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Ciprofloxacin Nano-Composite Carbon Paste and PVC Membrane Potentiometric Sensors

Farnoush Faridbod[1,2], *Tahereh Poursaberi*,[3] *Parviz Norouzi*[1,2], *Mohammad Reza Ganjali*[1,2,*]

[1] Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran
[2] Endocrinology & Metabolism Research Center, Tehran University of Medical Sciences, Tehran, Iran
[3] Research Institute of Petroleum Industry, Tehran, Iran
[*]E-mail: ganjali@khayam.ut.ac.ir

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Ciprofloxacin is a synthetic antibiotic of the fluoroquinolone drug class. Two kinds of potentiometric sensors were introduced for determination of ciprofloxacin. Ciprofloxacin-tetraphenyl borate ion-pair was synthesized and used as a sensing element in making both electrodes. Both sensors respond based on ion-exchange mechanism. The best PVC membrane electrode performance was achieved by a membrane composition of 30% PVC, 65% DBP, and 5% ion-pair. Then, carbon paste electrode was designed to improve the analytical responses and mechanical resistance. The best electrode was composed of 20% ion-pair, 20% IL, 5% MWCNTs and 55% graphite. The proposed method was successfully applied in determination of Ciprofloxacin in pharmaceutical formulations.

Keywords: Ciprofloxacin, Potentiometric Sensor, PVC membrane, Ion-Pair, Carbon Paste

1. INTRODUCTION

Ciprofloxacin (Figure 1) (1 – cyclopropyl – 6 – fluoro - 4 –oxo – 7- (piperazin-1-yl)-quinoline-3-carboxylic acid) is an antibiotic in a group of drugs called fluoroquinolones. It is used to fight bacteria in the body and treat different types of bacterial infections. Ciprofloxacin may also be used to prevent or slow anthrax after exposure.

Ciprofloxacin is used to treat a number of infections including: infections of bones and joints, endocarditis, gastroenteritis, malignant otitis externa, respiratory tract infections, cellulitis, urinary tract infections, prostatitis, anthrax, chancroid, among others [1].

A number of research describe the determination of Ciprofloxacin in biological fluids and pharmaceutical formulation by several methods including high performance liquid chromatography (HPLC) [2-4], spectrophotometry [5-7], chemiluminescence [8], and micellar liquid chromatography

[9]. Nowadays, various advanced electrochemical methods was used for determination of active component of a drug in its formulation [10,11]. However, potentiometric detection based on ion–selective electrodes (ISEs) offers the advantages of speed and ease of preparation and procedures, relatively fast response, reasonable selectivity thorough judicious choice of the membrane active materials, wide linear dynamic range, and low cost in analysis of pharmaceutical compound in their formulations [12-16].

PVC membrane electrodes are the wide subdivisions of potentiometric sensors. Although they are widely used in different applications [17-29], 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. Also, the best property of CPEs is ability to modify their compositions [30-34].

Here, Ciprofloxacin-tetraphenyl borate ion-pair was synthesized and used as a sensing element in making both kinds of potentiometric electrodes. Both sensors were responded according to the ion-exchange mechanism. PVC membrane electrode was made at first and then, a carbon paste electrode was designed to have a more stable electrode.

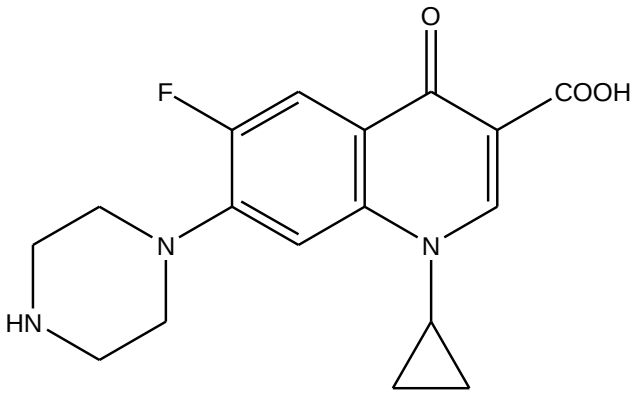

Figure 1. Chemical structure of Ciprofloxacin

2. EXPERIMENTAL PART

2.1. Apparatus

The glass cell, where the Ciprofloxacin 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 tetraphenyl borate (NaTPB), dibutyl phthalate (DBP), nitrobenzene (NB), benzylacetate (BA) and tetrahydrofuran (THF) (Merck Co., Germany). All materials were of the highest available purity without further modification. Graphite powder with a <50 μm particle size (Merck), and 2.2 g/cm^3 density; along with the paraffin oil (Aldrich) of the highest purity, and 1-n-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF_4, were used for the preparation of the carbon pastes. The multi-wall 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 (Iran). Ciprofloxacin and its pharmaceutical formulation were obtained from local pharmaceutical manufacturer as gift sample (Tehran, Iran).

2.3. Preparation of the sensing element (ion-pair)

Sensing element used in both sensors was an ion-pair compound composed of Ciprofloxacin-tetraphenyl borate (CF-TPB). It was prepared by mixing about 20 mL of 0.01 M solution of Ciprofloxacin.HCl with 20 mL of 0.01 M solution of tetraphenyl borate. The resulting precipitate was filtered, washed with water and dried in room temperature [12-16].

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 5 h. Afterwards, the tube was filled with an internal filling solution (1.0×10^{-3} M of Ciprofloxacin.HCl solution). The electrode was finally conditioned for 24 h by soaking in the same solution [12-16].

2.4.2. Nano-composite carbon paste electrodes preparations

General procedure for preparation of carbon paste electrode was as follows: various amounts of ion-pair along with appropriate amount of MWCNTs (in case of modified carbon paste), graphite powder, ionic liquids or paraffin oil (in case of modified or non-modified Carbon paste), 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 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 Ciprofloxacin.HCl solution [30-34].

2.5. Standard Ciprofloxacin solutions

A stock solution of 0.1 M Ciprofloxacin was prepared. The working standard solutions (1×10^{-6} to 1×10^{-2} M) were prepared by appropriately diluting of the stock solution with distilled water.

2.6. The emf Measurements

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

A: Ag-AgCl || internal solution, 1×10^{-3} M Ciprofloxacin.HCl | 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 [35-42].

Table 1. Optimization of PVC membrane ingredients

No.	Composition (%)				Slope (mV/decade)	LR (M)	DL (M)
	PVC	Plasticizer	Ion-pair	Additive			
1	30	DBP, 67	3	-	31.7±0.5	1.0×10^{-4}-1.0×10^{-2}	9.0×10^{-5}
2	30	DBP, 65	5	-	56.8±0.4	1.0×10^{-5}-5.0×10^{-2}	1.0×10^{-5}
3	30	DBP, 63	7	-	55.9±0.5	2.0×10^{-5}-5.0×10^{-2}	1.8×10^{-5}
4	30	DBP, 63	5	2	52.2±0.3	5.0×10^{-5}-1.0×10^{-2}	3.5×10^{-5}
5	30	NB, 60	5	-	20.4±0.3	1.0×10^{-4}-1.0×10^{-2}	1.0×10^{-4}
6	30	BA, 60	5	-	43.5±0.5	5.0×10^{-5}-1.0×10^{-2}	5.0×10^{-5}
7	30	DBP, 70	0	-	3.8±0.6	5.0×10^{-3}-5.0×10^{-2}	4.5×10^{-3}

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 [31-35]. As it can be seen in Table 1, the optimum amount of PVC was selected 30 mg.

Plasticizer mainly acts as a membrane solvent allowing homogeneous dissolution and diffusional mobility of the ion-pair inside the membrane [12-16]. 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 [27,28].

Nature of the plasticizer has an important effect on analytical responses *e.g.* slope, linear domain and selectivity of the 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 benzyl acetate (BA 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 Ciprofloxacin 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. 2 with the composition of 30% PVC, 5% ion-pair, and 65% DBP was the optimum one for the sensor design.

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 electrode composed of 20% paraffin oil, 20% ion-pair, and 60% graphite powder (no. 2) was found to be optimal for Ciprofloxacin carbon paste electrode. 20% IL, 20% ion-pair, 5% MWCNTs and 55% graphite powder (no. 10) was found to be optimal for Ciprofloxacin nano-composite carbon paste electrode. This nano-composition electrode was selected for further examination.

From Table 2, it was obvious that in the absence of ion-pair and presence of other components (no. 12), the response of the modified CPE was very low (slope of 5.7±0.6 mV/decade).

Replacement of paraffin oil, which is an organic binder, with IL, improved the sensitivity of the sensor to a near-Nernstian slope (no. 6). Enhancement of the electrochemical behavior of RTIL based electrodes can be related to its enhanced conductivity. Because of the good solubility and high viscosity, the IL can form a layer on the carbon particles and can fill in the empty spaces between carbon particles, so the conductivity of the IL-based electrodes was greatly enhanced compared to the traditional CPE. Also, IL can be a better solvent and extract the analyte from the solution to the electrode surface.

High conductivity of MWCNT increases the dynamic working range and response time of the sensor. Addition of 5% MWCNT to the composition was found to increase the response to a Nernstian slope of about 58.7 mV decade^{-1} (no. 10).

Table 2. The optimization of the carbon paste ingredients

CPE No.	Binder	Sensing Material	Graphite Powder	MWCNTs	Slope (mV/decade)	Linear Range (M)
1	Paraffin -20%	15%	65%	-	34.5±0.5	5.0×10^{-5}-1.0×10^{-2}
2	Paraffin -20%	20%	60%	-	43.7±0.6	1.0×10^{-5}-5.0×10^{-2}
3	Paraffin -20%	25%	55%	-	41.2±0.4	1.0×10^{-5}-1.0×10^{-2}
4	Paraffin -15%	20%	65%	-	28.9±0.5	5.0×10^{-4}-1.0×10^{-2}
5	Paraffin -25%	20%	55%	-	37.4±0.5	5.0×10^{-5}-5.0×10^{-2}
6	RTIL-15%	20%	65%	-	49.5±0.4	1.0×10^{-5}-1.0×10^{-2}
7	RTIL-20%	20%	60%	-	53.7±0.5	5.0×10^{-6}-1.0×10^{-2}
8	RTIL-25%	20%	55%	-	53.8±0.6	8.0×10^{-6}-1.0×10^{-2}
9	RTIL-20%	20%	57%	3%	57.5±0.6	5.0×10^{-6}-1.0×10^{-1}
10	RTIL-20%	20%	55%	5%	58.7±0.4	1.0×10^{-6}-1.0×10^{-1}
11	RTIL-20%	20%	53%	7%	56.7±0.5	3.0×10^{-6}-1.0×10^{-1}
12	RTIL-20%	-	75%	5%	5.7±0.6	5.0×10^{-4}-5.0×10^{-3}

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.

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 [36-45]. Calibration graph slope for PVC membrane electrode is 56.8 mV/decade of the Ciprofloxacin concentration and a standard deviation of ±0.4 mV after five replicate measurements. A linear response towards the Ciprofloxacin concentration was from 1.0×10^{-5}-1.0×10^{-2} M. Calibration graph slope for nano-

composite CPEs is 58.7 mV/decade of Ciprofloxacin concentration in the range of 1.0×10^{-6}-1.0×10^{-1} M.

Detection limit was calculated from the intersection of two extrapolated segments of the calibration graph. In this work, detection limit of proposed PVC membrane sensor was 1.0×10^{-5} M and nano-composite CPE was 1.0×10^{-6} M which were calculated by extrapolating the two segments of the calibration curves.

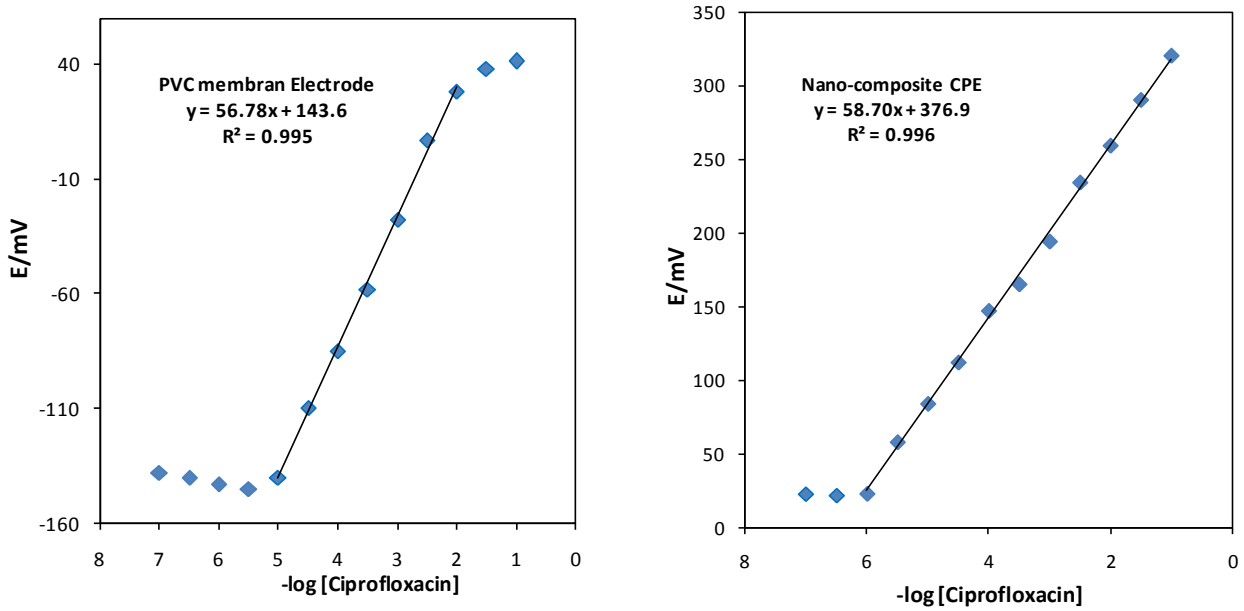

Figure 2. Calibration curves of nano-composite CPE and PVC membrane electrode. The results are based on 5 replicate measurements.

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 [43-51]. It is obtained by variation the Ciprofloxacin concentration in a series of solutions from 1.0×10^{-6} to 1.0×10^{-2} M and recording the time and potential changes. Both sensors were able to quickly reach its equilibrium response in the whole concentration range. This time for nano-composite CPE was about 15 seconds and for PVC membrane electrode was about 20 s in the whole concentrated range.

3.5. pH Effect on the Electrodes Response

To examine the effect of pH on both electrode responses, the potential was measured at specific concentration of the Ciprofloxacin.HCl solution (1.0×10^{-3} M) from the pH value of 2.0 up to 10.0 (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 8.0, which

indicates the applicability of this electrode in the specified pH range [52-55]. 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 8.0 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 and calculation of its response slope.

Table 3. Lifetime of CPE and PVC membrane electrode

Week	PVC membrane Slope (mV/ decade)	DL (M)	Nano-composite CPE Slope (mV/ decade)	DL (M)
First	56.8	1.0×10^{-5}	58.7	1.0×10^{-6}
Second	56.5	2.5×10^{-5}	58.6	2.0×10^{-6}
Third	56.3	3.5×10^{-5}	58.4	2.8×10^{-6}
Fourth	56.1	5.8×10^{-5}	58.2	3.7×10^{-6}
Fifth	55.8	6.6×10^{-5}	57.9	5.9×10^{-6}
Sixth	54.0	8.0×10^{-5}	57.6	6.5×10^{-6}
Seventh	47.6	2.3×10^{-4}	57.0	7.8×10^{-6}
Eighth	43.2	3.8×10^{-4}	56.2	9.0×10^{-6}
Ninth	38.5	5.2×10^{-4}	48.4	3.2×10^{-5}
Tenth	18.3	7.2×10^{-4}	34.2	7.5×10^{-5}

For this estimation, three 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 56.8 to 54.0 mV/decade) and an increase in the detection limit (from 1.0×10^{-5} M to 8.0×10^{-5} M). As can be seen from Table 3, this time in case of 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 decrease the membrane response and sensitivity. While in nano-composite 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 of a potentiometric electrode [52-60]. The detection limits and linear ranges were discussed above.

3.7.1. Recovery Test from pharmaceutical formulations

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

Table 4. Potentiometric determination of Ciprofloxacin in pharmaceutical formulations

Sample	Labeled amount (mg/tab.)	Found by PVC membrane electrode* (mg/tab.)	Found by Nano-composite CPE* (mg/tab.)
CIPROFLOXACIN HCL-ARYA	250	255.7±2.2	254.2±1.7
CIPROFLOXACIN-EXIR	250	258.4±1.9	255.2±1.4
CIPROFLOXACIN HCL-Toliddaru	250	246.9±2.3	249.0±2.0

* 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 98.7-103.4%.

3.7.2. Precision and accuracy

For repeatability monitoring, 5 replicate standard samples of were measured. The RSD values by PVC membrane were 3.7, 4.2, and 3.8% and for CPE were 3.3, 4.0, and 3.7%.

3.7.3. Ruggedness/Robustness

For ruggedness of the methods a comparison was performed between the intra- and inter-day assay results for Ciprofloxacin 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 4.3%. On the other hand, the robustness was examined while the parameter values (pH of the solution and the laboratory temperature) changed slightly. Ciprofloxacin recovery percentages were good under most conditions, and not showing

any significant change when the critical parameters were modified.

3.7.4. 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 Ciprofloxacin sensor were evaluated by the matched potential method (MPM) [60-65]. 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 Ciprofloxacin sensors

Interfering ion	K_{MPM} (PVC membrane electrode)	K_{MPM} (Nano-composite CPE)
Na^+	-3.6	-3.7
K^+	-4.0	-3.8
NH_4^+	-3.6	-3.5
Ca^{2+}	-3.8	-3.9
Mg^{2+}	-4.2	-4.1
Cl^-	-4.4	-4.5
NO_3^-	-4.2	-4.3
CO_3^{2-}	-3.8	-3.9
Lactose	-4.2	-4.3
Glucose	-4.4	-4.3

4. CONCLUSIONS

In the present work, two types of potentiometric electrodes were constructed for determination of Ciprofloxacin. The sensors demonstrated advanced performances with a fast response time, a lower detection limit of 1.0×10^{-5} M and 1.0×10^{-6} M and potential responses across the range of 1.0×10^{-5}-1.0×10^{-2} M and 1.0×10^{-6}-1.0×10^{-1} M. The sensors enabled the Ciprofloxacin determination in pharmaceutical formulations accurately. Both sensors respond based on ion-exchange mechanism. Ciprofloxacin-tetraphenyl borate ion-pair was employed as a sensing element in construction of both electrodes. The best PVC membrane electrode performance was achieved by a membrane composition of 30% PVC, 65% DBP, 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% IL, 5% MWCNTs and 55% graphite powder.

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