

Full Paper

Clomipramine Determination by Potentiometric PVC Membrane and Carbon Paste Sensors

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Abstract- Clomipramine hydrochloride, active component of an antidepressant drug, was determined in the pharmaceutical formulation by two kinds of potentiometric sensor; a PVC membrane sensor and a carbon paste electrode modified by MWCNTs and ionic liquid. Both sensors were incorporated with clomipramine-tetraphenylborate ion-pair complex and they respond based on ion exchange mechanism. The best PVC membrane sensor response was obtained by the membrane composition of 7% ion-pair, 30% PVC and 63% DBP, and in case of modified carbon paste electrode, the best response was obtained by a paste composed of 25% ion-pair, 5% MWCNTs, 25% ionic liquid and 45% graphite powder. The PVC membrane sensor showed a Nernstian response in the range of 1.0×10^{-4} - 1.0×10^{-2} mol L⁻¹ and modified carbon paste electrode 1.0×10^{-5} - 1.0×10^{-2} mol L⁻¹. The both sensors work well in laboratory conditions in analysis of clomipramine hydrochloride in the tablet.

Keywords- Clomipramine hydrochloride, Potentiometry, Ion-selective Electrode, PVC Membrane, Sensor, MWCNTs, Carbon Paste

1. INTRODUCTION

Clomipramine (CMIP), 3-(3-chloro-10,11-dihydro-5H-dibenzo[b,f]azepin-5-yl)-N,N-dimethylpropan-1-amine, with trade name of Anafranil, is a tricyclic antidepressant drug. It was developed in the 1960s by the Swiss drug manufacturer Geigy (now known as Novartis) and now it has been used in clinical worldwide ever since.

Clomipramine is used to treat people with obsessive-compulsive disorder. Clomipramine works by increasing the amount of serotonin, a natural substance in the brain that is needed to maintain mental balance.

Many analytical methods have been published for the determination of CMIP in biological fluids, and pharmaceutical formulations. Capillary gas chromatography [1], high performance liquid chromatography (HPLC) after solid phase extraction [2], double-radioisotope derivative technique [3], spectrofluorimetric method [4], high-performance liquid chromatography with on-line column-switching [5] and flow-injection analysis with acidic potassium permanganate–formic acid chemiluminescence detection [6] have been reported for clomipramine determination.

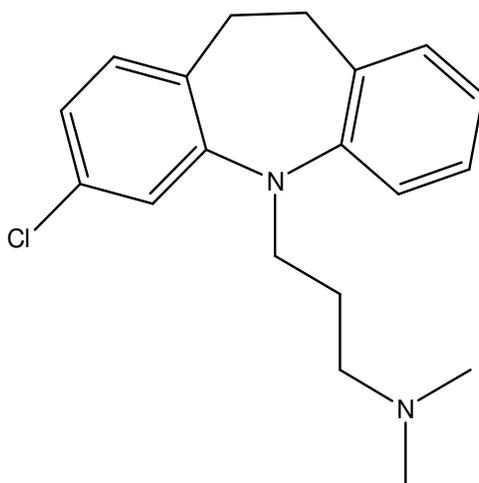


Fig. 1. Chemical structure of clomipramine

However, in this work we decide to introduce new electrochemical sensors for determination of CMIP in pharmaceutical formulations. These devices can be used alone in pharmaceutical matrix or in combination with other separation methods for determination of this drug in the complex matrixes. Like other potentiometric electrodes which have found wide applications in different fields [7-13], they offer advantages of low cost of analysis, high precision and rapidity, wide concentrations range of measurement, portability, and simplicity.

Both constructed electrodes reported here, respond according to the ion-exchange mechanism. CMIP hydrochloride and sodium tetraphenyl borate were used in synthesis of the ion-pair complex which acts as a sensing element in the both sensors.

2. EXPERIMENTAL PART

2.1. Reagents

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), tetrahydrofuran (THF) and ionic liquid (1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF₄) (Merck Co., Germany). 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). Clomipramine hydrochloride and its pharmaceutical formulations were obtained from a local pharmaceutical manufacturer (Tehran, Iran) as gift samples.

2.2. Apparatus

An Ag/AgCl electrode (Azar electrode, Iran) as a reference electrode and CMIP sensor as an indicator electrodes were connected to a mili-voltmeter (± 0.1).

The following cell assembly was used for the electromotive force (EMF) measurements:

In PVC membrane electrode:

Ag/AgCl–KCl (satd.) || internal filling solution of CMIP-HCl ($1.0 \times 10^{-3} \text{ mol L}^{-1}$)
| PVC membrane | CMIP-HCl sample solution || Ag/AgCl–KCl (satd).

In nano-composite electrode:

Modified carbon paste surface | CMIP-HCl sample solution || Ag/AgCl–KCl (satd).

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

2.3. Ion-pair complex preparation

The ion-pair complex used in construction of both sensors as a sensing material was made from the interaction of clomipramine hydrochloride and sodium tetraphenyl borate. It was synthesized by mixing about 20 mL of 0.01 mol L^{-1} CMIP-HCl 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 [12, 13].

2.4. Preparation of the sensors

2.4.1. General procedure to prepare PVC membrane

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. Then, THF was evaporated slowly until an oily concentrated solution 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} mol L⁻¹ of CMIP hydrochloride). The electrode was finally conditioned for 20 h by soaking in the same solution [11-13].

2.4.2. Carbon paste electrode preparation

Various amounts of ion-pair along with appropriate amount of graphite powder, MWCNTs, binder (ionic liquid or paraffin oil) were mixed well. After homogenization of the mixture, the paste was moved 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 CMIP hydrochloride solution [14-16].

2.5. Standard CMIP-HCl solutions

A stock solution of 0.01 mol L⁻¹ CMIP hydrochloride 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

CMIP-TPB ion-pair complex was synthesized and used as a sensing element in the composition of both PVC membrane and modified carbon paste electrodes. Ion-exchanging is the mechanism of the potential response. In both kinds of sensor, the used compositions have an important effect on the sensors responses. Every constituent plays a particular function in the electrode response. Thus, the type and amount of the component of the membrane and the paste was modified and optimized. The results have been given in Table 1 and 2.

3.1. PVC Membrane composition optimization

Previous studies showed that the membrane having a plasticizer/PVC ratio about 2.2 can show the best performance [7-13]. The optimum amount of PVC was selected 30 mg. Selectivity of the electrode based on ion-exchange mechanism, can be drastically influenced by the type of the plasticizer used. Plasticizer or solvent mediator allows a homogeneous dissolution and diffusional mobility of the ion-pair in the membrane phase.

Table 1. Optimization of PVC membrane components of the electrode

| No. | Composition (%) | | | Slope (mV decade ⁻¹) | LR (mol L ⁻¹) | R ² | Response time |
|-----|-----------------|-------------|----------|-------------------------------------|--|----------------|---------------|
| | PVC | Plasticizer | CMIP-TPB | | | | |
| 1 | 30 | DBP, 67 | 3 | 18.5±0.8 | 5.0×10 ⁻⁴ -5.0×10 ⁻³ | 0.900 | 74 s |
| 2 | 30 | DBP, 65 | 5 | 39.4±0.6 | 5.0×10 ⁻⁴ -5.0×10 ⁻³ | 0.965 | 58 s |
| 3 | 30 | DBP, 63 | 7 | 58.2±0.5 | 1.0×10 ⁻⁴ -1.0×10 ⁻² | 0.996 | 25 s |
| 4 | 30 | DBP, 61 | 9 | 57.1±0.6 | 1.0×10 ⁻⁴ -1.0×10 ⁻² | 0.992 | 31 s |
| 5 | 30 | NB, 63 | 7 | 17.8±0.6 | 5.0×10 ⁻⁴ -5.0×10 ⁻³ | 0.890 | 69 s |
| 6 | 30 | BA, 63 | 7 | 27.9±0.5 | 1.0×10 ⁻⁴ -1.0×10 ⁻² | 0.967 | 61 s |
| 7 | 30 | DBP, 70 | 0 | 2.9±0.8 | 5.0×10 ⁻³ -1.0×10 ⁻³ | 0.803 | 4 min |

Nature of the plasticizer affect on analytical responses such as slope, linear range and selectivity of PVC membrane electrodes. 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). The sensor responses showed that the membrane with DBP respond better. DBP among the used plasticizers provided an effective linear range and a lower detection limit due to the better extraction of clomipramine ions in the organic phase of the membrane. As it can be seen from Table 1, lack of ion-pair in the membrane components causes a very poor response (membrane no. 7), which confirm significance of the ion-pair. The electrodes behavior show that the best Nernstian slope is 58.2±0.5 mV per decade. Finally, membrane no. 3 with the composition of 30% PVC, 7% ion-pair, and 63% DBP was selected as the optimum one for the sensor design.

3.2. Carbon Paste Composition

Carbon paste electrodes (CPEs) are another category of potentiometric sensors which are mechanically strong. They have attracted more attention than membrane electrodes because of their advantages such as improved renewability, low ohmic resistance, more stable response, and no need to internal filling solutions. Three kinds of carbon paste electrode, unmodified, modified with MWCNTs and modified with ionic liquid carbon paste electrodes with different compositions were prepared and their potential responses were studied.

The carbon paste electrode composed of 20% paraffin oil, 20% CMIP-TPB, and 60% graphite powder (no. 4) was found to be optimal for unmodified or normal clomipramine hydrochloride electrode. This composition was selected for further examination. Then, the past was modified by ionic liquid instead of paraffin oil. ILs are a good choice as binders in

carbon paste electrodes due to their chemical stability, low vapor pressure, low toxicity, low melting temperature, high ionic conductivity and good electrochemical and thermal stability.

Table 2. Optimization of nano-composite carbon paste sensor ingredients

| No. | Composition (%) | | | | Slope (mV decade ⁻¹) | LR (mol L ⁻¹) | Response time | R ² |
|-----|-----------------|-------------|----------|--------|-------------------------------------|--|------------------|----------------|
| | Graphite | Binder | CMIP-TPB | MWCNTs | | | | |
| 1 | 80 | 20-Paraffin | - | - | - | - | - | - |
| 2 | 65 | 20-Paraffin | 15 | - | 19.3±0.7 | 5.0×10 ⁻⁴ -5.0×10 ⁻³ | 2 min | 0.905 |
| 3 | 60 | 20-Paraffin | 20 | - | 33.7±0.7 | 5.0×10 ⁻⁴ -5.0×10 ⁻³ | 58 s | 0.933 |
| 4 | 55 | 20-Paraffin | 25 | - | 47.6±0.6 | 1.0×10 ⁻⁵ -5.0×10 ⁻³ | 39 s | 0.942 |
| 5 | 50 | 20-Paraffin | 30 | - | 45.3±0.6 | 5.0×10 ⁻⁵ -5.0×10 ⁻³ | 40 s | 0.938 |
| 6 | 55 | 20-IL | 25 | - | 52.7±0.5 | 1.0×10 ⁻⁵ -1.0×10 ⁻² | 26 s | 0.954 |
| 7 | 50 | 25-IL | 25 | - | 54.5±0.4 | 1.0×10 ⁻⁵ -1.0×10 ⁻² | 24 s | 0.977 |
| 8 | 45 | 30-IL | 25 | - | 54.9±0.5 | 1.0×10 ⁻⁵ -1.0×10 ⁻² | 37 s | 0.964 |
| 9 | 47 | 25-IL | 25 | 3 | 55.7±0.3 | 1.0×10 ⁻⁵ -1.0×10 ⁻² | 22 s | 0.990 |
| 10 | 45 | 25-IL | 25 | 5 | 58.5±0.3 | 1.0×10 ⁻⁵ -1.0×10 ⁻² | 20 s | 0.997 |
| 11 | 43 | 25-IL | 25 | 7 | 57.8±0.5 | 1.0×10 ⁻⁵ -1.0×10 ⁻² | 27 s | 0.983 |
| 12 | 70 | 25-IL | - | 5 | 4.7±0.8 | 5.0×10 ⁻⁴ -1.0×10 ⁻³ | 4 min | 0.888 |

The third modification was done by using 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. 10). 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 too low (slope of 4.7±0.8 mV per decade). Finally, the best sensor response in was obtained by the paste composition of 25% ion-pair, 5% MWCNTs, 25% ionic liquid and 45% graphite powder.

3.3. Characterization of the PVC membrane sensor

The proposed PVC membrane sensor calibration curve has been shown in Fig. 2. According to this figure, the measuring range of the sensor which is the linear part of the calibration curve is in the range of 1.0×10⁻⁴-1.0×10⁻² mol L⁻¹. Detection limit was

calculated from the intersection of two extrapolated segments of the calibration graph. Detection limit of the PVC membrane sensor was calculated $8.5 \times 10^{-5} \text{ mol L}^{-1}$. Slope of the calibration curve is 58.2 mV per decade of the clomipramine hydrochloride concentration and a standard deviation of $\pm 0.5 \text{ mV}$ after five replicate measurements.

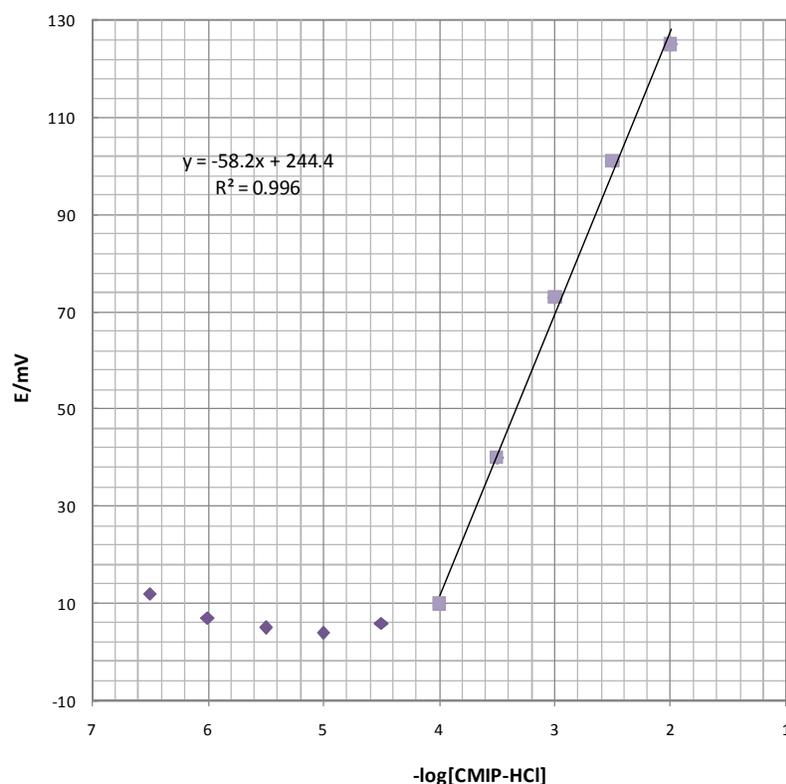


Fig. 2. Calibration curves of CMIP-HCl PVC membrane electrode (no. 3). The results are based on 5 replicate measurements

Dynamic response time which is the necessary time for the sensor to reach the values within $\pm 1 \text{ mV}$ of the final equilibrium potential, after successive immersions in the sample solutions [17-23]. It is obtained by variation and the recording of the clomipramine hydrochloride concentration in a series of the solutions from 1.0×10^{-5} to $1.0 \times 10^{-2} \text{ mol L}^{-1}$. The PVC membrane sensors were able to quickly reach its equilibrium response, about 25 s, in the whole concentration range. The sensor lifetime was estimated considering the calibration curve slope and detection limit periodically. Four same sensors were employed 1 h. per day for 10 weeks. After 5 weeks of utilization, a slight gradual decrease in the slope and an increase in the detection limit were observed. After several time of usage, the membrane ingredients leak from the organic layer of the membrane into the solution and affect the membrane response.

3.4 .Characterization of the nano-composite carbon paste sensor

The proposed nano-composite carbon paste sensor calibration curve has been shown in Fig. 3. Linear measuring range of this sensor is in the range of 1.0×10^{-5} - 1.0×10^{-2} mol L⁻¹. Detection limit was calculated 1.0×10^{-5} mol L⁻¹. Nernstian slope of the calibration curve is 58.5 mV per decade of the clomipramine hydrochloride concentration and a standard deviation of ± 0.3 mV after five replicate measurements.

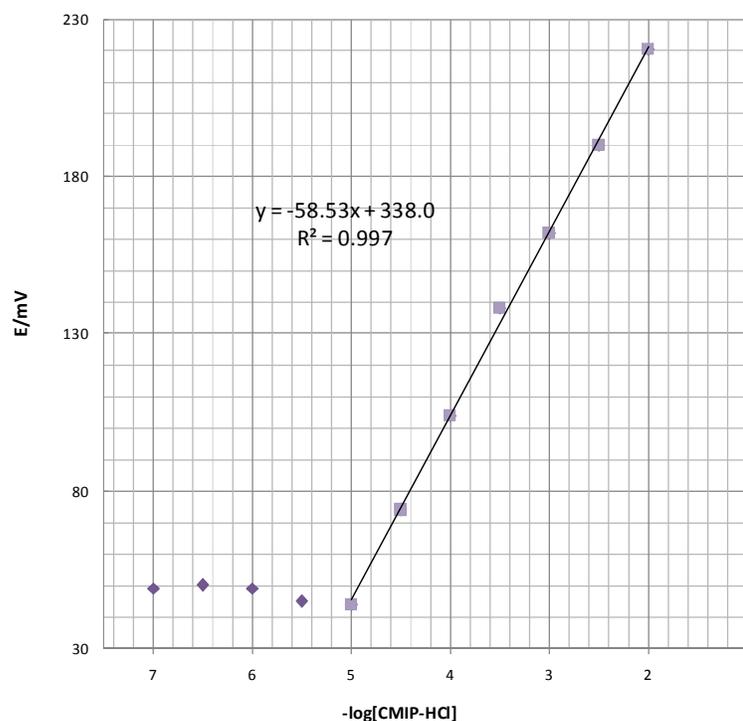


Fig. 3. Calibration curves of CMIP-HCl nano-composite electrode (no. 10) .The results are based on 5 replicate measurements

Dynamic response time of nano-composite carbon paste electrode, after successive immersions in the standard solutions from 1.0×10^{-5} to 1.0×10^{-2} mol L⁻¹, is obtained about 20 s. The nano-composite carbon paste sensor lifetime was estimated considering the calibration curve slope and detection limit periodically as mentioned for PVC membrane sensor. After 8 weeks of use, a decrease in the Nernstian slope and an increase in the detection limit were observed. In comparison with PVC membrane electrode this time is more because in CPEs the surface of the sensor can be renew and thus it can be used for longer time.

3.5. pH Effect on the sensors response

Fig. 4. shows the effect of pH on the sensors responses. To examine the effect of pH on the electrode responses, the potential was measured at specific concentration of the clomipramine hydrochloride solution ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) 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 3.0 to 6.5, 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 6.5 might be justified by removing the positive charge on the drug molecule. Fluctuations below the pH value of 3.0 were caused by removal of the membrane ingredients or analyte in the solution. In both electrodes the same trend were observed.

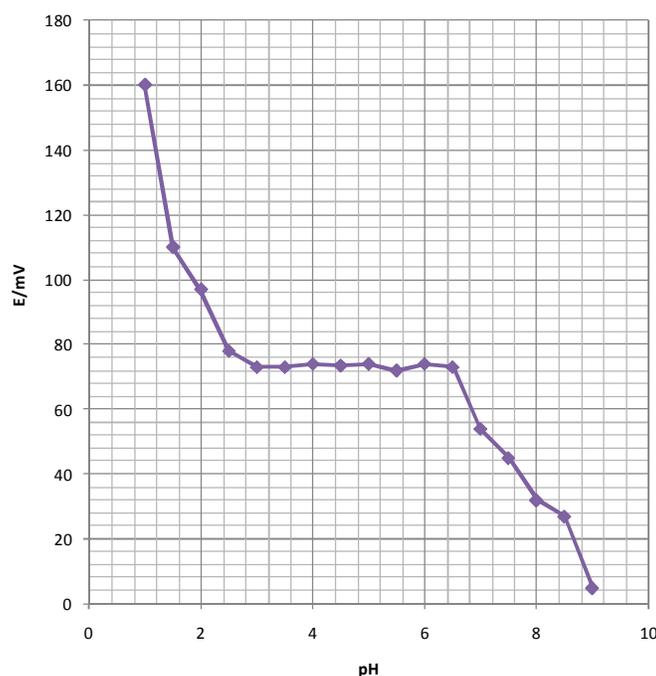


Fig. 4. Applicable pH of the electrodes in the test solution of $1.0 \times 10^{-3} \text{ mol L}^{-1}$

3.6. Selectivity

Selectivity, sensor specificity toward the target ion in the presence of interfering ions, is the most important factor for the analytical applications. The potentiometric selectivity coefficients of the clomipramine hydrochloride electrode were calculated by the matched potential method (MPM) [24-25]. In this method, a specified concentration of the primary ion

(A) is added to a reference solution and the potential is measured. In a separate experiment, interfering ions (B) are successively added to an identical reference solution, until the measured potential matches the one obtained before the primary ions addition. The matched potential method selectivity coefficient is then given by the resulting primary ion to the interfering in concentration ratio. The resulting values of the selectivity coefficients are shown in Table 3. The selectivity coefficients shows that the interferences from other species is negligible in the performance of the both sensors.

Table 3. Selectivity coefficients of various interfering compounds for clomipramine hydrochloride sensors

| Interfering ion | Log K_{MPM} (PVC membrane sensor) | Log K_{MPM} (Nano-composite CPE) |
|------------------------------|--|---------------------------------------|
| Na ⁺ | -3.7 | -3.5 |
| K ⁺ | -3.3 | -3.2 |
| NH ₄ ⁺ | -2.6 | -2.8 |
| Ca ²⁺ | -3.7 | -3.9 |
| Mg ²⁺ | -3.7 | -3.9 |
| Lactose | -4.0 | -4.3 |
| Glucose | -4.1 | -4.3 |

Table 4. Potentiometric determination of clomipramine hydrochloride in pharmaceutical formulations

| Sample | Found by PVC membrane electrode* | Found by Nano-composite CPE* |
|----------------------------|-------------------------------------|---------------------------------|
| CLOMIPRAMINE HCL 25MG TAB | 27.64±1.03 mg/Tab | 26.66±0.96 mg/Tab |
| CLOMIPRAMINE HCL 50MG TAB | 53.76±1.64 mg/Tab | 52.83±2.04 mg/Tab |
| CLOMIPRAMINE HCL 100MG TAB | 110.20±2.06 mg/Tab | 107.78±1.99 mg/Tab |

*The results are based on five replicate measurements

3.7. Analysis of clomipramine in pharmaceutical formulation

The proposed sensor was evaluated by measuring the clomipramine content of some pharmaceutical formulations (Table 4). The drug concentration of different tables was determined using calibration method with direct potentiometry. The results are in satisfactory agreement with the labeled amounts.

3.8. Precision, accuracy, and ruggedness/robustness

3 standard samples were analyzed for repeatability study. The RSD values by PVC membrane were 3.7, 3.9, and 3.6% and for nano-composite CPE were 3.5, 3.3, and 3.7%.

For ruggedness of the methods a comparison was performed between the intra- and inter-day assay results for clomipramine 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 two analysts did not exceed 4.8%. On the other hand, the robustness was examined while the parameter values (pH of the solution and the laboratory temperature) changed slightly. Clomipramine 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 clomipramine hydrochloride. The sensors showed advanced performances with a fast response time, a lower detection limit of $8.5 \times 10^{-5} \text{ mol L}^{-1}$ for PVC membrane electrodes and of $1.0 \times 10^{-5} \text{ mol L}^{-1}$ for nano-composite electrode across the range of 1.0×10^{-4} – $1.0 \times 10^{-2} \text{ mol L}^{-1}$ and 1.0×10^{-5} – $1.0 \times 10^{-2} \text{ mol L}^{-1}$, respectively. The sensors enabled the clomipramine hydrochloride determination in some 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, 63% DBP and 7% ion-pair complex. Then, a carbon paste electrode was designed to improve the analytical responses. The best electrode was composed of 25% ion-pair, 25% IL, 5% MWCNTs and 45% graphite powder.

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