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Potentiometric Determination of Loperamide Hydrochloride by Loperamide PVC Membrane and Nano-Composite Electrodes

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In this work, two new loperamide potentiometric electrodes were prepared and used for pharmaceutical analysis. In case of liquid membrane electrode, the best results were obtained from the electrode with the membrane composition of 5% ion-pair, 1% NaTPB, 30% PVC, and 64% DBP. The proposed sensor shows a Nernstian response (slope of 57.2 mV per decade) in the range of 3.0×10^{-5}-1.0×10^{-2} mol L^{-1}. In case of carbon paste electrode modified by MWCNTs, calibration graph slope is about 58.5 mV per decade in the concentration range of loperamide hydrochloride 1.0×10^{-5}-1.0×10^{-2} mol L^{-1}. Both sensors work well in the laboratory conditions and successfully applied in analysis of loperamide in some pharmaceutical formulations.

Keywords: Loperamide, Sensor, Potentiometry, Ion-selective electrode, PVC membrane, Carbon paste, Multi-walled carbon nanotubes

1. INTRODUCTION

Loperamide, Fig. 1, (4-(p-chlorophenyl)-4-hydroxy-N,N,-dimethyl-α,α-diphenyl-1-piperidinebutyr amide hydrochloride), an opiate-receptor agonist, is broadly used as an efficient drug for control and symptomatic relief of acute non-specific diarrhea and chronic diarrhea associated with inflammatory bowel diseases [1]. Recently, it has been also reported that loperamide could have some attention as an antihyperalgesic agent reducing pain without any central nervous system side effects [2].

Many methods have been reported for determination of loperamide in pharmaceutical or biological samples, including gas chromatography-mass spectrometry (GC-MS) [3] colorimetry [4], radioimmunoassay [5], high-performance liquid chromatography (HPLC) [6], spectrofluorimetry and spectrophotometry [7], non-aqueous titration [8] and liquid chromatography-mass spectrometry (LC–MS) [9].

Ion-selective electrodes (ISEs) have found wide applications in different fields of analysis [10-20]. They offer a low cost, high precision and rapid analysis with enhanced selectivity and sensitivity over a wide concentrations range. Additionally, they are easy constructed and operated without need to complex sample pretreatment before the analysis. Short response times, in the order of seconds, make ISEs appropriate devices for process control. Portable ability and online determination are also two important advantages of them.

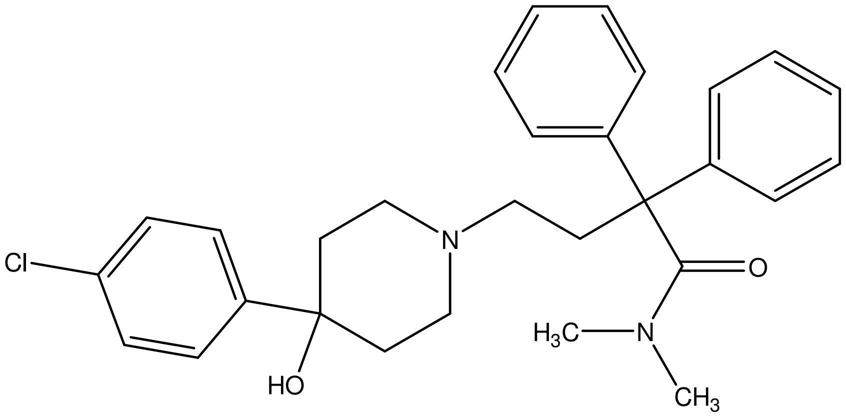

Figure 1. Chemical structure of loperamide

Here, lopramide hydrochloride and sodium tetraphenyl borate were used in synthesis of the ion-pair complex which acts as a sensing element in the electrodes. The synthesized ion-pair was used in making the both kinds of electrodes. Two kinds of ion selective electrode, PVC membrane electrode and carbon paste one are made and characterized and then used for pharmaceutical analysis of loperamide in some formulations.

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 loperamide selective electrode 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:

In PVC membrane electrode:

Ag/AgCl–KCl (satd.) || internal filling solution of loperamide hydrochloride (1.0×10^{-3} mol L^{-1}) |
PVC membrane | loperamide hydrochloride sample solution || Ag/AgCl–KCl (satd.)

In nano-composite electrode:

Nanocomposite surface| loperamide hydrochloride sample solution || Ag/AgCl–KCl (satd.)

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

2.2. Reagents and materials

Chemicals (of analytical reagent grade) were high-molecular weight polyvinylchloride (PVC) (Fluka Co., USA), sodium tetraphenyl borate (NaTPB), dibutyl phthalate (DBP), nitrobenzene (NB), benzyl acetate (BA) and tetrahydrofuran (THF) (Merck Co., Germany). All materials were of the highest available purity without further modification. Loperamide hydrochloride and its pharmaceutical formulation were obtained from a local pharmaceutical manufacturer (Tehran, Iran) as gift samples. The multi-walled carbon nanotubes (MWCNTs) with 10-40 nm diameters, 1-25 µm length, core diameter: 5-10 nm, SBET: 40-600 m^2/g, V_{total}: 0.9 cm^3/g, bulk density 0.1 g/cm^3, true density 2.1 g/cm^3 and with 95% purity were purchased from a local company (Research Institute of the Petroleum Industry, Iran).

2.3. Ion-pair synthesis

Sensing element used in both sensors was an ion-pair complex made from the interaction of loperamide hydrochloride and sodium tetraphenyl borate. It was prepared by mixing about 20 mL of 0.01 mol L^{-1} loperamide hydrochloride with equivalent value of tetraphenyl borate solution. The resulting precipitate was then filtered, washed with distilled water and dried in room temperature to use in construction of the sensors [21,22].

2.4. Preparation of the Electrodes

2.4.1. PVC membrane electrode

General procedure to prepare 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 thick transparent membrane was formed. The tube was then pulled out from the mixture and kept at room temperature for about 5 h. Afterwards, the tube was filled with an internal filling solution of loperamide hydrochloride (1.0×10^{-3} mol L^{-1}). The electrode was finally conditioned for 20 h by soaking in the same solution [20-22].

2.4.2. Nano-composite Electrode

Two kinds of carbon paste electrode were prepared to study the effect of MWCNTs in the paste. The procedure for preparation of carbon paste electrode was as follows: various amounts of ion-pair along with appropriate amount of graphite powder, MWCNTs, paraffin oil, 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 resistant. A copper wire was inserted into the opposite end of the tube to make an 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} mol L^{-1} of loperamide hydrochloride solution [23-28].

2.5. Standard loperamide solutions

A stock solution of 0.01 mol L^{-1} loperamide hydrochloride solution was prepared. The working standard solutions (1×10^{-7} to 1×10^{-3} mol L^{-1}) were prepared by properly dilution of the stock solution with distilled water.

3. RESULTS AND DISCUSSION

3.1. PVC Membrane Composition Selection

Since characteristics of a PVC membrane electrode can significantly affect the electrode responses, changes in the potential responses of the PVC membrane electrode were study by changing the composition of the membrane ingredients. The main components of a membrane are PVC as a polymeric matrix, solvent mediator and a suitable sensing element. Every ingredient plays a particular role in the electrode function and response.

Previous studies showed that the membrane having a plasticizer/PVC ratio about 2.2 can show the best performance [29-33]. As it can be seen in Table 1, the optimum amount of PVC was selected 30 mg.

The plasticizer is a water-immiscible liquid with 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.

Table 1. Optimization of PVC membrane components

No.	Composition (%)				Slope (mV decade^{-1})	LR (mol L^{-1})	R^2	Response time
	PVC	Plasticizer	Ion-pair	Additive (NaTPB)				
1	30	DBP, 67	3	0	29.6±0.6	1.0×10^{-4}-5.0×10^{-3}	0.908	57 s
2	30	DBP, 65	5	0	52.4±0.4	5.0×10^{-5}-5.0×10^{-3}	0.957	46 s
3	30	DBP, 63	7	0	51.3±0.5	5.0×10^{-5}-5.0×10^{-3}	0.942	50 s
4	30	DBP, 64	5	1	57.2±0.4	3.0×10^{-5}-1.0×10^{-2}	0.997	26 s
5	30	DBP, 63	5	2	54.5±0.6	3.0×10^{-5}-1.0×10^{-2}	0.990	33 s
6	30	NB, 64	5	1	21.8±0.6	5.0×10^{-5}-1.0×10^{-2}	0.905	1 min
7	30	BA, 64	5	1	27.7±0.5	1.0×10^{-4}-1.0×10^{-2}	0.894	53 s
8	30	DBP, 69	0	1	3.7±0.6	5.0×10^{-4}-1.0×10^{-3}	-	4 min

Plasticizer or solvent mediator mainly acts as a membrane solvent allows a homogeneous dissolution and diffusional mobility of the ion-pair in the membrane [34-40]. Nature of the plasticizer has a noticeable effect on analytical responses e.g. slope, linear domain and selectivity of PVC membrane electrode. 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 benzylacetate (BA with DC of about 5.7), as listed in Table 1. The electrode responses showed that membrane had DBP better respond. DBP among the used plasticizers provided an effective linear range and a lower detection limit due to the better extraction of loperamide hydrochloride ions in the organic layer of the membrane. Addition of ionic additive such as sodium tetraphenyl borate (NaTPB) to the membrane composition improved the slope, linear range and the response time. In fact, it helps to the ion-exchange of the lopermide from aqueous solution to organic layer of the membrane. As it can be seen from Table 1, absence of the ion-pair in the membrane causes a very poor response (membrane no. 8), which confirm significance of the ion-pair. The electrodes behavior show that the best Nernstian slope is 57.2±0.4 mV per decade. As a conclusion, membrane no. 4 with the composition of 30% PVC, 5% ion-pair, 1% NaTPB and 654% DBP was the optimum one for the sensor design.

3.2. Carbon Paste Composition

As mentioned above, two kinds of carbon paste electrode, modified and unmodified carbon paste electrodes with different compositions were prepared and their potential responses were studied. The results are given in Table 2. The carbon paste electrode composed of 20% paraffin oil, 20% ion-pair, and 60% graphite powder (no. 3) was found to be optimal for loperamide hydrochloride electrode. This composition was selected for further examination. Then, the past was modified by multi-walled carbon nanotubes (MWCNTs). Because of their particular physicochemical properties, such as ordered structures with high aspect ratios, ultra-light weight, high thermal conductivity, metallic or semi-metallic behavior, high surface area, high electrical conductivity and remarkable mechanical strength. High conductivity of MWCNTs increases the dynamic working range and response time of the carbon paste electrode. Addition of 5% MWCNT to the composition increased the response to a Nernstian slope of about 58.5±0.3 mV per decade (no. 7). From Table 2, it was obvious that in the absence of ion-pair and presence of other components (no. 9), the response of the modified CPE was very low (slope of 3.2±0.8 mV per decade).

Table 2. Optimization of nano-composite carbon paste electrode composition

No.	Composition (%)				Slope (mV decade^{-1})	LR (mol L^{-1})	Response time	R^2
	Graphite	Paraffin	Ion-pair	MWCNTs				
1	80	20	-	-	-	-	-	-
2	70	20	10	-	36.8±0.7	5.0×10^{-4}-5.0×10^{-3}	1.1 min	0.899
3	60	20	20	-	45.5±0.5	1.0×10^{-5}-1.0×10^{-2}	50 s	0.915
4	55	20	25	-	46.3±0.6	1.0×10^{-5}-1.0×10^{-2}	54 s	0.912
5	55	25	20	-	30.2±0.8	5.0×10^{-5}-5.0×10^{-3}	1.5 min	0.927
6	57	20	20	3	53.6±0.3	1.0×10^{-5}-1.0×10^{-2}	31 s	0.9
7	55	20	20	5	58.5±0.3	1.0×10^{-5}-1.0×10^{-2}	20 s	0.997
8	53	20	20	7	56.6±0.5	1.0×10^{-5}-1.0×10^{-2}	44 s	0.945
9	55	20	-	5	3.2±0.8	5.0×10^{-4}-1.0×10^{-3}	3 min	0.811

3.3. Calibration curve

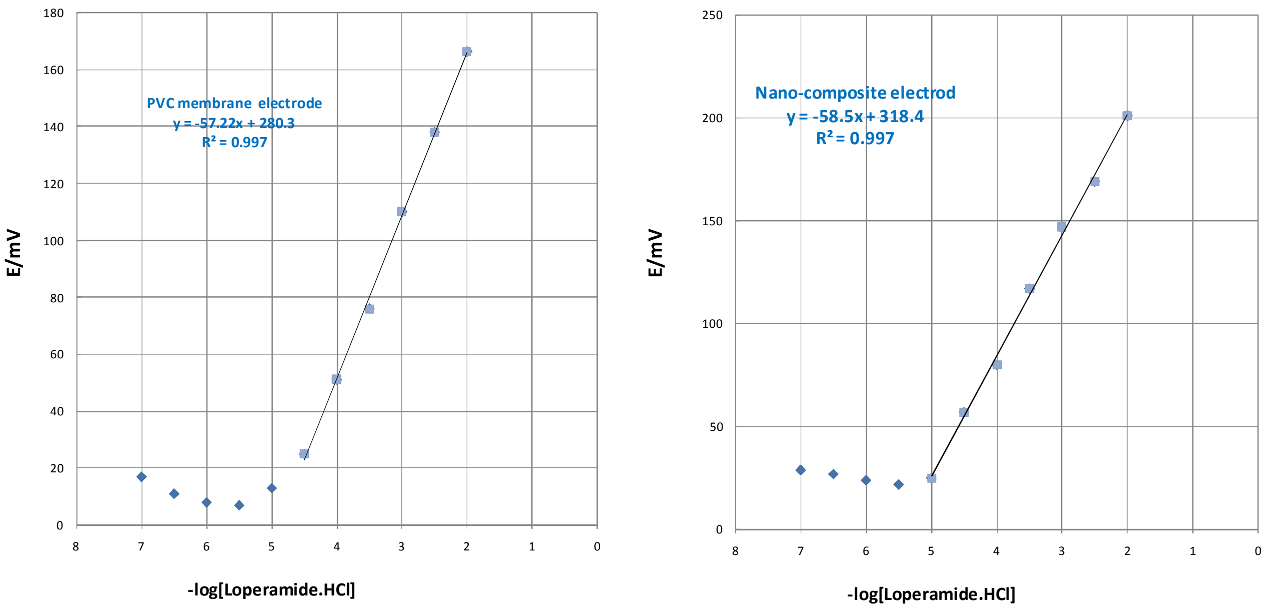

Figure 2. Calibration curves of loperamide nano-composite and PVC membrane electrode. The results are based on 5 replicate measurements.

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

For many ion-selective electrodes the measuring range can extend from 1 molar to 10^{-6} or even 10^{-7} molar concentrations [41-44]. Slope of the calibration curve of PVC membrane electrode is 57.2 mV per decade of the loperamide hydrochloride concentration and a standard deviation of ±0.4 mV after five replicate measurements. A linear response towards the loperamide hydrochloride concentration was from 3.0×10^{-5}-1.0×10^{-2} mol L^{-1}. Calibration graph slope for CPEs is 58.5 mV per decade of loperamide hydrochloride concentration in the range of 1.0×10^{-5}-1.0×10^{-2} mol L^{-1} with a standard deviation of ±0.3 mV after eight replicate measurements. Detection limit was calculated from the intersection of two extrapolated segments of the calibration graph. In this work, detection limit of the PVC membrane sensor was 1.0×10^{-5} mol L^{-1} and in case of nano-composite carbon paste electrode was 9.0×10^{-6} mol L^{-1} 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 [45-50]. Its calculation involved the variation and the recording of the loperamide hydrochloride concentration in a series of solutions from 1.0×10^{-5} to 1.0×10^{-2} mol L^{-1}. Both sensors were able to quickly reach its equilibrium response in the whole concentration range. This time for CPE was about 20 seconds and for PVC membrane electrode was about 26 s in the whole concentrations.

3.5. pH Effect on the Electrodes Responses

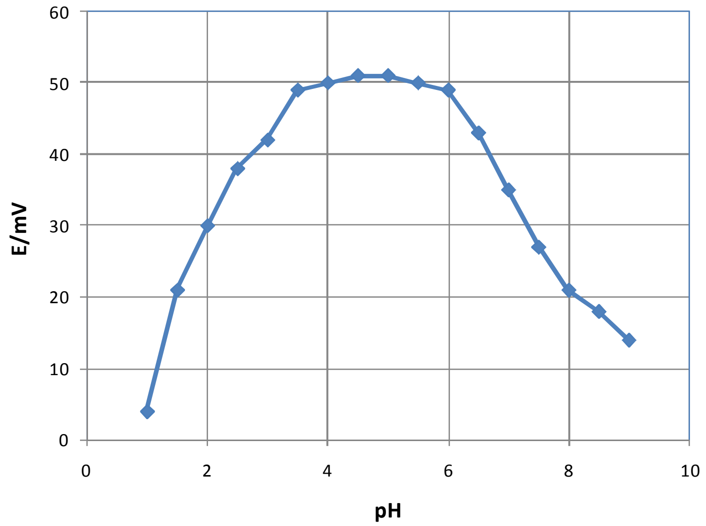

Figure 3. Applicable pH of the electrodes in the test solution of 1.0×10^{-4} mol L^{-1}

To examine the effect of pH on the electrode responses, the potential was measured at specific concentration of the loperamide hydrochloride solution (1.0×10^{-4} mol L^{-1}) from the pH value of 1.0 up to 9.0 (concentrated NaOH or HCl solutions were employed for the pH adjustment) by PVC membrane electrode. The results showed that the potential remained constant despite the pH change in the range of 3.5 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 3.5 were caused by removal of the membrane ingredients or analyte in the solution. In both electrodes the same trend were observed.

3.6. Life-time Study

Both electrodes lifetime was estimated by the calibration curve, periodical test of a standard solution and calculation of its response slope.

Table 3. Lifetime of CPE and PVC membrane electrode

Week	PVC membrane Slope (mV per decade)	DL (mol L^{-1})	Nano-composite CPE Slope (mV per decade)	DL (mol L^{-1})
First	57.2	1.0×10^{-5}	58.5	9.0×10^{-6}
Second	57.0	1.5×10^{-5}	58.4	9.5×10^{-6}
Third	56.8	3.0×10^{-5}	58.2	1.0×10^{-5}
Fourth	56.4	5.5×10^{-5}	58.0	2.5×10^{-6}
Fifth	56.1	7.0×10^{-5}	57.7	4.0×10^{-5}
Sixth	52.5	1.0×10^{-4}	57.4	5.0×10^{-5}
Seventh	51.3	3.5×10^{-4}	55.5	9.0×10^{-5}
Eighth	49.2	7.5×10^{-4}	53.2	2.5×10^{-4}
Ninth	42.0	1.5×10^{-3}	50.0	7.0×10^{-4}
Tenth	33.7	3.5×10^{-3}	46.0	9.5×10^{-4}

For this estimation, three electrodes were employed extensively (1 hour per day) for 10 weeks. After 5 weeks utilization of PVC membrane electrode, two changes were observed: a slight gradual decrease in the slope and an increase in the detection limit. As it can be seen from Table 3, this time in case of carbon paste was 6 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 were the parameters used for the method validation.

3.7.1. Recovery Test from Tablet

The proposed sensor was evaluated by measuring the drug concentration in some pharmaceutical formulations of loperamide hydrochloride (Table 4). The drug concentration was determined using calibration method. The results are in satisfactory agreement with the labeled amounts. The corresponding recovery percentage value varied from 97.6-104.0%.

Table 4. Potentiometric determination of loperamide hydrochloride in some pharmaceutical formulations

Sample	Labeled amount	Found by PVC membrane electrode*	Found by Nano-composite CPE* (mg/1ml)
Sample 1	2 mg/CAP	2.17±0.13 mg/CAP	2.10±0.10 mg/CAP
Sample 2	2 mg/CAP	2.15±0.08 mg/CAP	2.14±0.09 mg/CAP
Sample 3	2 mg/Tab	2.09±0.11 mg/Tab	2.10±0.07 mg/Tab
Sample 4	2 mg/Tab	1.93±0.07 mg/Tab	1.92±0.10 mg/Tab

* The results are based on four replicate measurements.

3.7.2. Selectivity

Table 5. Selectivity coefficients of various interfering compounds for loperamide hydrochloride sensors

Interfering ion	Log K_{MPM} (PVC membrane electrode)	Log K_{MPM} (Nano-composite CPE)
Na^+	-3.2	-3.5
K^+	-3.4	-3.6
NH_4^+	-3.0	-3.1
Ca^{2+}	-4.1	-4.1
Mg^{2+}	-4.0	-4.2
Cl^-	-3.9	-3.7
NO_3^-	-4.0	-4.2
Lactose	-4.4	-4.5
Glucose	-4.1	-4.0

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 loperamide hydrochloride electrode were evaluated by the matched potential method (MPM) [55-60]. 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.

3.7.3. Precision and accuracy

For repeatability monitoring, 3 standard samples were measured. The RSD values by PVC membrane were 3.6, 3.4, and 3.3% and for nano-composite CPE were 3.1, 3.2, and 3.0%.

3.7.4. Ruggedness

For ruggedness of the methods a comparison was performed between the intra- and inter-day assay results for loperamide hydrochloride 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 4.1%. On the other hand, the robustness was examined while the parameter values (pH of the solution and the laboratory temperature) changed slightly. Loperamide hydrochloride 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 loperamide hydrochloride. The sensors demonstrated advanced performances with a fast response time, a lower detection limit of 1.0×10^{-5} mol L^{-1} for PVC membrane electrodes and 9.0×10^{-6} mol L^{-1} potential responses across the range of 3.0×10^{-5}-1.0×10^{-2} mol L^{-1} and 1.0×10^{-5}-1.0×10^{-2} mol L^{-1}. The sensors enabled the loperamide hydrochloride determination in pharmaceutical formulations. Both sensors respond based on ion-exchange mechanism. The best PVC membrane electrode performance was achieved by a membrane composition of 30% PVC, 64% DBP, 1% NaTPB and 5% ion-pair. Then, a carbon paste electrode was designed to improve the analytical responses. The best electrode was composed of 20% ion-pair, 20% paraffin, 5% MWCNTs and 55% graphite.

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