher dielectric constant of the ionic liquids as binder compared to paraffin oil [35]. As it can be seen from Table 1, using [bmim]BF_4 instead of paraffin oil in the carbon paste composition yields more efficient extraction of CLZ ion (which is a rather high charge density cation having two positive charges) from the solution into the surface of NCCPE.

Finally, the electrode composed of 20% IL, 20% CLZ-MIP, 54% graphite powder 1% nano-silica and 5% MWCNTs (no. 10) was found to be optimal for CLZ carbon paste electrode. This composition was selected for further examination.

Table 1. Optimization of the carbon paste ingredients

No.	Graphite	CLZ-MIP	Paraffin	RTIL	MWCNT	NS	Slope (mV decade^{-1})	Linear Range (mol L^{-1})	Response Time
1	75	10	15	-	-	-	15.8±0.5	1.0×10^{-4}-5.0×10^{-3}	2 min
2	70	15	15	-	-	-	18.4±0.4	5.0×10^{-5}-5.0×10^{-3}	1 min
3	65	20	15	-	-	-	20.9±0.5	1.0×10^{-5}-8.0×10^{-3}	52s
3	60	25	15	-	-	-	20.2±0.6	1.0×10^{-5}-8.0×10^{-3}	55s
4	65	20	-	15	-	-	22.3±0.4	8.0×10^{-6}-1.0×10^{-2}	38s
5	60	20	-	20	-	-	23.2±0.5	5.0×10^{-6}-1.0×10^{-2}	31s
6	55	20	-	25	-	-	22.9±0.5	5.0×10^{-6}-1.0×10^{-2}	32s
7	57	20	-	20	3	-	24.7±0.3	3.0×10^{-6}-1.0×10^{-2}	28s
8	55	20	-	20	5	-	26.8±0.3	2.0×10^{-6}-1.0×10^{-2}	25s
9	53	20	-	20	7	-	26.5±0.4	6.0×10^{-6}-8.0×10^{-3}	29s
10	54	20	-	20	5	1	28.8±0.3	1.0×10^{-6}-1.0×10^{-2}	20s
11	52	20	-	20	5	3	27.1±0.5	5.0×10^{-6}-5.0×10^{-3}	35s
12	74	-	-	20	5	1	5.2±0.6	1.0×10^{-4}-5.0×10^{-3}	50s

3.2. Measuring range and detection limit

The measuring range of an ion selective electrode is defined as the activity range between the upper and lower detection limits. The response of the optimal modified CLZ carbon paste electrode (no. 10) was tested across CLZ concentration in the range of 1.0×10^{-7}-1.0×10^{-1} mol L^{-1}. The applicable range of the proposed sensor extends from 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} as seen in Fig. 2.

By extrapolating of the linear portion of the calibration curve, the detection limit of an ion selective electrode can be calculated [40-49]. In this work, the detection limit of the proposed membrane sensor was 1.0×10^{-6} mol L^{-1}.

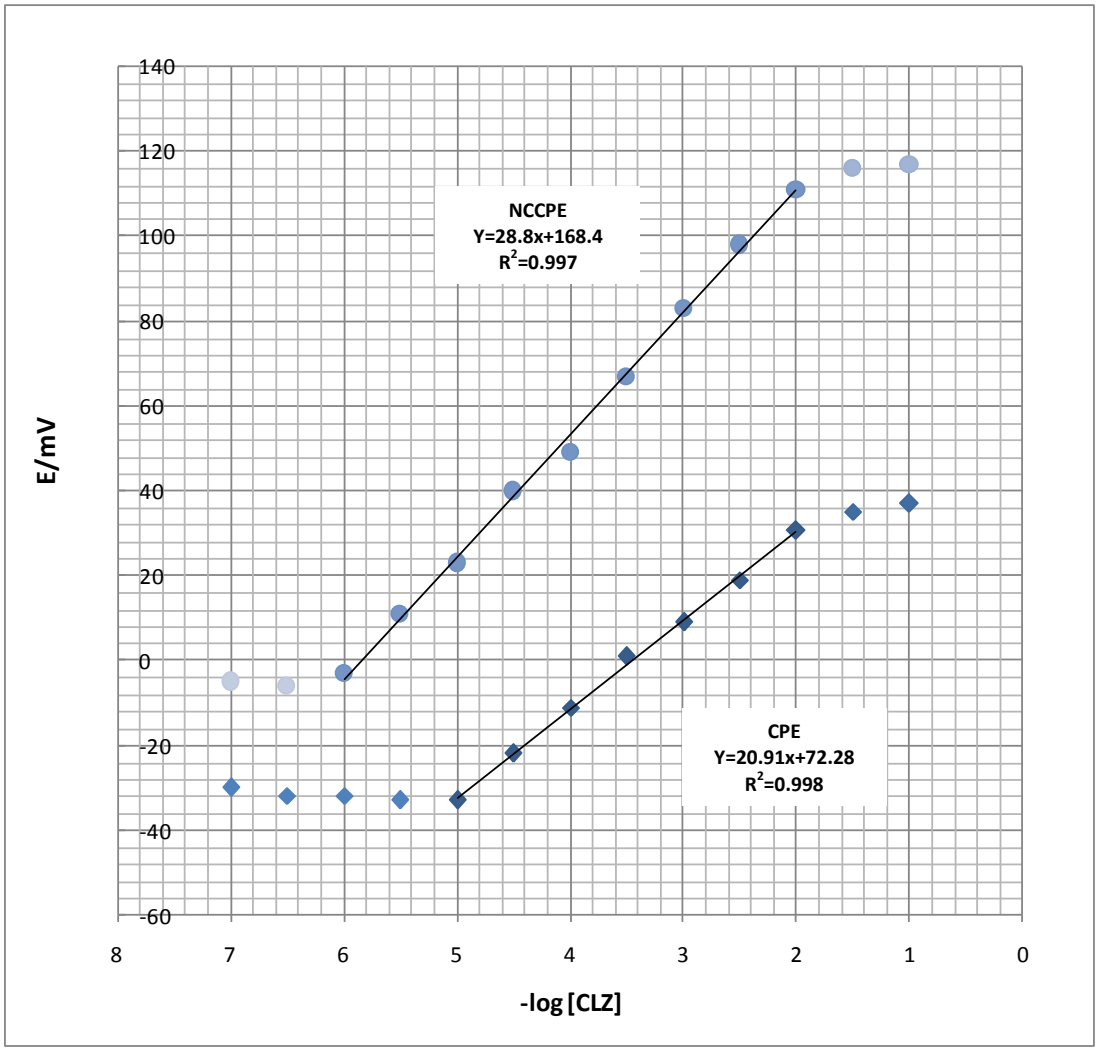

Figure 2. The calibration curve of NCCPE (no. 10) and CPE (no. 3)

3.3. pH effect on the electrode response

In order to study the effect of pH on the response of NCCPE (no. 10), the potential was measured for a certain concentration of CLZ solutions (10^{-3} mol L^{-1}) at different pH values. The pH

was varied from (2-10) by addition of concentrated HNO_3 or NaOH. The changes in potential as a function of pH show that the response of the sensor is independent of pH in the range from 3.5-5.0. In addition, there is no visible interference from H^+ or OH^- in this pH range. Fluctuations at pH greater than 5.0 might be due to the remove of the charges on CLZ compound and the fluctuations at pH values lower than 3.5 were attributed to the protonation of MIP active sites in the carbon paste.

3.4. Response time

Response time is an important factor for any sensor. For electrochemical sensors, this parameter is evaluated by measuring the average time required to achieve a potential within ±0.1 mV of the final steady-state potential upon successive immersion of a series of interested ions, each having a ten-fold difference in concentration [50-57].

Experimental conditions such as stirring or the flow rate, the ionic concentration and composition of the test solution, the concentration and composition of the solution to which the electrode was exposed before performing the experiment measurement, any previous usage or preconditioning of the electrode, and the testing temperature can all affect the experimental response time of a sensor. For the proposed modified mercury sensor, the response time was less than 15 s in the concentrated solution (10^{-3}-10^{-2} M) and about 25 s in diluted solutions (10^{-6}-10^{-4} M).

3.5. Selectivity

Selectivity is the most important characteristic of any sensor, and describes an ion selective electrode's specificity toward the target species in the presence of interfering species, the potentiometric selectivity coefficients of the proposed nano-composite carbon paste electrode were evaluated by matched potential method (MPM) [58-62], and the results are depicted in Table 2. Concentration of the reference solution of CLZ was 1.0×10^{-6} mol L^{-1} and the concentration of interfering ions was between 1×10^{-6} to 1.0×10^{-2} mol L^{-1}.

Table 2. The selectivity coefficients of various interfering cations for NCCPE

Cation	Selectivity Coefficients
Na^+	$<10^{-4}$
K^+	$<10^{-4}$
Mg^{2+}	1.4×10^{-4}
Ca^{2+}	$<10^{-4}$
Cl^-	$<10^{-4}$
CO_3^-	$<10^{-4}$
Co^{2+}	1.3×10^{-4}
Lactose	5.3×10^{-4}
Glucose	6.5×10^{-4}
NH_4^+	4.5×10^{-4}

3.6. Lifetime

The average lifetime for most ion selective sensors ranges from 4–10 weeks. After this time the slope of the sensor decreases, and the detection limit increases. The lifetime of the proposed nano-composite sensor was evaluated for a period of 12 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 9 weeks. After this time, a gradual decrease in the slope from 28.8 to 18.6 mV per decade is observed, as an increase in the detection limit from 1.0×10^{-6} mol L^{-1} to 5.0×10^{-5} mol L^{-1} (Table 3). It is well understood that the loss of sensing material is the primary reason for limited lifetimes of carbon paste electrode.

Table 3. Lifetime of mercury nano-composite carbon paste electrode

Week	Slope mV per decade	Detection Limit (mol L^{-1})
1	28.8±0.3	1.0×10^{-6}
2	28.5±0.4	1.0×10^{-6}
3	28.3±0.4	2.5×10^{-6}
4	28.2±0.3	3.3×10^{-6}
5	28.0±0.3	4.1×10^{-6}
6	27.7±0.4	4.4×10^{-6}
7	27.5±0.3	5.0×10^{-6}
8	27.2±0.4	5.5×10^{-6}
9	26.8±0.3	6.0×10^{-6}
10	18.6±0.4	5.0×10^{-5}
11	14.6±0.5	1.0×10^{-4}
12	12.3±0.6	6.7×10^{-4}

3.7. Analytical application

Linearity, limit of detection, recovery test, selectivity, precision, accuracy, and ruggedness/robustness were the parameters used for the method validation. As mentioned before, the sensors were measured between 1×10^{-6} and 1×10^{-2} mol L^{-1}. The calculated detection limit of the sensors was 1.0×10^{-6} mol L^{-1} (0.3 µg/mL).

3.7.1. Recovery Test from Tablet

The proposed sensor was evaluated by measuring the drug concentration in some pharmaceutical formulations (Table 4).

Table 4. Potentiometric determination of CLZ in pharmaceutical formulations

Sample	Labeled amount (mg/tab.)	Found by NCCPE* (mg/tab.)
Tablet 1	100	105.4±1.1
Tablet 2	100	110.3±0.8
Tablet 3	100	96.2±1.2

* The results are based on five replicate measurements

The drug concentration was determined with the calibration method. The results are in satisfactory agreement with the labeled amounts. The corresponding recovery percentage value varied from 96.2-110.3%.

3.7.3. Precision and accuracy

For repeatability monitoring, 5 replicate standard samples of 5, 50, 500 µg/mL were measured. The mean concentrations were 5.4±0.3, 54.4±2.1, 510.6±6.2 µg/mL with respective RSD values of 5.2, 3.8, and 1.2%.

3.7.4. Ruggedness/Robustness

For ruggedness of the methods a comparison was performed between the intra- and inter-day assay results for CLZ obtained by two analysts.

The RSD values for the intra- and inter-day assays in the cited formulations performed in the same laboratory by the two analysts did not exceed 4.7%. On the other hand, the robustness was examined while the parameter values (pH of the solution and the laboratory temperature) changed slightly. CLZ recovery percentages were good under most conditions, and not showing any significant change when the critical parameters were modified.

4. CONCLUSION

A CLZ selective nano-composite carbon paste electrode based on a novel biomimetic recognition element is constructed. Molecular imprinted polymer (MIP) as a sensing element, multi-walled carbon nanotube (MWCNT), nanosilica (NS), graphite powder, and room temperature ionic liquid (RTIL) were formed the carbon paste. The best results were obtained from the nano-composite sensor with the electrode composition of 5% MWCNT, 1% NS, 20% CLZ-MIP, 20% RTIL, and 54% graphite powder. The nano-composite sensor shows a Nernstian response (28.8±0.3 mV decade^{-1}) in the range of 1.0×10^{-6}-1.0×10^{-2} mol L^{-1} with detection limit of 1.0×10^{-6} mol L^{-1}. The response of the

sensor is independent of pH in the range of 3.5-5.0. The nano-composite sensor displayed very good selectivity, response time, and specially, lifetime.

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