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Surface morphology changes of polymer membrane and carbon paste sertraline sensors

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ABSTRACT

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

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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

Effect of anionic additives on the performance characteristics of the sensors was examined by addition of variable percentages of different additives such as NaTPB, KTPB, NaTFMPB, and KTFMPB to the mixture of both membrane and CMCP sensors.

Effect of pH and temperature [13] and interfering ions on the sensor potential were also examined [13–17].

2.5. Surface characterization

To study the change in surface morphologies of the prepared membrane films in part 2.3, freshly prepared membranes containing PVC only (blank), (PVC+plasticizer), (PVC+plasticizer+Ser-TPB), and (PVC+plasticizer+ion-pair+additives) were prepared. The surface characterizations were carried out by SEM and AFM.

2.6. Potentiometric determination of the pure Ser-Cl

Potentiometric titrations were applied by transferring solutions containing 0.34–34.27 mg Ser-Cl into a 100- mL titration cell and diluting to 50 mL by doubly distilled water. The resulting solutions were titrated against 10 mmol L^{-1} NaTPB using the prepared sensor. The end points were determined from S-shape and the first derivative plots.

The standard addition technique was also applied [18] by adding known volumes of standard drug solution to a 50- mL solution containing different amounts of Ser-Cl.

Under the optimized conditions, 1.0 mmol L^{-1} standard Ser-Cl injected into FIA system and its peak height was measured. These measurements were repeated at least thrice, and the average height was calculated. The peak heights are compared with those obtained from injecting different concentrations of the pharmaceutical preparations under the same conditions, where the percentage recovery and RSD can be calculated.

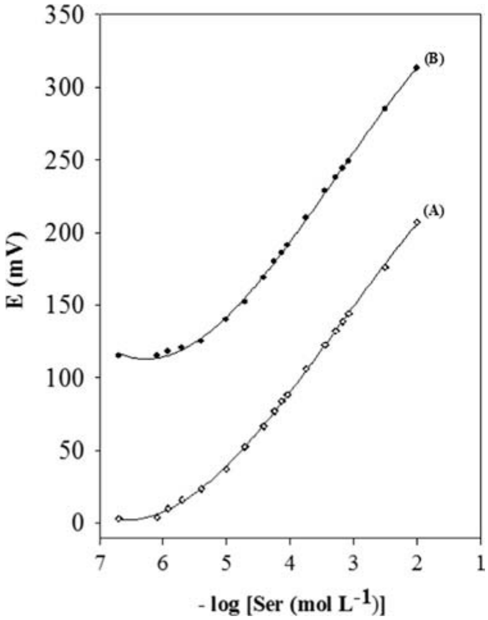

Fig. 1. The calibration plots for Ser-TPB membrane (A) and CMCP (B) sensors in batch analysis.

2.7. Analysis of tablets

10 Serlift® or Moodapex® tablets were weighed and ground to a fine powder; an appropriate weight from this powder was taken and dissolved in hot doubly distilled water. Then, the solution was filtered in a 50- mL measuring flask and completed to the mark. Different volumes of this solution were taken and analyzed as the pure Ser-Cl.

3. Results and discussion

3.1. Potentiometric behavior of Ser-TPB sensors

The potentiometric behavior of the prepared Ser-TPB sensors based on different compositions (1–5% w/w) is collected in Table 1. The sensor exhibited a nernastian response for Ser-ion over a wide concentration range (0.01–10.0 mmol L^{-1}) with a limit of detection 2.80 and 9.55 μmol L^{-1} for membrane and CMCP sensors, respectively. These poteniometric characteristics were reached on using 3.00, 48.50, and 48.50% Ser-TPB, PVC, or carbon and plasticizer (sensors 3 and 12, Table 1), respectively. Although some sensors have a lower detection limit compared with sensor 3, it is clear that the latter sensor is stable and gives repeatable results. In order to have a homogeneous mixture, the solvent mediator should be physically compatible with the ion pair used in the preparation of the sensor. In this work, several mediators were tested as potential plasticizers (Table 1). The membrane and CMCP sensor containing TCP and DBP were the appropriate selection with regard to high sensitivity and a wider concentration range (Fig. 1).

The pH dependence of the potentials of the investigated membrane and CMCP sensors was tested over the pH range 2.0–12.0 at three different Ser-Cl concentrations (0.1, 1.0, and 10.0 mmol L^{-1}). It can be seen from Fig. 2 that the potentials are fairly constant in the pH range 2.11–7.64 and 2.06–7.44 for membrane and CMCP sensors, respectively. The decrease in potential observed at higher pH values

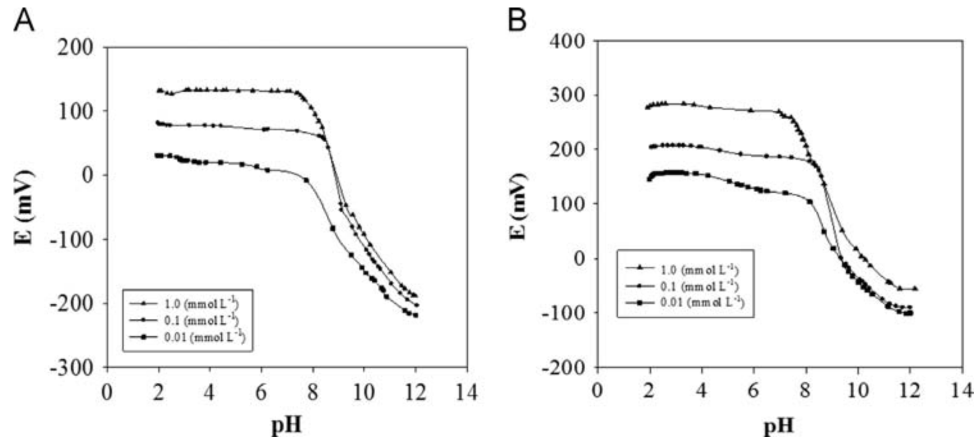

Fig. 2. The pH effect on the response of membrane (A), CMCP (B) sensors.

could be due to the deprotonation of Ser-ion producing the free base.

The response time of the investigated sensors was tested by measuring the average time required to achieve a steady potential within ± 1 mV of the final steady-state value on successive immersion of the sensor in a series of the drug solutions; each having a 10-fold increase in concentration (from 0.1 to 10.0 mmol L^{-1}) according to IUPAC definition [17,18] was ≤ 10 s. The potential stayed constant for at least 3 min.

Table 2
Effect of anionic additives on membrane and CMCP sensors behaviors.

Sensor	Plasticizer %	Additive %	Slope (mVdecade^{-1})	Linear range (mmol L^{-1})	LOD (μmol L^{-1})
Membrane Sensor using TCP as plasticizer					
3	48.5	–	56.60	0.01–10.00	2.80
18	48.25	0.5 KTFMPB	55.76	0.02–10.00	5.01
19	48	1.0 KTFMPB	50.20	0.02–10.00	3.38
20	48.25	0.5 NaTFMPB	55.50	0.01–10.00	2.34
21	48	1.0 NaTFMPB	47.17	0.01–4.46	2.29
22	48.25	0.5 KTPB	58.79	0.01–10.00	3.98
23	48	1.0 KTPB	59.95	0.01–10.00	3.63
24	48.25	0.5 NaTPB	58.39	0.01–10.00	3.89
25	48	1.0 NaTPB	58.79	0.01–10.00	3.89
CMCP Sensor using DBP as plasticizer					
12	48.5	–	59.60	0.01–10.00	9.55
26	48.25	0.5 KTFMPB	60.37	0.005–10.00	4.50
27	48	1.0 KTFMPB	58.60	0.004–10.00	2.95
28	48.25	0.5 NaTFMPB	63.26	0.004–10.00	2.45
29	48	1.0 NaTFMPB	68.35	0.004–10.00	1.32
30	48.25	0.5 KTPB	60.67	0.01–10.00	4.67
31	48	1.0 KTPB	55.70	0.01–10.00	3.8
32	48.25	0.5 NaTPB	81.74	0.01–2.69	5.88
33	48	1.0 NaTPB	67.18	0.01–7.24	3.72

The reproducibility of sensors was investigated by preparing 5 similar sensors of optimum composition, and the slope of each sensor was determined. The average slopes and relative standard deviations were 55.76 ± 0.36 and 59.28 ± 0.52 mV decade^{-1}, 1.29 and 1.90% for membrane and CMCP sensors, respectively.

For repeatability study, the calibration curves of the selected sensors were obtained from 5 replicate measurements. The average slopes and relative standard deviations obtained were 56.09 ± 0.19 and 59.9 ± 0.47 mV decade^{-1}, 0.67 and 1.7% for membrane and CMCP sensors, respectively. The life spans were 17 and 30 days for membrane and CMCP sensors, respectively.

Calibration plots were constructed in the temperature range 30–60 °C for membrane and CMCP sensors. The intercept at -log [Ser, mol L^{-1}]=0 gives the value of the standard cell potentials,E^{o}_{cell}. The cell temperature coefficient$(dE^{o}/dt)_{cell}$ and the sensor temperature coefficient$(dE^{o}/dt)_{sens.}$ were obtained by plotting E^{o}_{cell}(intercept of the calibration curves in the temperature range 30–60 °C) and $E^{o}_{sens.}$(E^{o}_{cell} + and E^{o}_{ref}in the temperature range 30–60 °C) versus t-25 °C, respectively. The temperature coefficients obtained from the slope of these straight lines, $(dE^{o}/dt)_{cell}$and $(dE^{o}/dt)_{sens.}$were $1.68 \times 10^{-3}$and 1.74×10^{-3} and 2.42×10^{-3} and 1.01×10^{-3} V/°C for membrane and CMCP sensors, respectively. These low values reveal high thermal stability of these sensors within the studied temperature range.

The effect of ionic additives on the response characteristics of ISSs have been reported [19–22]. In our investigation, we studied the effect of different anionic additives such as NaTPB, KTPB, NaTFMPB, and KTFMPB on the response characteristics of the selected sensors (Table 2). In the absence of anionic additive, the sensor slopes were 56.60 and 59.60 mV decade^{-1}; the linear range was 0.01–10 mmol L^{-1} with LOD 2.80 and 9.55 μmol L^{-1} for membrane and CMCP sensors, respectively. Addition of 0.5% NaTFMPB in case of the membrane sensors decreased LOD to 2.34 μmol L^{-1}. LOD improvement was highly observed in the case of CMCP sensor than in the membrane one.

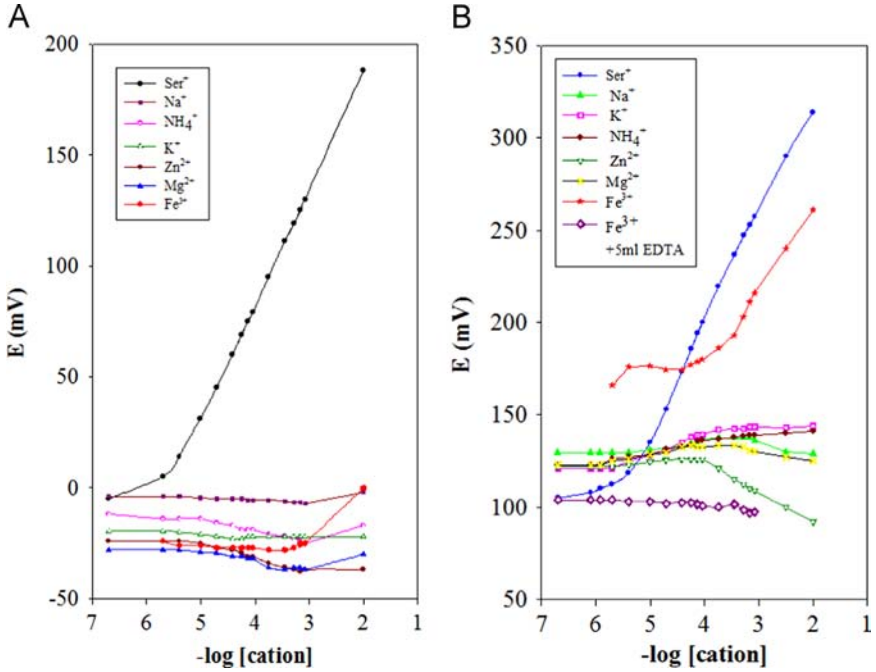

Fig. 3. Response to Ser-Cl and some inorganic cations using Ser-TPB membrane (A) and CMCP sensors (B).

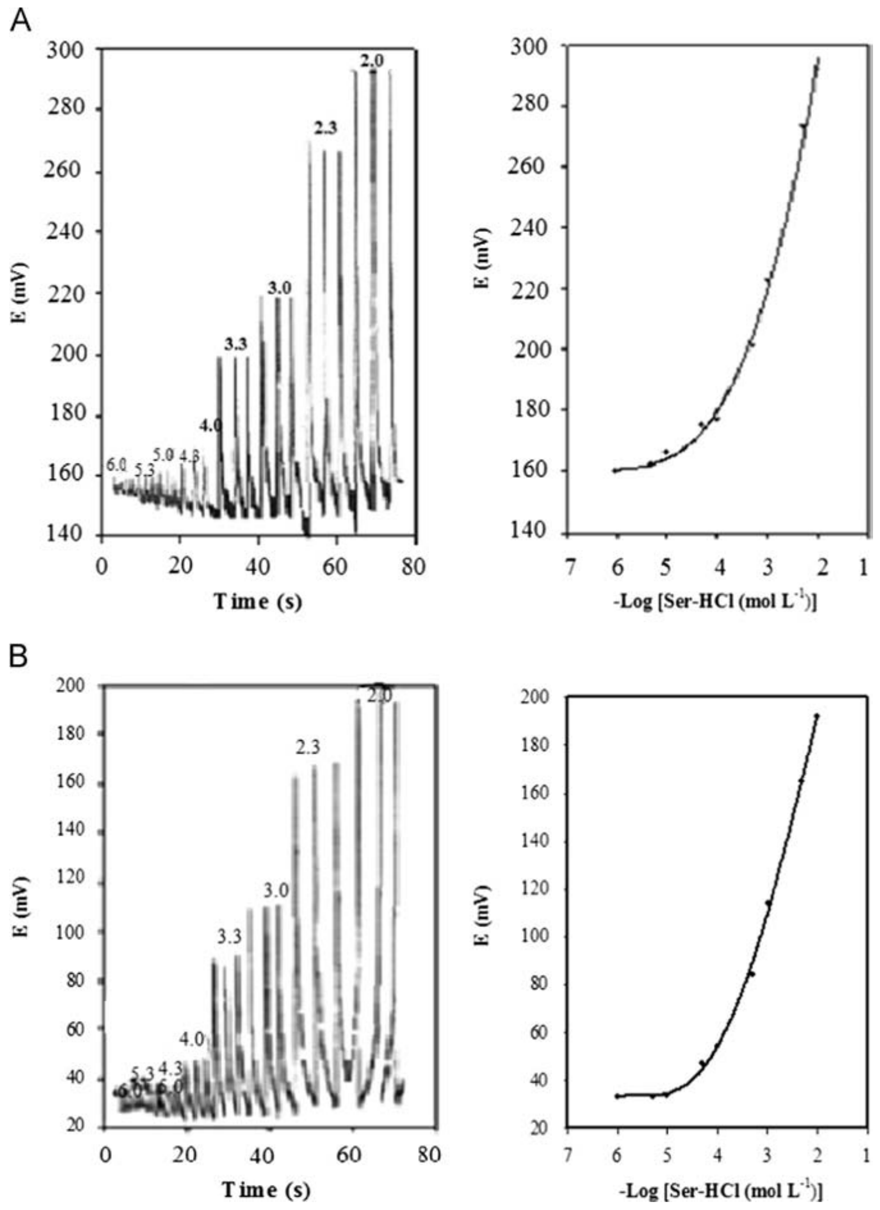

Fig. 4. Calibration graph of Ser-TPB CMCP (A) and membrane sensors in FIA (B).

The selectivity of the sensor is dependent on the ion-exchange process at the sensor-test solution interface and the mobility of the respective ions in the matrix of the sensor [23,24]. The influence of some inorganic cations (Na^+, K^+, NH_4^+, Mg^{2+}, Zn^{2+}, and Fe^{3+}) on the behavior of the investigated sensor was studied graphically by plotting the potential responses for all different cationic species against -log [concentration] of the added cation. The obtained calibration curves show that the Ser sensors are selective for Ser-Cl. However, the ferric ion shows interference at a higher concentration in the case of CMCPS. After several trials, it was found that addition of 5 mL 1.00 mmol L^{-1} EDTA to the test solution solves this problem. There was a negligible effect of this volume of EDTA on the response of the sensor (Fig. 3).

3.2. Flow injection analysis

The dispersion coefficient, the carrier composition, the injection volume, and the flow rate effects were studied. The maximum peak height was reached at volume of the sample loops (V_{inj},μL) 150 and 75 μL for membrane and CMCP sensors, respectively. The optimum flow rate (Fm, mL min^{-1}) value was 12.50 mL min^{-1} for both membrane and CMCP sensors, respectively. The low flow rate observed below 12.5 mL min^{-1} produces a steady-state high signal but leads to increased response time due to increased residence time of the sample at the active surface of the sensor. The conditions mentioned earlier enabled analyses to be carried out using a low dispersion system and a carrier stream that is 0.033 mol L^{-1} Na_2SO_4 and 0.1 μmol L^{-1} Ser-Cl. The optimized factors of the FIA along with the response characteristics of the sensor were evaluated according to the IUPAC recommendations. The slope, linear concentration range, and limit of detection were 70.46 and 59.89 mV $decade^{-1}$, 0.17–10.00 and 0.23–10.00 and 0.13 and 0.19 mmol L^{-1} for membrane and CMCP sensors, respectively. Fig. 4 represents the recordings obtained by the studied sensors at optimum FIA conditions and the corresponding calibration graph.

3.3. Surface characterization of membrane sensors

Surface characterization of membrane sensors was studied to show the effect of adding the electro-active material to the prepared

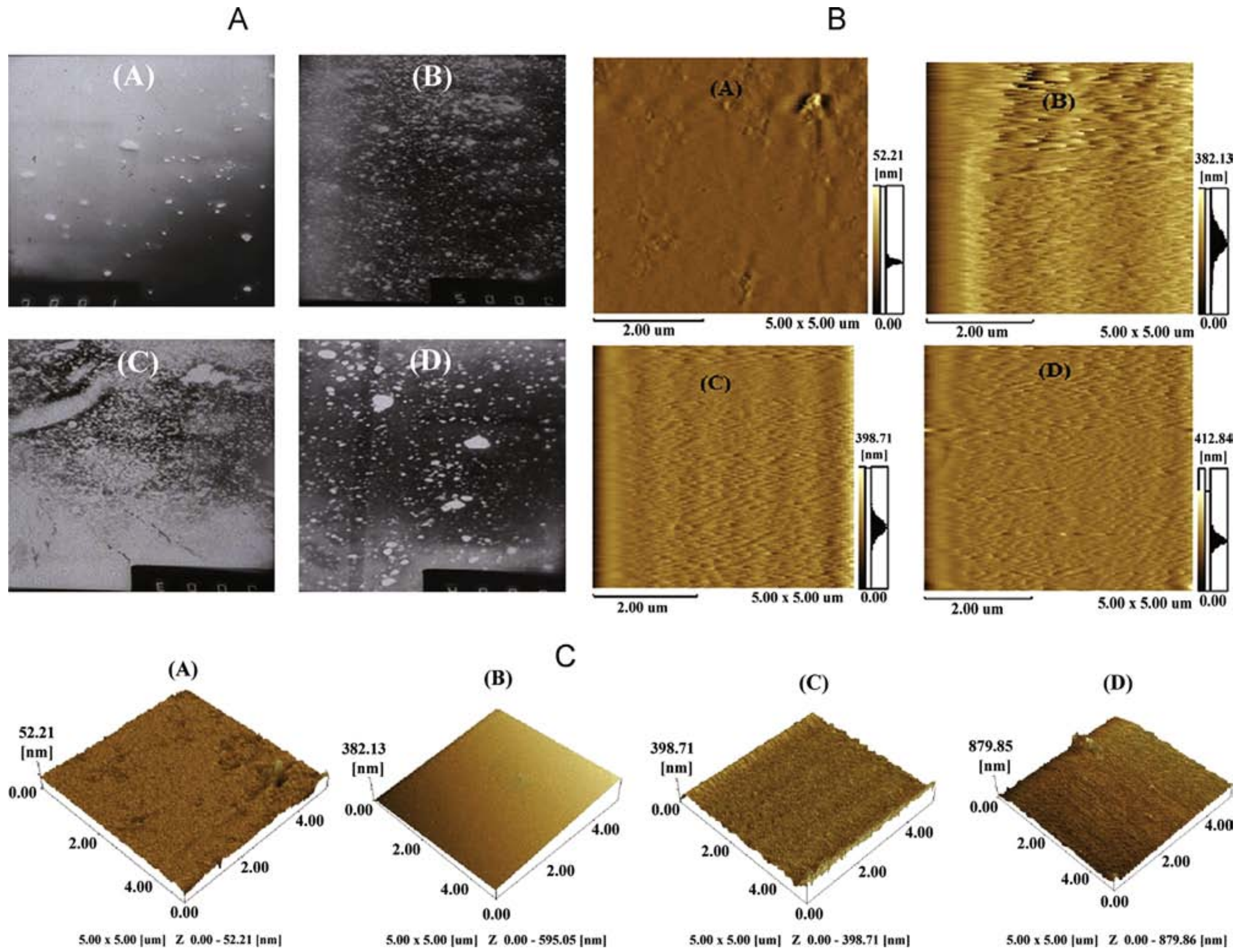

Fig. 5. Comparison of surface morphologies of PVC membranes - 100.00% PVC (A), 50.00% PVC+50.00% TCP (B), 48.50% PVC+48.50% TCP+3.00% Ser-TPB (C), and 48.25% PVC+48.25% TCP+3.00% Ser-TPB+0.50% NaTFMPB (D) membrane films (total weight, 200 mg) at 400x, total weight, 200 mg using SEM (a), 2D AFM (b), and 3D AFM (c).

Table 3
Determination of Ser-HCl in pure and its pharmaceutical preparations using membrane and CMCP sensors.

Sample type	Weight (mg)	Membrane sensor		CMCP sensor	
		Recovery ± S.E%	RSD%	Recovery–S.E%	RSD%
Potentiometric titration					
Pure solution	0.34	113.00 ± 0.95	1.87	100.00 ± 0.12	0.28
	1.03	107.26 ± 0.11	0.20	102.5 ± 0.19	0.41
	1.71	107.26 ± 0.16	0.29	102.52 ± 0.37	0.82
	6.85	102.42 ± 0.21	0.10	109.00 ± 0.30	0.61
	17.14	102.15 ± 0.23	0.13	106.50 ± 0.40	0.85
	34.27	102.15 ± 0.10	0.13	101.60 ± 0.21	0.41
Moodapex® (50 mg/tablet)	1.99	103.1 ± 0.15	0.11	103.8 ± 0.85	1.82
	5.96	102.25 ± 0.24	0.28	99.74 ± 0.09	0.19
	9.94	103.32 ± 0.16	0.31	100.66 ± 0.11	0.24
Serlift® (100 mg/tablet)	1.99	100.5 ± 0.25	0.41	98.06 ± 0.34	0.76
	5.96	101.42 ± 0.31	0.23	98.10 ± 0.25	0.56
	9.94	98.95 ± 0.36	0.24	98.34 ± 0.14	0.32
Standard addition method					
Pure	0.017	105.80 ± 0.37	0.79	98.20 ± 0.37	0.85
	0.174	102.90 ± 0.34	0.72	107.00 ± 0.35	0.74
	1.714	99.40 ± 0.26	0.59	106.60 ± 0.68	1.42
Serlift® (100 mg/tablet)	1.00	99.40 ± 0.26	1.50	97.70 ± 0.54	1.22
	1.99	105.20 ± 0.71	1.37	95.20 ± 0.37	0.88
Moodapex® (50 mg/tablet)	1.00	98.70 ± 0.61	1.35	95.60 ± 0.19	0.42
	1.99	96.20 ± 0.58	0.72	98.20 ± 0.37	0.85

membrane and to verify the results obtained earlier. Since the response of electrochemical sensors is related to the physical morphology of its surface, scanning electron microscope (SEM) and two- and three-dimension atomic force microscope (AFM) were used to study their surface morphologies. The SEM images at 400x for these membranes are shown in Fig. 5(a) (A-D). Results show that

Table 4
Comparison between the suggested and some of the other published methods for determination of Ser-ion.

Reagent/method	Linear range mmol L^{-1}	LOD μmol L^{-1}	Slope	r^2	ε	λmax nm	Ref.
Spectrophotometric			a, $Lg^{-1}cm^{-1}$				
Chloranil	0.047–0.47	–	0.0084	0.9930	28.31×10^2	450	[4]
DDQ	0.043–0.30	–	0.0092	0.9950	31.25×10^2	455	[4]
Iodine	0.018–0.14	–	0.0250	0.9980	85.50×10^2	290	[4]
CAA	0.014–0.29	3.79	0.0007	0.9999	6.00×10^2	530	[5]
Spectroflourimetry	0.014–1.46	0.05	16.04	0.9995	–	Ex. 280 Emi. 560	[6]
Electrometric				–	–	–	
Voltammetry	0.2×10^{-3}–1.2×10^{-3}	0.15	–	0.9950	–	–	[2]
GCE	3.0×10^{-3}–9.0×10^{-3}	1.00	–	0.9964	–	–	[3]
Ion Selective Sensor			mV/decade				
molecularly imprinted polymers	0.001–10.00	0.80	57.70	–	–	–	[1]
Ser-TPB + 1.0 NaTFMPB CMCP	0.004–10.00	1.32	68.35	0.9995			[C.S]
Ser-TPB CMCP	0.01–10.00	9.55	59.60	0.9997			[C.S]
Ser-TPB membrane	0.01–10.00	2.80	56.60	0.9997			[C.S]

r^2: Correlation coefficient
ε: Molar absorptivity
R%: Mean recovery%
t: tested range
C.S: Current study
DDQ: 2, 3 dichloro-5, 6-dicyanoquinone
CAA: p-Chloranilic acid
GCE: Glassy carbon electrode
Ex: Excitation
Emi: Emission
t: tested range
GC: Glassy carbon

the blank membrane (only PVC) had a smooth surface containing small surface defects (Fig. 5(a) (A) (slope = 1.43 mV decade^{-1})). The membrane containing TCP and PVC showed formation of grains (Fig. 5(a) (B) (slope = 22.74 mV decade^{-1})). After adding Ser-TPB to the prepared mixture containing TCP and PVC, the number of grains increased and was rearranged to another form (Fig. 5(a) (C)), which reflects the improvement of the sensor response (slope = 56.60 mV decade^{-1} and LOD 2.80 μmol L^{-1}). On the other hand, adding NaTFMPB affected the rearrangement and size of the formed grains, causing a small change in the slope value, 55.50 mV decade^{-1}, and lowering the LOD value to 2.34 μmol L^{-1} (Fig. 5(a) (D)). Typical 2 and 3D AFM images of these membranes are shown in Figs. 5(b) (A-D) and 5(c) (A-D). Since AFM is a powerful tool to measure topography and properties of surfaces, it showed a close agreement with the data obtained from SEM.

3.4. Analytical applications

The proposed sensors were successfully applied for the titration of Ser-ion solution with NaTPB. The amount of Ser-ions in 50 mL solution can be accurately determined in the range 0.34–34.27 mg with recoveries from 98.06 to 113.00% and RSD% 0.11 from 1.87 (Table 3). It is interesting to note that before the titration end point, the measured potential shows logarithmic change with mL NaTPB added, whereas the potential response after the end point remains almost constant. The latter is due to an extremely low concentration of free Ser-ion in solution.

The standard addition method was also applied successfully for determination of Ser-Cl in aqueous solution of pure raw material (0.017–1.714 mg) and pharmaceutical preparations (1.00–1.99 mg), using membrane and CMCP sensors. The average recovery values ranged from 95.20 to 107.00%, with relative standard deviation values ranging from 0.42 to 1.42 (Table 3).

Potentiometric determination of Ser-Cl in pharmaceutical preparations was carried out using FIA. The recovery values ranged from 99.6 to 102.2 and from 96.0 to 102.5% for membrane and CMCP sensors, respectively, revealing high accuracy of the proposed method.

Statistical treatment (F and t-tests) of the data was carried out to compare the experimental data with those of the reference method [25] (Table 3). It was found that values were lower than the tabulated ones, 5% critical values (95% confidence level).

4. Conclusion

Sertraline HCl sensors based on Ser-TPB have been prepared. The sensors were found to exhibit good Nernastian slope, low LOD, wide linear range, high selectivity, and repeatable results. The obtained data were proved by using SEM and AFM showing the surface morphology change on adding the active ingredients (Ser-TPB) and additives as NaTFMPB.

This study was compared with some previously published data. The results of this study showed wider linear range, 0.004–10.00 μmol L^{-1}, and lower LOD, 1.23 μmol L^{-1}, than methods [4–6]. It is less expensive than methods [2,3]. It is characterized by wide linear range and low LOD and near Nernastian value, 59.60 mV/decade, than that in case of the method [1] in Table 4, thus proving that it is a good Ser-ion selective sensor for the pure and pharmaceutical preparations with high accuracy and precision.

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