Talanta 134 (2015) 546–553

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Surface morphology changes of polymer membrane and carbon paste sertraline sensors

M.M. Khater [1], H.B. Hassib [1], Y.M. Issa *,[1], S.H. Mohammed [1]

Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt

A R T I C L E I N F O

Article history:
Received 8 July 2014
Received in revised form
9 November 2014
Accepted 10 November 2014
Available online 27 November 2014

Keywords:
Sertraline HCl
Graphite
Tetraphenylborate
Membrane sensor
Carbon paste sensor
SEM

A B S T R A C T

Polymer membrane and chemically modified carbon paste (CMCP) sensors for determination of sertraline HCl (Ser-Cl) incorporating sertraline tetraphenylborate (Ser-TPB) as an electro-active material were constructed. They showed a rapid and linear response for Ser-ion over the concentration range 0.01–10.00 mmol L^{-1}. The limits of detection were 2.80 and 9.55 μmol L^{-1}, and Nernastian slopes were 56.60, 59.60 mV $decade^{-1}$ for membrane and CMCP sensors for batch method. In flow injection analysis (FIA), the electrodes revealed comparatively good selectivity for Ser-ion with regard to a wide variety of different cations, sugars, and amino acids. The addition of different anionic additives, namely sodium tetraphenylborate (NaTPB), potassium tetraphenylborate (KTPB), potassium tetrakis[3,5-bis-(triflouromethyl)phenyl]borate (KTFMPB), and sodium tetrakis[3,5-bis(trifluoro-methyl)phenyl]borate (NaTFMPB), to the prepared mixture improved their response characteristics. The surface morphologies of membrane films containing PVC only (blank), plasticizer+PVC, Ser-TPB+plasticizer+PVC, and Ser-TPB +plasticizer+PVC+additive were studied using scanning and atomic force electron microscopes. These sensors had been used in the potentiometric titration of Ser-ion against NaTPB. Standard addition method for the pure raw material and some of its pharmaceutical tablets was used for Ser-Cl determination. The obtained results were tested for their repeatability and reproducibility and were statistically treated by F- and t- tests.

1. Introduction

(1 S-cis)-4-(3,4-dichlorophenyl)-l,2,3,4-tetrahydro-N-methyl-l-naphthalenamine hydrochloride, known as Sertraline HCl (M. wt. 342.7 g mol^{-1}), is a white crystalline powder that is slightly soluble in water and isopropyl alcohol and sparingly soluble in ethanol. It is widely used as an antidepressant and belongs to the selective serotonin reuptake inhibitor class. It is used in the treatment of major depression, obsessive compulsive and panic disorders as well as for eating, premenstrual dysphoric, and post-traumatic stress disorders.

Several methods have been published for the determination of sertraline in pharmaceutical and biological materials. Potentiometric chemo sensors for selective determination of sertraline based on the molecular imprinting technique and electrometric methods using voltammetric technique were developed [1–3]. Several spectroscopic methods have been reported for the determination of Ser^+ and their metabolites in pharmaceutical formulation [4–6]. Different HPLC methods were reported for the drug. Different methods used for the determination of the drug till the year 2008 were collected in a review [7].

Ion-selective sensors have been used for analytical determination of a wide variety of pharmaceutical compounds [8–10]. They have replaced other analytical methods due to their utility and simplicity. FIA, a widespread method, is characterized by its versatility, high sampling frequency, and minimum sample treatment before injection into the system, reduced time of analysis, and low consumption of reagents compared with the manual procedure [11]. Characterization of a surface of different solids is often of vital importance in a number of fields, including heterogeneous catalysis, semiconductor thin-film technology, corrosion and adhesion mechanisms, activity of metal surfaces, embrittlement properties, and studies of the behavior and functions of biological membranes. The surface of a solid is considered a part of the solid that differs in composition from the average structure of its bulk [12].

The aim of this article is to study the surface morphologies of a new membrane sensor for the determination of sertraline HCl. Construction of CMCP sensor is another part in this work. Finally, these new sensors were applied in the potentiometric

---

* Corresponding author.
E-mail address: yousrymi@yahoo.com (Y.M. Issa).
[1] Tel.: +002 01005600793; fax: +0020235728843.

http://dx.doi.org/10.1016/j.talanta.2014.11.018
0039-9140/© 2014 Elsevier B.V. All rights reserved.

determination of the pure form and some of its pharmaceutical formulations using potentiometric titration, standard addition method, and FIA.

2. Materials and methods

2.1. Reagents

All reagents used were of chemically pure grade. Ser-Cl and Serlift® tablets (100 mg/tablet) were obtained from Global Napi Pharmaceuticals, Egypt. Moodapex® tablets (50 mg/tablet) were obtained from Multi-Apex phama-Badr City-Cairo, Egypt. Reagent-grade sodium tetraphenylborate (NaTPB) Na[$C_{24}H_{20}B$], potassium [3,5-bis-(triflouro-methyl)phenyl]borate (KTFMPB), sodium [3,5-bis (trifluoromethyl)phenyl]borate (NaTFMPB), Dibutyl phthalate (DBP), dioctyl phthalate (DOP), tricresyl phosphate (TCP), ethylhexyl adipate (EHA), orthonitrophenyl phenyl ether (o-NPPE), ethylhexyl sebacate (EHS), graphite powder, poly (vinyl chloride) (PVC) of high relative molecular weight, and tetrahydrofuran (THF) were obtained from Aldrich and used as received. Potassium tetraphenylborate (KTPB) used throughout the work was prepared by addition of 100 mL 10.0 mmol L^{-1} KCl to 100 mL 10.0 mmol L^{-1} NaTPB. Doubly distilled water was used throughout all experiments.

2.2. Apparatus

Potential was measured using a Jenway 3010 (Essex, England) digital pH/mV meter. Ag/AgCl/Sat. KCl electrode was used as the reference electrode. The pH of the sample solutions was monitored with Jenway pH glass electrode. The temperature control system used was Techne, FTU-20 DE, Temp. Unit, England.

A single-stream FIA manifold mentioned in our previous work [11] was used in this study. The carrier and reagent solutions were degassed by means of vacuum suction.

SEM and AFM investigations were carried out using JEOL JSM-6360LA, Philips XL30, and Shimadzu Wet-SPM Scanning Probe microscope, Japan, respectively, at the Micro Analytical Center, Faculty of Science, Cairo University.

2.3. Preparations

Sertraline-tetraphenylborate was prepared by addition of 100 mL 10.0 mmol L^{-1} Ser-Cl solution to 10.0 mmol L^{-1} NaTPB. After complete coagulation of the precipitate, it was filtered and thoroughly washed with distilled water, dried at room temperature, and ground to fine powder. Its chemical composition was confirmed by C, H, and N elemental analysis using an automatic CHN analyzer (Perkin-Elmer model 2400) in the Micro Analytical Center, Faculty of Science, Cairo University. The C, H, and N percentages are 74.48, 6.00, and 2.02% and the corresponding calculated ones are 74.27, 6.34, and 2.11%, respectively. The stoichiometric ratio of the ion pair was also determined using conductimetric titration, and it was found to be 1:1.

1–5% (w/w) Ser-TPB sensors were prepared. The required amount of high-molecular-weight PVC needed to make the membrane film was dissolved in 5 mL THF. The calculated amount of Ser-TPB was dissolved in THF and mixed with the PVC solution in a 5.0-cm-diameter Petri dish; then, the calculated plasticizer volume was added. The total constituent weight is fixed at 0.2 g. The membranes were left to dry freely in air for 24 h to obtain homogenous and uniform thickness. Next, 7.5-mm disks were punched from the cast films and mounted in a homemade glass sensor body. The sensors were filled with a solution that is 10.0 mmol L^{-1} KCl and 1.0 mmol L^{-1} drug solution and preconditioned by soaking in 5 mL 1.0 mmol L^{-1} of the drug solution. The electrochemical system is represented as follows: Ag/AgCl//inner solution/ membrane/ test solution// Ag/AgCl/Sat. KCl.

A 12-cm-long teflon holder with a hole at one end (7 mm diameter, 3.5 mm deep) for the carbon paste filling served as the sensor body. Electrical contact was made with a stainless steel rod through the center of the holder. The modified paste of each sensor was prepared by dissolving 1–5% Ser-TPB in the calculated amount of the plasticizer, and high-purity carbon (graphite powder) was added to the obtained mixture. The latter is used as a support and diluent for the active ingredients. Very intimate homogenization was then achieved by careful mixing with a glass rod in agate mortar and afterward rubbing by intensive pressing with a pestle. The ready-prepared paste was then packed into the hole of the electrode body. The electro-chemical system is represented as follows: CMCPS/test solution//Ag/AgCl/Sat. KCl.

2.4. Construction of calibration curves

Suitable increments of standard Ser-Cl solution were added to 50 mL doubly distilled water so as to cover the concentration range 1.0×10^{-4}-10.0 mmol L^{-1}. The sensor and the reference electrodes were immersed in the solution in batch measurements. After each addition, the emf value was recorded at 25 ± 1 °C, and the values were plotted versus the negative logarithmic value of Ser-Cl concentration (-log [Ser-Cl, mol L^{-1}]).

In FIA measurements, a solution of 1.0×10^{-3} mmol L^{-1} was injected to the flow stream to determine the optimum conditions (dispersion coefficient, the carrier composition, the injection volume, and the flow rate). The dispersion coefficients, D, were 1.5 and 1.4 for membrane and CMCP sensors, respectively. The effect of different sample injection volumes on the performance of the sensor response was assessed by using 19.0, 37.5, 75.0, 150.0, 340.0, and 500.0 µL of 1.0 mmol L^{-1} Ser-Cl standard solution. The sensor response was studied at different flow rates (5.35, 7.50, 9.70, 12.50, 17.85, 23.25, and 25.00 mL min^{-1}) using 1.0 mmol L^{-1} Ser-Cl solution. After optimization, a series of Ser-Cl solutions covering the range 1.0×10^{-3}-10.0 mmol L^{-1} was injected into the flow stream; the corresponding peak heights were recorded; and the calibration curve was constructed.

Table 1
Composition and slope of calibration curves for Ser-TPB membrane and CMCP sensors at 25.0 ± 1.0 °C, response time (t_{resp}) ≤ 6 s.

Sensor	Ser-TPB%	Plasticizer %	Slope (mV $decade^{-1}$)	Linear range (mmol L^{-1})	LOD (µmol L^{-1})
Membrane sensor					
1	1.00	49.50 TCP	55.05	0.01–10.00	1.47
2	2.00	49.00 TCP	56.20	0.01–10.00	1.49
3	3.00[a]	48.50 TCP	56.60	0.01–10.00	2.80
4	5.00	47.50 TCP	55.90	0.01–10.00	4.48
5	3.00	48.50 DOP	48.73	0.04–10.00	5.88
6	3.00	48.50 EHA	52.39	0.06–10.00	4.89
7	3.00	48.50 DBP	55.40	0.01–10.00	2.67
8	3.00	48.50 DNP	50.62	0.04–10.00	5.13
9	3.00	48.50 DOTP	50.77	0.04–10.00	5.24
CMCP sensor					
1	1.00	49.50 DBP	47.50	0.01–10.00	8.13
2	2.00	49.00 DBP	56.20	0.01–10.00	9.12
3	3.00[a]	48.50 DBP	59.60	0.01–10.00	9.55
4	5.00	47.50 DBP	58.60	0.01–10.00	9.77
5	3.00	48.50 DOP	34.70	0.02–10.00	2.42
6	3.00	48.50 EHA	31.6	0.04–10.00	4.50
7	3.00	48.50 TCP	58.60	0.03–10.00	25.00
8	1.00	49.50 DBP	47.50	0.01–10.00	8.13

Plasticizer: PVC or carbon is 1:1

[a] Selected composition