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Full Paper

PVC Membrane Sensors for Potentiometric Determination of Metoclopramide in Pharmaceutical Preparations and in presence of its Degradate

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Abstract- Two novel polymeric membrane sensors were developed for determination of Metoclopramide (MCP), based on the use of metoclopramide-barbiturate (MCP-B) and metoclopramide-flavinate (MCP-F) ion pairs as electroactive materials in PVC matrix, in presence of *o*-nitrophenyloctylether (*o*-NPOE) as a solvent mediator, in plasticized PVC membranes. The suggested two-sensors show a near-Nernstian response for MCP over a wide concentration range of 1×10^{-5}-1×10^{-2} M. The proposed sensors have a fast response time and can be used for more than 4 weeks without any considerable divergence in potentials. They exhibit comparatively good selectivity with respect to related substances, dosage forms additives, acidic-degradates, alkaline earth and some transition and heavy metal ions.

Keywords- Metoclopramide, Barbiturate, Flavinate, Potentiometry

1. INTRODUCTION

Metoclopramide (MCP), 4-Amino-5-chloro-N-(2-diethylaminoethyl)-2-methoxy benzamide is a dopamine-receptor antagonist active for gastrointestinal motility [1]. It is a white or almost white crystalline powder and it is odorless. At 25 °C, 1 g MCP is soluble in 0.7 g of water, 3 g of ethanol (96%) and 55 g of chloroform, though it is practically insoluble

in ether. It is soluble in dilute hydrochloric acid. It shows two ionization constants; pK_1=0.42 and pK_2=9.71 [2]. It is used as an anti-emetic in the treatment of some forms of nausea and vomiting and to increase the gastrointestinal motility. MCP is of little benefit in the prevention or treatment of motion sickness or in the treatment of nausea and vertigo due to Ménière's disease or other labyrinth disturbances. Also it is used in higher doses for the prevention of cancer chemotherapy-induced emesis [1-3].

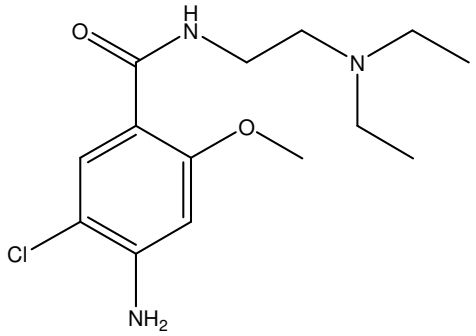

Fig. 1. Chemical Structure of Metoclopramide

Many analytical methods have been developed for analysis of metoclopramide hydrochloride in both clinical and experimental medicine which has promoted extensive interest in its determination. Current analytical methods employed for the determination of MCP can involve potentiometry [4-12], fluorimetry [13], spectrometry [14-22], chromatography [23-28], capillary electrophoresis [29,30], differential scanning calorimetry (DSC) and X-ray diffraction [31], gas chromatography-mass spectrometry (GC-MS) [32], voltammetry [33], fast stripping continuous cyclic voltammetry [34], square wave anodic stripping voltammetry [35], ^{1}H-NMR [36], chemiluminescence [37-38] and electrochemiluminesce [39].

Recently, Miao Yan et al. [40] developed a LC-MS application for determination of MCP in human plasma as bioequivalence studies, also Attia et al. [41] determined MCP in pharmaceutical preparations and serum samples using Eu^{3+} ion doped in sol-gel matrix.

Most of the mentioned methods are complicated and need sophisticated instruments; also the chromatographic method is costly and time-consuming, limiting its application. Other methods often are typically less sensitive or have their own intrinsic disadvantages such as technical complexity or require expensive instrumentation. The present work establishes a new simple, accurate, rapid and reproducible technique for determination of MCP, by construction and electrochemical evaluation of novel potentiometric sensors. These sensors incorporate the ion association complexes of MCP cation with barbiturate and flavinate as counter anions in a plasticized polyvinyl chloride (PVC) matrix. The metoclopramide-barbiturate (MCP-B) and metoclopramide-flavinate (MCP-F) ion-pair association PVC

sensors have fast response and near-Nernstian slopes. These sensors have been successfully applied for the determination of MCP in simple and complex matrices. In comparison with other techniques, Table 1, the suggested procedures are simple, relatively free from interference with coexisting substances and can be applied to the determination of the drug MCP in pharmaceutical preparations and in presence of its degradates with satisfactory results.

Table 1. Comparison of the adopted potentiometric technique with some existing methods for determination of MCP

Method	Linear range	Detection limit	Reference
PVC matrix membrane sensor for potentiometric determination of MCP HCl	1×10^{-2} - 6×10^{-5} mol L^{-1}	4×10^{-5} mol L^{-1}	[10]
Spectrophotometric method	5-25 µg mL^{-1}	0.5 µg mL^{-1}	[18]
Flow injection spectrophotometric determination of MCP HCl	0.5-85 mg mL^{-1}	0.05 µg mL^{-1}	[19]
Square wave anodic stripping voltammetric determination of MCP HCl	0.067-0.269 ng mL^{-1}	0.06 ng mL^{-1}	[34]
Chemiluminescent determination of MCP HCl	0.005-3.5 µg mL^{-1}	1.0 ng mL^{-1}	[38]
Optical sensor Eu^{3+} doped in sol-gel	5×10^{-9} - 1×10^{-6} mol L^{-1}	2.2×10^{-11} mol L^{-1}	[41]
High performance liquid chromatography	1-10 µg mL^{-1}	0.5 µg mL^{-1}	[42]
Novel PVC Membrane Sensors for potentiometric determination of MCP HCl	1×10^{-5}-1×10^{-3} mol L^{-1}	1×10^{-5} mol L^{-1}	Present work

2. EXPERIMENTAL

2.1. Chemicals and reagents

Metoclopramide was kindly supplied by Sanofi-aventis Egypt and certified to contain 99.99%. Primperan® tablet, ampoule and syrup with batch number 19E13, 19E38/C, and 18E06, respectively manufactured by Sanofi Aventis Company. Each tablet and ampoule was

labeled to contain 10 mg of metoclopramide hydrochloride and each 5 ml of syrup was labeled to contain 5 mg of metoclopramide hydrochloride.

2-nitrophenyloctyl ether (*o*-NPOE), tetrahydrofuran (THF), bi-distilled water (Riedel-dehaen, Sigma-Aldrich, Germany), Polyvinyl chloride powder (PVC) (Fluka), Flavinic acid and sodium barbiturate [Sigma Chem. Co. (St. Louis, MO., USA)].

All chemical and reagents used through this work are of analytical grade. Bi-distilled water is used throughout the whole work and is indicated by the word "water".

2.2. Instruments

All potentiometric measurements were made with an Orion (Model 720) pH / mV meter, in conjunction with single junction Ag/AgCl reference electrode, Orion electrode (Model 90-01) filled with 10% (w/v) potassium chloride and the proposed metoclopramide PVC membrane sensor at ambient temperature. Combination glass electrode, a Ross pH electrode (Orion Model 81-02) was used for all pH measurements.

2.3. Standard Solutions

2.3.1. Standard solutions of metoclopramide

Stock standard solution of MCP having a concentration of 1×10^{-2} M was prepared and it was further diluted with 0.01 M acetate buffer (pH 5) to produce working standard solutions with the concentration range of 1×10^{-2} -1×10^{-6} M.

2.3.2. Standard solutions of metoclopramide acidic-degradate

Stock standard solution of metoclopramide acidic-degradate was prepared by refluxing 0.0299 gm of MCP with 10.0 ml of 0.1 M HCl for 8 h at 100 ˚C followed by cooling, neutralizing the media with 0.1 M NaOH and completing to 100 ml final volume with 0.01 M acetate buffer (pH 5). Working standard solutions were prepared by appropriate dilution with 0.01 M acetate buffer (pH 5) to obtain a concentration range of 1×10^{-2}-1×10^{-6} M.
Complete degradation was checked by using TLC system; silica gel 60 F_{254} plates and chloroform: methanol (80: 20, v/v) was used as a developing system [2].

2.4. Preparation of metoclopramide membrane electrodes

Metoclopramide barbiturate and metoclopramide flavinate ion–pair complexes were prepared by slow addition of 20 ml of 1×10^{-2} M solution of sodium barbiturate, and flavinic acid reagents, respectively to 20 ml aliquots of 1×10^{-2} M aqueous metoclopramide hydrochloride solution. The mixtures were stirred for 10 min, filtered on whatmann filter

paper no., 42, washed with bi-distilled water, dried at room temperature and ground to fine powder. Elemental analysis revealed the formation of 1:1 ion-pair complexes. Three mg portion of metoclopramide ion-pair complex was thoroughly mixed in a glass Petri dish (5-cm diameter) with 0.198 ml of 2-nitrophenyloctyl ether (o-NPOE) and 99 mg of polyvinyl chloride (PVC). The mixture was dissolved in a 4 ml of tetrahydrofuran (THF). The Petri-dish was covered, and left to stand overnight to allow slow evaporation of the solvent at room temperature. A master PVC membrane (0.1 mm thickness) was obtained.

The PVC master membranes were sectioned with a cork porer (10 mm diameter) and glued to a polyethylene tubing (2-cm length, 8 mm i.d) using THF. A homemade electrode body was used, which consisted of a glass tube, to which the polyethylene tubing was attached to one end and filled with the internal reference solution (equal volumes of 1×10^{-2} M aqueous metoclopramide and 1×10^{-2} M KCl). An Ag/AgCl internal reference wire electrode (1.0 mm diameter) was immersed in the internal solution.

The electrodes were conditioned by soaking the prepared electrode in 1×10^{-2} M MCP solution for 2h and stored in the same solution when not in use [11].

2.5. Sensor Calibration

Aliquots (10ml) of 1×10^{-2}-1×10^{-6} M aqueous metoclopramide in 0.01 M acetate buffer of pH 5 were transferred into 50 ml beakers. The metoclopramide PVC membrane sensor (indicator electrode) together with the single junction Ag/AgCl reference electrode were immersed in the MCP solution. The solution was stirred and the potential reading was recorded after stabilization to ±0.3 mV. The electromotive force (e.m.f.) was plotted as a function of log (metoclopramide concentration). The calibration plot was used for measuring samples of unknown concentration under the same conditions.

2.6. Determination of metoclopramide in pharmaceutical preparations

Twenty tablets were accurately weighed and finely powdered. A portion of powder equivalent to one tablet of MCP was accurately weighed, transferred to 100 ml volumetric flask, dissolved and shaked for 15 minutes with 50 ml of 0.05 M acetate buffer of pH 5. The solution was then completed to the mark. Three milliliters aliquot were transferred to a 100 ml calibration flask and diluted to the mark with 0.05 M acetate buffer of pH 5. Also, the content of twelve MCP ampoules was mixed and a volume equivalent to one ampoule of MCP was transferred into 100 ml calibrated flask and completed to the mark with acetate buffer pH 5. Finally, twenty milliliters of MCP syrup-solution was transferred into 100 ml measuring flask and complete to the mark with acetate buffer pH 5.

The e.m.f of the solution was measured as described above and the corresponding concentration was determined using the calibration plot.

3. RESULTS AND DISCUSSION

The present work exhibits new membrane sensors, metoclopramide-barbiturate (MCP-B) and metoclopramide-flavinate (MCP-F), in which PVC was used as polymeric matrix. The used sensors exhibit a good selectivity with respect to related substances, additives in dosage forms, acidic-degradates alkaline earth and some transition and heavy metal. The conventional design are prepared, characterized and compared according to IUPAC recommendations [43].

3.1. Membrane composition and potentiometric response

Metoclopramide cation reacts readily with barbiturate or flavianate anion to form 1:1 ion-pair complexes as confirmed by IR spectrometry and elemental analysis of the solid reaction products. Suitability and sensitivity of membranes, based on these ion-pair complexes as electroactive compounds were examined. The best membrane composition for sensors based on metoclopramide–barbiturate and metoclopramide-flavianate are 2: 64: 34 weight % for ion–pair complex, plasticizer and PVC, respectively. The plasticizer *o*-NPOE proved to be a suitable plasticizer. Typical response curves of the two MCP membrane sensors are shown in Fig. 2. Table 2 summarizes the response characteristics of the metoclopramide membrane sensors, from data collected over a period of 3 months for 5 different membrane sensors of each type. Calibration plots obtained with MCP at pH 5 using both MCP membrane sensors show near Nernstian slope of 52.4 and 53.2 mV/concentration decade over the concentration range 1×10^{-5}-1×10^{-2} M for metoclopramide-barbiturate and metoclopramide-flavianate, respectively. The two sensors displayed good stability at ambient temperature, potential reproducibility and good selectivity.

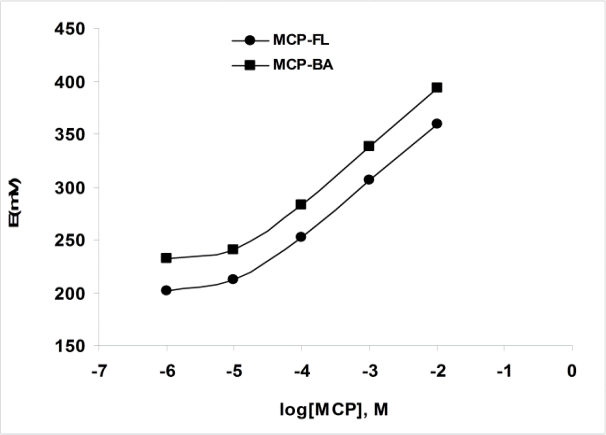

Fig. 2. Potentiometric response of metoclopramide PVC membrane based sensors

Table 2. Response characteristics of PVC metoclopramide membrane electrode system

Parameter [a]	MCP-FL	MCP-BA
Slope, mV/decade	53.2	52.4
Correlation coefficient (r)	0.998	0.997
Lower limit of linear range (M)	5×10^{-5}	5×10^{-5}
Lower limit of detection (M)	1×10^{-5}	1×10^{-5}
Response time for 10^{-3} M (s)	25±2	25±2
Life span (week)	4	4
Working pH range	3-7	3-7

[a] average of five measurements

3.2. Response time

The sensors showed rapid response within 25 seconds for drug solutions $\geq 1\times10^{-3}$ M and 45 seconds for 1×10^{-4} M. The lifetime of the sensors were examined by repeated calibration every 2 days. Over a period of 30 days there was no noticeable deterioration in the sensor performance in terms of detection limit, calibration curve slope and response time.

3.3. Effect of pH

The effect of pH on the potential readings of the two electrode systems was studied by immersing the Ross combination glass electrode, PVC based MCP sensors and a single junction Ag/AgCl reference electrode in 100 ml beakers containing 30 ml aliquots of 1×10^{-3} and 1×10^{-4} M MCP aqueous solutions. The pH of each solution was gradually changed by adding small aliquots of dilute sodium hydroxide and/or hydrochloric acid solutions. The potential reading at each pH value was recorded. The mV-pH profile of each metoclopramide concentration was plotted for each electrode system.

The influence of pH of the test solution on the potential response of the membrane sensor was tested in the pH range 2-11 and the results are shown in Fig. 3, as can be seen, potentials remain constant from pH 3-7, beyond which the potential changes considerably. The potential did not vary over this range by more than ±2 mV.

Above pH 7 the displayed potentials decreased due to the formation of non-protonated form of MCP which results in a noisy and unbalanced response. Below pH 3, there is an increased solution acidity which could lead to extraction of H^+ by the membrane, thus leading to noisy responses.

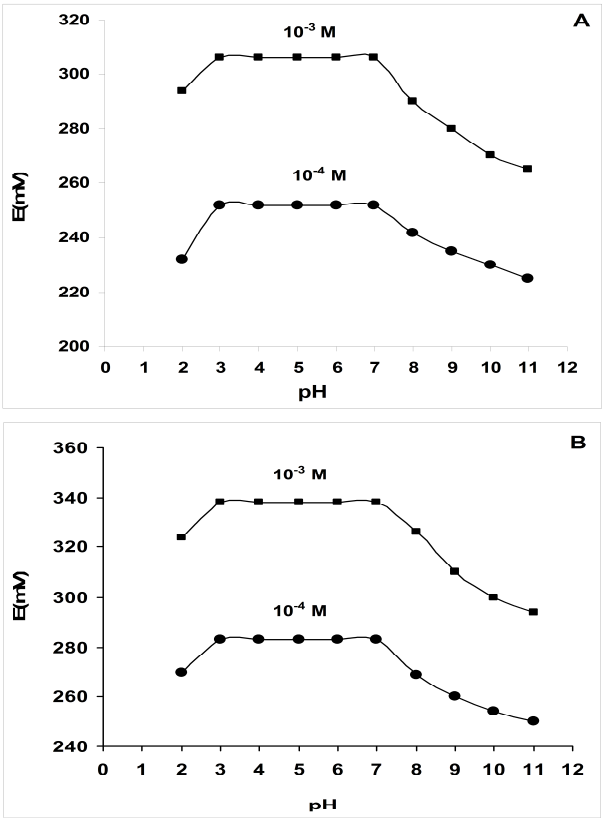

Fig. 3. Effect of pH on the potentiometric response of (A) MCP–FL and (B) MCP–BA PVC membrane based sensors

3.4. Sensor Selectivity

The potentiometric selectivity coefficients ($K^{Pot}_{MCP,I}$) of the metoclopramide sensors were measured by the separate solutions method [44]. In this method, the potentials of 1×10^{-3}M concentration of both MCP and the interfering species in 0.01 M acetate buffer of pH 5 were determined. The selectivity coefficients were calculated using the Eisenman-Nicolsky equation:

$$-\text{Log}\,(K^{Pot}_{MCP,I}) = (E_1-E_2) / S$$

where, E_1 and E_2 are the potential readings observed after 1 min of exposing the sensors to the same concentration of MCP and interferent in separate solutions, respectively, and S is the slope of the MCP calibration graph (mV/concentration decade).

The potentiometric selectivity coefficient of the metoclopramide based sensors depends on the selectivity of the ion-exchange process at the membrane-sample interface, the mobility of the respective ions in the membrane, and the hydrophobic interactions between the primary ions and the organic membrane. The free energy transfer of the MCP ions between the

aqueous and the organic phases could also control the selectivity of the proposed sensor. Thus, the potentiometric selectivity of 1×10^{-3} M MCP solution and 1×10^{-3} M of the foreign ion at pH 5 was critically investigated by the separate solution method. The influences of 24 different organic and in organic cations on the response of metoclopramide membranes were examined. The results obtained are summarized in Table 3. The proposed sensors exhibited a high selectivity towards metoclopramide with respect to the test ions.

Table 3. Potentiometric selectivity coefficients ($K^{Pot}_{MCP,B}$) for some common cation with metoclopramide-PVC membrane sensors

Interfering ion, B	$K^{Pot}_{MCP,B}$	
	MCP-FL	MCP-BA
Na^+	1.3×10^{-3}	1.4×10^{-3}
K^+	2.2×10^{-3}	2.3×10^{-3}
NH_4^+	8.2×10^{-3}	7.2×10^{-3}
Mg^{2+}	2.7×10^{-3}	3.1×10^{-3}
Cu^{2+}	5.6×10^{-3}	6.8×10^{-3}
Ni^{2+}	2.6×10^{-3}	2.8×10^{-3}
Fe^{2+}	6.8×10^{-3}	5.6×10^{-3}
Co^{2+}	3.6×10^{-3}	3.5×10^{-3}
Mn^{2+}	4.6×10^{-3}	3.8×10^{-2}
Vitamin C	6.8×10^{-2}	2.3×10^{-2}
Vitamin B_2	5.3×10^{-3}	1.4×10^{-3}
Glycine	5.4×10^{-3}	3.4×10^{-3}
Cysteine	4.7×10^{-3}	7.8×10^{-3}
Histidine	7.5×10^{-3}	5.3×10^{-3}
Tyrosine	3.3×10^{-3}	5.7×10^{-3}
p-aminophenol	1.1×10^{-3}	2.2×10^{-3}
p-aminobenzoate	6.6×10^{-2}	2.5×10^{-2}
Catecholate	7.8×10^{-2}	3.4×10^{-3}
Resorcinolate	5.8×10^{-3}	6.5×10^{-2}
Pyrogallate	2.8×10^{-2}	2.1×10^{-3}
p-Nitroaniline	1.1×10^{-3}	3.1×10^{-3}
Vit B6	3.9×10^{-3}	9.1×10^{-3}
Sorbitol	5.7×10^{-3}	1.2×10^{-2}
Paracetamol	5.5×10^{-3}	9.8×10^{-3}
Acidic-degradate	1.4×10^{-3}	1.1×10^{-3}

3.5. Determination of metoclopramide in pharmaceutical preparations

Metoclopramide in various drug formulations was determined by direct potentiometric measurements using both sensors. The potentials measured by these sensors were recorded and compared with the calibration graph. The obtained data were compared with that obtained using UV-VIS method [16] as can be seen from Table 4. The results revealed good agreement with the reference method.

Table 4. Determination of metoclopramide in pharmaceutical preparations by the proposed sensors

Pharmaceutical preparation	Accuracy, [a] %		
	MCP-FL	MCP-BA	UV-VIS [16]
Primperan® Tablets (10 mg)	99.3±0.4	101.3±0.6	97.5±1.0
Primperan® Syrup (5 mg/5ml)	99.5±0.9	102.6±0.8	98.6±0.7
Primperan® Injection (10 mg/ampoule)	103.3±0.8	99.1±0.7	96.2±0.8
F-Test	1.791 (6.388)[b]	3.947 (6.388)[b]	
Student's t-Test	1.684 (2.306)	2.117 (2.306)[b]	

[a]average of five measurements

[b]Figures in parenthesis are the corresponding theoretical values for F and t at the 95% confidence level

4. CONCLUSION

The proposed method is precise, specific and accurate one. Metoclopramide can be determined in bulk powder and in pharmaceutical preparations without interference from common excipients using the proposed sensors. The suggested potentiometric sensors are easy to fabricate and can easy and directly assay metoclopramide even in the presence of it's degradate. Thus, the suggested method can be applied for routine and quality control analysis.

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