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Nano-Composite Carbon Paste Electrode and PVC membrane Sensor for Potentiometric Determination of Erythromycin

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In this work, two kinds of potentiometric sensor were introduced. Both sensors respond based on ion-exchange mechanism. Erythromycin-tetraphenyl borate ion-pair was employed as a sensing element in construction of both electrodes. First, PVC membrane electrode was made after series of experiments. The best PVC membrane electrode performance was achieved by a membrane composition of 30% PVC, 60% DBP, and 10% ion-pair. Then, a nano-composite carbon paste electrode was designed to improve the analytical responses. The carbon paste electrode incorporation of multi-walled carbon nano-tube (MWCNTs) and nano-silica showed a better response especially in term of lifetime and response time. The best nano-composite electrode was composed of 25% ion-pair, 4% MWCNTs, 1% nano-silica, 30% paraffin and 40% graphite. The proposed method was successfully applied in determination of erythromycin in some formulations.

Keywords: Erythromycin, potentiometric sensor, PVC membrane, ion-pair, carbon paste

1. INTRODUCTION

Erythromycin (Figure 1) is a macrolide antibiotic that has an antimicrobial spectrum (nearly all Gram-positive and Gram-negative bacteria) similar to penicillin and it is often used for people who have an allergy to penicillins. It is an important antibiotic currently used in clinical applications.

Erythromycin is a complex 14-carbon lactone ring with two deoxy sugars, which one of them has an amino group with pK_a of 8.8. It is highly lipophilic and poorly water-soluble (Log $P_{(octanol/water)}$ is 3.1). High performance liquid chromatography (HPLC) is a routine method for measurement of

erythromycin [1]. However, some other methods have been also reported for determination of erythromycin; e.g. electrochemical method [2], capillary electrophoresis combined with chemiluminescence [3] and fluorimetric method [4].

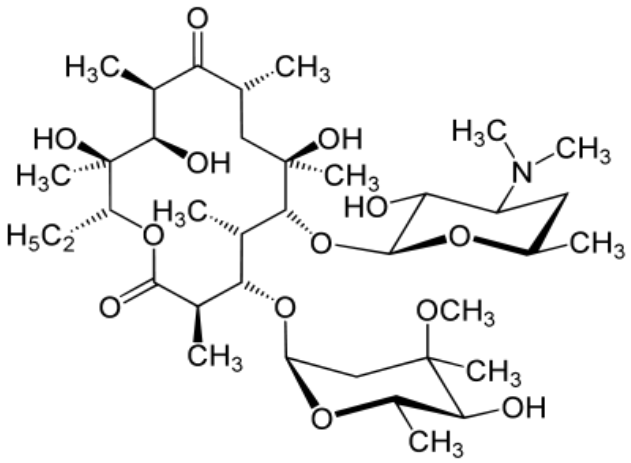

Figure 1. Chemical structure of erythromycin

In comparison with these accurate and complex methods, potentiometric detection based on suitable designed electrodes offers advantages of speed, ease of operation and procedure, relatively fast response time, reasonable selectivity thorough appropriate choice of sensing element, wide linear range, and cost-effectiveness [5,6]. These characteristics have led to preparation of many sensors for several ionic species, and the list of available electrodes has grown substantially over the past years [7-18]. Although potentiometric drug sensors cannot be used in complex matrix like biological samples, they may be a useful device for analysis of drugs in pharmaceutical formulation.

PVC membrane electrodes are one of the subdivisions of potentiometric sensors. Although they are widely used, they have not adequate mechanical stability for long-term usage. In contrast, carbon paste electrodes (CPEs) are another category of potentiometric sensors which are mechanically strong. In addition, CPEs have attracted attention more than membrane electrodes because of their advantages such as improved renewability, stable response, and low ohmic resistance and no need for internal solutions [19-21].

Recently, to improve the response of CPEs, the paste is modified by nano-materials [22-25]. Carbon nano-tubes (CNTs) have very interesting physicochemical properties, such as an ordered structure with a high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior and high surface area [26,27]. The combination of these characteristics makes CNTs unique materials with the potential for various applications.

In this work, two kinds of potentiometric sensor were made. Both electrodes respond based on ion-exchange mechanism. Erythromycin-tetraphenyl borate ion-pair was employed as a sensing material in construction of both electrodes. First, PVC membrane electrode was made after series of

experiments. Afterward, a nano-composite carbon paste electrode using MWCNTs and nano-silica was designed to improve the mechanical stability and analytical responses.

2. EXPERIMENTAL SECTION

2.1. Apparatus

The glass cell, where the erythromycin indicator electrodes (PVC membrane or carbon paste electrodes) were placed, consisted of two R684 model Analion Ag/AgCl double junction reference electrodes as internal and external reference electrodes. Both electrodes were connected to a Corning ion analyzer with a 250 pH/mV meter with ±0.1 mV precision.

2.2. Materials and Reagents

Chemicals (of analytical reagent grade) were; high-molecular weight polyvinylchloride (PVC) (Fluka Co., USA), sodium tetraphenylborate (NaTPB), dibutyl phthalate (DBP), nitrobenzene (NB), nitrophenyloctylether (*o*-NPOE) and tetrahydrofuran (THF) (Merck Co., Germany). All materials were of the highest available purity without further modification. MWCNTs (diameter 10–40 nm, length 1–25 µm, SBET: 40–600 m^2/g, purity 95%) was purchased from Shenzhen Nanotech Port Co. Ltd. (Shenzhen, China). Nano-silica used was Wacker HDK®H20 with BET surface of the hydrophilic silica of 170–230 m^2/g, V_{total}: 0.81 cm^3/g and tamped density 40 g/lit. Erythromycin and its pharmaceutical formulation were obtained from local pharmaceutical manufacturer (Tehran, Iran).

2.3. Preparation of sensing element

Sensing element used in both sensors was an ion-pair compound composed of erythromycin-tetraphenylborate (E-TPB). It was prepared by mixing about 20 mL of 0.01 M acidic solution of erythromycin with 20 mL of 0.01 M solution of tetraphenylborate. The resulting precipitate was filtered, washed with water and dried in room temperature [28-30].

2.4. Preparation of the Electrodes

2.4.1. PVC membrane electrode

General procedure for preparation of PVC membrane was as follow: different amounts of ion-pair along with appropriate amounts of PVC, plasticizer and additive were dissolved in tetrahydrofuran (THF), and the solution was mixed well into a glass dish of 2 cm diameter. Then THF was evaporated slowly until an oily concentrated mixture was obtained. A plastic tube (about 3 mm o.d.) was dipped into the mixture for about 10 s so a transparent membrane of about 0.3 mm in thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 10 h. Afterwards, the tube was filled with an internal filling solution (1.0×10^{-3} M of aciidic erythromycin

solution (pH=5)). The electrode was finally conditioned for 24 h by soaking in the same solution [28-32].

2.4.2. CPEs

General procedure for preparation of carbon paste electrode was as follows: various amounts of ion-pair along with appropriate amount of graphite powder, paraffine oil, 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. The electrode was finally conditioned for about 48 h by soaking it in a 1.0×10^{-3} M of aciidic erythromycin solution [33-35].

2.5. Standard erythromycin solutions

A stock solution of 0.02 M erythromycin was prepared. The working standard solutions (1×10^{-6} to 1×10^{-2} M) were prepared by appropriately diluting of the stock solution with water.

2.6. emf Measurements

Following cell assembly for the conduction of emf (electromotive force**)** measurements were used:

A: Ag-AgCl || internal solution, 1×10^{-3} M erythromycin | PVC membrane | sample solution || Ag-AgCl, KC1 (satd.)

B: Nano-composite CPE | sample solution || Ag-AgCl, KC1 (satd.)

These measurements were preceded using calibration of the electrodes with several standard solutions.

3. RESULTS AND DISCUSSION

3.1. PVC Membrane Composition Selection

Membrane composition effect on potential responses of the sensor was tested. The operating characteristics of PVC membrane sensor can be significantly modified by changing the relative proportions of the electrode membrane components. The main components of a membrane are PVC

matrix, plasticizer and ion-pair. Each membrane component plays a special role in the membrane function and electrode response. Previous studies shows that the membrane prepared with a plasticizer/PVC ratio about 2.2 can show the best performance [36-38]. As can be seen in Table 1, the optimum amount of PVC was selected 30 mg.

Table 1. Optimization of PVC membrane ingredients

No.	Composition (%)				Slope (mV per decade)	LR (M)	R^2
	PVC	Plasticizer	Ion-pair	NaTPB			
1	30	DBP, 65	5	-	49.6±0.3	8.0×10^{-4} -5.0×10^{-3}	0.723
2	30	DBP, 63	7	-	53.6±0.5	5.0×10^{-5} -1.0×10^{-2}	0.799
3	30	DBP, 60	10	-	58.7±0.4	1.0×10^{-5} -1.0×10^{-2}	0.999
4	30	DBP, 55	15	-	50.3±0.3	3.0×10^{-5} -1.0×10^{-2}	0.901
5	30	NB, 60	10	-	30.2±0.3	5.5×10^{-4} -3.0×10^{-2}	0.897
6	30	NPOE, 60	10	-	27.4±0.5	1.0×10^{-3} -1.0×10^{-2}	0.923
7	30	DBP, 70	0	-	3.3±0.2	5.0×10^{-5} -5.0×10^{-2}	0.963
8	30	DBP, 58	10	2	57.3±0.3	5.0×10^{-3} -1.0×10^{-2}	0.921

Plasticizer mainly acts as a membrane solvent allowing homogeneous dissolution and diffusional mobility of the ion-pair inside the membrane [28-30]. The plasticizer should be water-immiscible liquid of low vapor-pressure, compatible with PVC, no functional groups which can undergo protonation reactions. The selectivity of such electrode can be drastically influenced by the choice of the membrane solvent [39-45]. Nature of the plasticizer has a marked effect on analytical responses e.g. slope, linear domain and selectivity of PVC membrane electrodes. Here, three plasticizers with different polarity (dielectric constant) were tested, dibutyl phthalate (DBP with DC of 6.4), nitrobenzene (NB with DC of 35.7) and nitrophenyloctyl ether (*o*-NPOE with DC of about 25), as listed in Table 1. The electrode responses showed that membrane had DBP better respond. DBP had the lowest dielectric constant among the used plasticizers, and provided an effective linear range and a lower detection limit due to the better extraction of the erythromycin in the organic layer of the membrane.

As it can be seen from Table 1, absence of ion-pair in the membrane causes a very poor response (membrane no. 7), which confirm significance of the ion-pair. As a conclusion, membrane no. 3 with the composition of 30% PVC, 10% ion-pair, and 60% DBP was the optimum one for the sensor design.

Addition of 2 mg NaTPB (membrane No. 8) to the membrane composition has no remarkable improvement in the electrode response.

3.2. Carbon Paste Composition Selection

Two kinds of carbon paste were made; modified and unmodified CPEs with a variety of compositions. The results for these CPEs are given in Table 2. The unmodified CPE with optimized composition (electrode no. 3) shows a sub-Nernstian slope of 47.4 mV per decade. However, the electrode composed of 30% paraffin oil, 25% ion-pair, 40% graphite powder 1% nano-silica and 4% MWCNTs (no. 9) was found to be optimal for erythromycin carbon paste electrode. This composition was selected for further examination.

Table 2. Optimization of carbon paste electrode composition

No.	Composition (%)					Slope (mV decade^{-1})	LR (M)	R^2
	Ion-pair	Graphite	Paraffin	Nano-silica	MWCNTs			
1	-	70	30	-	-	2.1 ± 0.6	-	-
2	15	55	30	-	-	7.8 ± 0.4	1.0×10^{-4} - 1.0×10^{-3}	0.756
3	25	45	30	-	-	47.4 ± 0.3	5.0×10^{-5} - 1.0×10^{-2}	0.888
4	35	35	30	-	-	29.5 ± 0.5	1.0×10^{-5} - 1.0×10^{-2}	0.908
5	25	55	20	-	-	37.8 ± 0.4	3.0×10^{-5} - 1.0×10^{-2}	0.987
6	25	43	30	-	2	54.7 ± 0.2	1.0×10^{-2} - 4.0×10^{-2}	0.993
7	25	41	30	-	4	53.8 ± 0.3	1.0×10^{-2} - 4.0×10^{-2}	0.993
8	25	39	30	-	6	51.7 ± 0.4	1.0×10^{-2} - 2.0×10^{-2}	0.976
9	25	40	30	1	4	59.2 ± 0.3	1.0×10^{-5} - 1.0×10^{-2}	0.998
10	25	38	30	3	4	53.9 ± 0.4	1.0×10^{-2} - 7.5×10^{-2}	0.981
11	-	65	30	1	4	4.6 ± 0.3	1.0×10^{-4} - 5.0×10^{-2}	0.845

From Table 2, it was obvious that in the absence of ion-pair and presence of other components (no. 11), the response of the modified CPE was very low (slope of 4.6±0.3 mV per decade).

Using MWCNTs in the carbon paste improves the conductivity and, therefore, conversion of the chemical signal to an electrical signal. 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 CPE. Also, it enhances the mechanical properties of the electrode.

3.3. Calibration Graph and Statistical Data

The measuring range of a potentiometric sensor is the linear part of the calibration graph as shown in Figure 2.

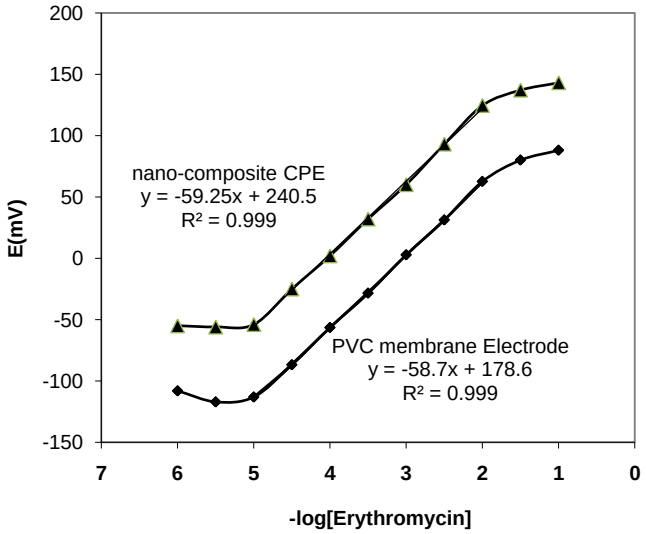

Figure 2. Calibration curves of nano-composite CPE and PVC membrane electrode. The results are based on 8 measurements.

Measurements could be performed in this lower range, but noted that more closely spaced calibration points are required for more precise determinations. For many electrodes the measuring range can extend from 1 molar to 10^{-6} or even 10^{-7} molar concentrations [46-51]. Calibration graph slope for PVC membrane electrode is 58.7 mV per decade of the erythromycin concentration and a standard deviation of ±0.3 mV after eight replicate measurements. A linear response towards the erythromycin concentration was from 1.0×10^{-5}-1.0×10^{-2} M. Calibration graph slope for nano-composite CPEs is 59.2 mV per decade of erythromycin concentration in the range of 1.0×10^{-5}-1.0×10^{-2} M.

Detection limit was calculated from the intersection of two extrapolated segments of the calibration graph. In this work, detection limit of both proposed sensor was 1.0×10^{-5} M which was calculated by extrapolating the two segments of the calibration curves.

3.4. Dynamic Response Time

Dynamic response time is the required time for the electrode to achieve values within ±1 mV of the final equilibrium potential, after successive immersions in the sample solutions [52-58]. Its calculation involved the variation and the recording of the erythromycin concentration in a series of solutions from 1.0×10^{-5} to 1.0×10^{-2} M. Both sensors were able to quickly reach its equilibrium

response in the whole concentration range. This time for nano-composite CPE was about 6 seconds and for PVC membrane electrode was about 10 s in concentrated solutions (10^{-3}-10^{-2} M) and 13 s in low concentration solutions (10^{-5}-10^{-4} M).

3.5. pH Effect on the Electrodes Response

To examine effect of pH on both electrode responses, the potential was measured at two specific concentrations of the erythromycin solution (1.0×10^{-3} M and 1.0×10^{-4} M) from the pH value of 2.0 up to 12.0 (concentrated NaOH or HCl solutions were employed for the pH adjustment). The results showed that the potential remained constant despite the pH change in the range of 4.0 to 6.0, which indicates the applicability of this electrode in the specified pH range.

Relatively noteworthy fluctuations in the potential *vs.* pH behavior took place below and above the formerly stated pH limits. In detail, the fluctuations above the pH value of 6.0 might be justified by removing the positive charge on the drug molecule. Fluctuations below the pH value of 4.0 were caused by removal of the ion-pair in the membrane or analyte in the solution. In both electrodes the same trend were observed.

3.6. Life-time Study

Both electrodes lifetime was estimated with the calibration curve, periodical test of a standard solution (1.0×10^{-5}-1.0×10^{-2} M) and calculation of its response slope.

Table 3. Lifetime of nano-composite CPE and PVC membrane electrode

Week	PVC membrane electrode		nano-composite CPE	
	Slope (mV per decade)	DL (M)	Slope (mV per decade)	DL (M)
First	58.7	1.0×10^{-5}	59.2	1×10^{-5}
Second	58.5	2.1×10^{-5}	59.0	1.5×10^{-5}
Third	57.9	3.4×10^{-5}	58.6	2.9×10^{-5}
Fourth	57.1	5.7×10^{-5}	58.2	3.7×10^{-5}
Fifth	56.8	6.9×10^{-5}	57.9	4.9×10^{-5}
Sixth	56.0	8.5×10^{-5}	57.5	5.6×10^{-5}
Seventh	55.1	1.6×10^{-4}	57.0	7.3×10^{-5}
Eighth	54.2	3.2×10^{-4}	56.5	9.2×10^{-5}
Ninth	52.9	5.6×10^{-4}	53.1	1×10^{-4}
Tenth	48.6	7.3×10^{-4}	50.5	2.7×10^{-4}

For this estimation, four electrodes were employed extensively (1 hour per day) for 10 weeks. After 6 weeks utilization of PVC membrane electrode, two changes were observed: a slight gradual decrease in the slope (from 58.7 to 48.6 mV/decade) and an increase in the detection limit (from 1.0×10^{-5} M to 7.3×10^{-4} M). As can be seen from Table 3, this time in case of nano-composite carbon paste was 8 weeks which shows the long-term stability of this kind of sensor in comparison with PVC membrane electrodes. In PVC membrane electrodes after several time of usage, the membrane ingredients leak from the organic layer and affect the membrane response. While in CPEs the surface of the electrode are renewable and can be used for longer time.

3.7. Analytical Applications

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^{-5} and 1×10^{-2} M. The calculated detection limit of the sensors was 1.0×10^{-5} M (7.3 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 erythromycin in pharmaceutical formulations

Sample	Labeled amount	Found by PVC membrane electrode*	Found by nano-composite CPE*
Tablet 1	400 mg/tab.	405.2±1.3 mg/tab.	403.2±1.5 mg/tab.
Tablet 2	400 mg/tab.	407.5±2.1 mg/tab.	406.3±1.8 mg/tab.
Tablet 3	400 mg/tab.	393.6±2.3 mg/tab.	388.7±2.0 mg/tab.
Solution 1	2%	2.3±0.5%	1.9±0.3%
Solution 2	2%	2.1±0.3%	2.3±0.4%
Solution 3	2%	2.4±0.3%	2.3±0.2%
Gel 1	4%	4.3±0.4%	3.9±0.2%
Gel 2	4 %	3.8±0.5%	4.1±0.4%
Gel 3	4 %	4.5±0.3%	4.4±0.4%

* 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 95.0-112.5%.

3.7.2. Selectivity

Selectivity, which describes an ion-selective electrode's specificity toward the target ion in the presence of interfering ions, is the most important characteristic of these devices. The potentiometric selectivity coefficients of the citalopram sensor were evaluated by the matched potential method (MPM) [59-63]. The resulting values of the selectivity coefficients are shown in Table 5. Note that all selectivity coefficients are about 10^{-3}, suggesting were interferences negligible in the performance of the electrode assembly.

Table 5. Selectivity coefficients of various interfering compounds for erythromycin sensors

Interfering ion	K_{MPM} (PVC membrane electrode)	K_{MPM} (nano-composite CPE)
Na^+	-3.9	-3.7
K^+	-3.9	-3.8
Ca^{2+}	-4.1	-4.2
Mg^{2+}	-4.3	-4.4
Glucose	-4.7	-4.3
NH_4^+	-3.6	-3.5
NO_3^-	-4.6	-4.4
CO_3^{2-}	-4.8	-4.9
Cl^-	-4.7	-4.7

3.7.3. Precision and accuracy

For repeatability monitoring, 5 replicate standard samples of 9, 90, 900 µg/mL were measured. The mean concentrations by PVC membrane were 9.3±0.3, 97.5±5.1, 917.5±9.6 µg/mL with respective RSD values of 3.2, 5.2, and 1.4% and for nano-composite CPE were 9.2±0.4, 93.7±4.2, 913.8±10.8 µg/mL with respective RSD values of 4.3, 4.4, and 1.3%.

3.7.4. Ruggedness/Robustness

For ruggedness of the methods a comparison was performed between the intra- and inter-day assay results for erythromycin 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 5.4%. On the other hand, the robustness was examined while the parameter values (pH of the solution and the laboratory temperature) changed slightly. Erythromycin recovery percentages were good under most conditions, and not showing any significant change when the critical parameters were modified.

4. CONCLUSIONS

In the present work, two types of potentiometric electrodes were constructed for determination of erythromycin. The sensors demonstrated advanced performances with a fast response time, a lower detection limit of 1.0×10^{-5} M and potential responses across the range of 1.0×10^{-5}-1.0×10^{-2} M. The sensors enabled the erythromycin determination in pharmaceutical formulations. Both sensors respond based on ion-exchange mechanism. Erythromycin-tetraphenyl borate ion-pair was employed as a sensing element in construction of both electrodes. First, PVC membrane electrode was made after series of experiments. The best PVC membrane electrode performance was achieved by a membrane composition of 30% PVC, 60% DBP, and 10% ion-pair. Then, a nano-composite carbon paste electrode was designed to improve the analytical responses. The carbon paste electrode incorporation of multi-walled carbon nano-tube (MWCNTs) and nano-silica showed a better response especially in term of lifetime and response time. The best nano-composite electrode was composed of 25% ion-pair, 4% MWCNTs, 1% nano-silica, 30% paraffin and 40% graphite.

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