Sibutramine Selective Electrodes for Batch and Flow Injection Determinations in Pharmaceutical Preparations

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The construction and electrochemical response characteristics of two new polyvinyl chloride (PVC) membrane sensors for the determination of sibutramine hydrochloride were described. The sensors are based on the ion association complexes of sibutramine with sodium tetraphenylborate (NaTPB) or phosphotungstic acid (PTA) using dibutyl phthalate as plasticizing solvent. The sensors display a fast, stable response over the concentration range 3.84×10^{-5} – 1.00×10^{-2} M sibutramine hydrochloride monohydrate (SibuCl), with cationic slopes of 57.7 ± 0.57 and 59.7 ± 1.79 mV concentration decade⁻¹ and detection limits of 8.91×10^{-6} and 1.47×10^{-5} M in case of sibutramine-tetraphenylborate (Sibu-TPB) and sibutramine-phosphotungstate ((Sibu)₃-PT), respectively. The proposed sensors have been successfully applied for the determination of sibutramine hydrochloride in Regitrim capsules in batch and flow injection (FI) conditions.

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Introduction

Sibutramine hydrochloride monohydrate (SibuCl) chemically is (±)-1-(*p*-chlorophenyl)- α -isobutyl-*N,N*-dimethylcyclobutylamine hydrochloride monohydrate [125494-59-9] (Scheme 1). It is an orally administered agent for treatment of obesity, as an appetite suppressant; it is a centrally acting serotonin-norepinephrine reuptake inhibitor structurally related to amphetamines.^{1,2}

Limited methods of determination of this drug have been reported in the literature, including high performance liquid chromatographic (HPLC),³⁻⁶ and spectrophotometric⁷⁻¹⁰ and derivative fluorescence spectroscopic¹¹ methods. The development and application of ion selective-electrodes continue to be of interest in pharmaceutical analysis because these sensors offer the advantages of simple design and operation, reasonable selectivity, fast response, low cost and applicability to turbid and colored solutions. A literature survey revealed that no potentiometric sensors for sibutramine have been published yet. In the present work, two new plastic membrane sensors for sibutramine have been constructed. The sensors are based on incorporation of sibutramine-tetraphenylborate (Sibu-TPB) or

sibutramine-phosphotungstate ((Sibu)₃-PT) association complexes in polyvinyl chloride (PVC) plasticized with dibutyl phthalate (DBP). Application of these sensors to the determination of SibuCl in pharmaceutical preparations for batch and flow injection systems are being described.

Experimental

Reagent and materials

All chemicals were of analytical grade. Double distilled water was used throughout all experiments. Pure grade sibutramine hydrochloride monohydrate and the pharmaceutical preparation Regitrim capsules were provided by Medical Union Pharmaceuticals, Abu-Sultan, Ismailia, Egypt. Sodium tetraphenylborate (NaTPB), phosphotungstic acid (PTA) and dioctyl sebacate (DOS) were from Fluka; tetrahydrofuran (THF), dibutyl phthalate (DBP) and dioctyl phthalate (DOP) were from Merck. PVC of relatively high molecular weight was from Aldrich.

Apparatus

Potentiometric and pH measurements were carried out using a Seibold G-103 digital pH/mV meter (Vienna, Austria). A Technic circulator thermostat Model C-100 was used to control the temperature of the test solutions. A saturated calomel electrode (SCE) was used as the external reference, while a Ag/AgCl wire was used as the internal electrode. The electrochemical system of the conventional electrode may be represented as follows: Ag/AgCl/filling solution (1×10^{-1} M NaCl and 1×10^{-2} M SibuCl)/membrane/test solution//KCl salt bridge//saturated calomel electrode.

The flow injection setup is that previously reported.¹² Figure 1 represents the schematic diagram of the flow injection system used in the measurements.

Scheme 1

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Fig. 1 Schematic diagram of the flow injection system used in the measurements.

Preparation of Sibul-PVC membrane sensors

The Sibul-TPB and (Sibu)₃-PT ion associates were prepared by mixing 50 ml of 1×10^{-2} M SibulCl solution with an equal amount of 1×10^{-2} M NaTPB solution or mixing 150 ml of 1×10^{-2} M SibulCl solution with 50 ml of 1×10^{-2} M PTA solution, respectively. The formed precipitates were filtered, washed thoroughly with bidistilled water until chloride free and dried at room temperature. The compositions of the ion associates were found to be 1:1 and 3:1 in cases of Sibul-TPB and (Sibu)₃-PT ion associates, respectively, as confirmed by elemental analysis data obtained at the microanalytical research laboratory in National Research Centre, Dokki, Cairo, Egypt. The percentage values found are 79.71, 7.17 and 2.21, and the calculated values are 79.80, 7.35 and 2.27 for C, H and N in case of Sibul-TPB, while in case of (Sibu)₃-PT the percentage values found are 16.76, 2.43 and 1.14, and the calculated values are 16.25, 2.17 and 1.12 for C, H and N, respectively. The membranes were prepared by dissolving the required amount of the ion associates, PVC and the plasticizers in about 10 ml of THF. This cocktail was poured into a 6-cm Petri dish and left to dry in air. The thickness of the membrane was about 0.2 mm; Disks of the membrane were used to assemble the electrodes by the general procedure previously described.¹³

Potentiometric determination of SibulCl

The standard additions method¹⁴ was applied, in which small increments of standard solution (3×10^{-2} M) of SibulCl were added to 50 ml aliquot samples of various concentrations from pure drug or pharmaceutical preparation. The change in mV reading was recorded for each increment and used to calculate the concentration of SibulCl sample solution using the following equation:

$$C_x = C_s \left(\frac{V_s}{V_x + V_s} \right) \left(10^{n(\Delta E/S)} - \frac{V_x}{V_x + V_s} \right)^{-1}$$

where C_x and V_x are the concentration and the volume of the unknown, respectively, C_s and V_s the concentration and the volume of the standard SibulCl solution, respectively, s the slope of the calibration graph and ΔE the change in mV due to the addition of the SibulCl standard solution.

Determination of SibulCl in Regitrim capsules

The contents of twenty capsules were accurately weighed and powdered in a mortar. The required amount of powder from the capsules to prepare 10^{-3} M SibulCl solution was dissolved in 30 ml of bidistilled water and the mixture was filtered in a

Table 1 Composition of different Sibul membrane and slopes of the corresponding calibration graphs at $25 \pm 1^\circ\text{C}$ and 15 min of soaking in 1×10^{-3} M SibulCl solution

Membrane	Composition, % w/w			Slope/mV decade ⁻¹	SD
	Ion associate	PVC	DBP		
Sibul-TPB	3	48.5	48.5	53.3	1.51
	5	47.5	47.5	55.5	0.60
	7	46.5	46.5	57.7	0.57
	10	45.0	45.0	52.5	2.61
(Sibu) ₃ -PT	3	48.5	48.5	57.0	2.00
	5	47.5	47.5	57.5	3.07
	10	45.0	45.0	59.7	1.79

100-ml measuring flask. The residue was washed three times with bidistilled water and the volume was completed to the mark by the same solvent. Fifty-milliliter solutions having concentrations (5×10^{-5} – 1×10^{-4} M SibulCl) were prepared by accurate dilutions. The prepared solutions were transferred into a 100-ml titration cell and subjected to potentiometric determination of SibulCl.

In FI conditions, a series of solutions of different concentrations was prepared from the capsules. The peak heights were measured and then compared with those obtained from injecting a standard solution of the same concentration prepared from pure SibulCl.

Results and Discussion

Composition of the membranes

Different membrane compositions were prepared by varying the percentages of the electroactive complex Sibul-TPB and (Sibu)₃-PT (Table 1). The results indicated that the electrodes made by membrane with 7% Sibul-TPB or 10% (Sibu)₃-PT electroactive complex exhibited the best performance characteristics (slope, 57.7 mV concentration decade⁻¹ at 25°C ; usable concentration range, 3.84×10^{-5} – 1.00×10^{-2} M SibulCl; detection limit,¹⁵ 8.91×10^{-6} M; response time, ≤ 10 s) for Sibul-TPB electrode. For (Sibu)₃-PT electrode the characteristics are: slope, 59.7 mV concentration decade⁻¹ at 25°C ; usable concentration range, 3.84×10^{-5} – 1.00×10^{-2} M SibulCl; detection limit, 1.47×10^{-5} M; response time, ≤ 10 s. The PVC acts as a regular support matrix for the plastic membrane ion-selective electrode, but its use requires a plasticizer which acts as a fluidizer allowing homogeneous dissolution and diffusional mobility of the electroactive complex inside the membrane.¹⁶ Three plasticizers, DBP, DOP and DOS, were examined (Table 2). The result indicated that DBP is the best of the plasticizers tested. It dissolves the ion associate complexes and adjusts both the membrane permittivity and the ion exchanger site mobility to give the highest possible sensitivity and selectivity.¹⁷ The potential response characteristics of the proposed electrodes were evaluated according to IUPAC recommendations (Table 3).¹⁸

Influence of pH and effect of electrolytes

The influence of the solution pH on the electrode response was checked for two concentrations of SibulCl (1×10^{-3} and 1×10^{-4} M) by following the variation in potential with change in pH by addition of very small volumes of hydrochloric acid and sodium hydroxide (each 0.1 – 1.0 M). The results indicated that

Table 2 Effect of plasticizers on Sibuprofen responsive membrane and slopes of the corresponding calibration graphs at $25 \pm 1^\circ\text{C}$ and 15 min of soaking in 10^{-3} M Sibuprofen

Plasticizer	Slope/mV decade ⁻¹	Usable concentration range/M	Detection limit ¹⁵ /M
Sibu-TPB			
DBP	57.7 + 0.57	$3.84 \times 10^{-5} - 1 \times 10^{-2}$	8.91×10^{-6}
DOP	47.5 + 0.65	$3.84 \times 10^{-5} - 1 \times 10^{-2}$	9.27×10^{-6}
DOS	49.0 + 1.37	$3.84 \times 10^{-5} - 1 \times 10^{-2}$	1.58×10^{-5}
(Sibu) ₃ -PT			
DBP	59.7 + 1.79	$3.84 \times 10^{-5} - 1 \times 10^{-2}$	1.47×10^{-5}
DOP	58.4 + 2.13	$3.84 \times 10^{-5} - 1 \times 10^{-2}$	1.71×10^{-5}
DOS	54.7 + 5.24	$3.84 \times 10^{-5} - 1 \times 10^{-2}$	2.51×10^{-5}

Table 3 Response characteristics of Sibuprofen sensors according to IUPAC recommendations¹⁸

Parameter	Sibu-TPB	(Sibu) ₃ -PT
Slope/mV decade ⁻¹	57.7	59.7
Intercept/mV	172.1	170.8
Correlation coefficient	0.9998	0.9995
Linear range/M	$3.84 \times 10^{-5} - 1.00 \times 10^{-2}$	$3.84 \times 10^{-5} - 1.00 \times 10^{-2}$
Detection limit/M	8.91×10^{-6}	1.47×10^{-5}
Working pH range	2.0 – 6.6	2.0 – 5.6
Response time/s	< 10	< 10

the electrode did not response to the pH change in the range 2.0 – 6.6 and 2.0 – 5.6 for Sibu-TPB electrode and (Sibu)₃-PT electrode, respectively (Fig. 2). The decrease in potential occurring at higher pH values can most probably be attributed to the formation of the free sibutramine base in the solution, leading to a decrease in the concentration of sibutraminium cation. The electrodes response was checked in bidistilled water, 0.04 M Britton-Robinson buffer pH 4.0, 0.1 M acetate buffer pH 4.0 and 0.05 M phthalate buffer pH 4.2. The results reveal that the electrodes in bidistilled water provided not only a higher Nernstian slope but also a stable potential reading; in cases of buffer medium, in addition to the poor sensitivities of the electrodes, there is no stable reading for potentials. Therefore we used bidistilled water medium for further studies.

Lifetime and stability of the electrodes

Lifetimes for the electrodes were examined by performing calibration plots (pSibuCl versus E , mV) as a function of soaking time. The results indicate that, in the case of Sibu-TPB electrode, the slope of the calibration graph was near 58 mV concentration decade⁻¹ for up to 49 days soaking in 1×10^{-3} M Sibuprofen solution; the slope then decreased, reaching about 54 and 49.5 concentration decade⁻¹ after 58 and 68 days, respectively. In case of (Sibu)₃-PT electrode, the slope of the calibration graph remained constant near 60 concentration decade⁻¹ for 7 days; then it decreased, reaching 55, 50 and 40 concentration decade⁻¹ after 17, 20 and 23 days, respectively. The day-to-day precision for the slopes of the calibration plot of the proposed electrodes gave RSD ($n = 4$) of 0.63 and 1.13% for Sibu-TPB and (Sibu)₃-PT electrode, respectively.

Effect of temperature

To study the thermal stability of the electrodes, we constructed calibration graphs at different temperatures, and we calculated, the isothermal coefficients (dE/dT) of the selected electrodes¹⁹ to

Fig. 2 Effect of the pH of the test solution containing 1×10^{-3} and 1×10^{-4} M Sibuprofen on the potential response of the Sibuprofen electrodes: a and b, Sibu-TPB; c and d, (Sibu)₃-PT.

Fig. 3 Recording (a) and corresponding calibration graph (b) for Sibu-TPB electrode under FI conditions.

be -0.0024 and -0.0021 V/ $^\circ\text{C}$ for Sibu-TPB and (Sibu)₃-PT electrodes, respectively.

FI conditions

FI parameters were optimized in order to achieve the best signal sensitivity. The dispersion coefficients were found to be 1.15 for Sibu-TPB or (Sibu)₃-PT electrode; this limited dispersion aids the optimum sensitivity and the fast response of the electrodes.²⁰

Samples of different volumes (4.7 – 500.0 μl) from the drug solution were injected at constant flow rate. The higher the sample volume, the higher the peak height and the longer the residence time of the sample at the electrode surface; such samples require a longer time to reach a steady state and greater consumption of sample.²¹ The optimum sample loop size was found to be 75 and 150 μl for Sibu-TPB and (Sibu)₃-PT electrodes, respectively, giving maximum peak height, less consumption of reagents, and a shorter time to reach the baseline. The effect of flow rate on the electrode response was

studied at different flow rates (4.15 – 30.00 ml/min), with constant injection sample loop size of 75 or 150 μ l in case of Sibutramine-TPB and (Sibutramine)₃-PT electrodes, respectively. The residence time of the sample was inversely proportional to the flow rate.²² It was found that, as the flow rate increases, the peak becomes higher and narrower until flow rates of 17.85 and 12.50 ml/min are reached in cases of Sibutramine-TPB and (Sibutramine)₃-PT electrode, respectively; the peaks obtained above these flow rates were nearly the same. These flow rates were used throughout this work providing the maximum peak height, a shorter time to reach the base line and less consumption of the carrier solution. Under these conditions, the performance characteristics are: slope, 64.9 and 73.5 mV concentration decade⁻¹, for Sibutramine-TPB and (Sibutramine)₃-PT electrode, respectively; usable concentration range, 5.0×10^{-5} – 1.0×10^{-2} M SibutramineCl; detection limit, 2.0×10^{-5} M for both electrodes. Figure 3 represents a typical recording and the calibration graph for Sibutramine-TPB electrode.

Selectivity of the electrodes

The selectivity of some inorganic cations, sugar, amino acids, vitamins and urea were investigated. The selectivity coefficients were determined by the separate solution method (SSM)²³ in which the Nicolsky-Eisenman equation was used:

$$\log K_{\text{Sibu}, J^{z+}}^{\text{pot}} = (E_2 - E_1)/S + \log[\text{Sibu}] - \log[J^{z+}]^{1/z}$$

where E_1 and E_2 are the electrode potential in a 1×10^{-3} M SibutramineCl solution and interfering ions J^{z+} , respectively, and S is the slope of the calibration graph in mV concentration decade⁻¹. In FI conditions, a series of standard solutions of SibutramineCl of concentration between 10^{-5} and 10^{-2} M were prepared; their corresponding potentials were measured and used to determine the slope of the calibration graph. Solutions of 1×10^{-3} M of interfering ions were prepared; their corresponding peak heights were measured. The selectivity coefficients were calculated using the above equation. The selectivity coefficients in cases of species without charges were determined using the matched potential method (MPM).²⁴ The potentiometric selectivity coefficient is defined in this method as the activity ratio of primary ions and interfering ions that give the same potential change under identical conditions. At first, a known activity of sibutramine ion solution is added into a reference solution which contains a fixed activity of sibutramine ion solution α_{Sibu} , ($\alpha'_{\text{Sibu}} - \alpha_{\text{Sibu}}$ is the change in activity), and the corresponding potential change (ΔE) is recorded. Next, a solution of an interfering ion is added to the reference solution until the same potential change (ΔE) is recorded. The change in potential produced at the constant background of the primary ion must be the same in both cases.

Table 4 Selectivity coefficients ($-\log K_{\text{Sibu}, J^{z+}}^{\text{pot}}$) for the Sibutramine electrodes in batch (SSM and MPM) and FI conditions

Interferent	Sibutramine-TPB			(Sibutramine) ₃ -PT		
	SSM	MPM	FI	SSM	MPM	FI
Na ⁺	1.802	—	1.75	1.91	—	1.97
K ⁺	1.970	—	1.68	1.98	—	1.83
Ca ²⁺	3.507	—	3.05	3.51	—	3.12
Mg ²⁺	3.451	—	3.00	3.56	—	3.05
Fe ³⁺	3.895	—	3.37	3.23	—	3.27
Zn ²⁺	3.163	—	3.07	3.64	—	3.02
Co ²⁺	3.191	—	3.11	2.87	—	2.93
Vitamin B ₁	1.315	—	1.60	1.59	—	1.35
Vitamin B ₆	1.384	—	1.68	1.67	—	1.77
Glucose	—	2.65	—	—	2.52	—
Fructose	—	2.80	—	—	2.51	—
Lactose	—	2.79	—	—	2.59	—
Maltose	—	2.57	—	—	2.23	—
Glycine	—	2.03	—	—	1.35	—
Alanine	—	2.06	—	—	1.61	—
Urea	—	1.68	—	—	1.86	—

$$K_{\text{Sibu}, J^{z+}}^{\text{pot}} = \frac{\alpha'_{\text{Sibu}} - \alpha_{\text{Sibu}}}{\alpha_J}$$

where α_J is the activity of the added interferent.

The selectivity coefficients values $-\log K_{\text{Sibu}, J^{z+}}^{\text{pot}}$ of the electrodes listed in Table 4 reflect a high selectivity of these electrodes towards sibutramine cation, under both batch and flow injection conditions.

Analytical applications

The usefulness of the proposed electrodes was examined by using the investigated electrodes for the potentiometric determination of SibutramineCl in pure solutions and in pharmaceutical preparation Regitrim capsules (15 mg SibutramineCl/capsule) in batch and FI conditions. The mean recovery and the relative standard deviation values are summarized in Table 5. The data indicate that there is no interference from the excipients used in the formulations of the capsules. As the drug is not listed in any pharmacopoeia yet, the results were compared with the UV spectrophotometric published method⁹ (Table 6). The results are in good agreement with those obtained from the reference

Table 5 Determination of SibutramineCl in pure form and pharmaceutical preparations by applying standard addition method and FI technique

	Pure solution				Regitrim capsule							
	Standard addition				Standard addition				FI			
	Taken/M	Found/M	Rec., %	RSD, %	Taken/M	Found/M	Rec., %	RSD, %	Taken/M	Found/M	Rec., %	RSD, %
Sibutramine-TPB	5.00×10^{-5}	4.95×10^{-5}	99.0	1.55	5.00×10^{-5}	4.98×10^{-5}	99.6	0.936	5.00×10^{-5}	4.94×10^{-5}	98.80	1.012
	1.00×10^{-4}	9.68×10^{-5}	96.8	1.51	8.00×10^{-5}	7.98×10^{-5}	99.8	1.013	8.00×10^{-5}	7.97×10^{-5}	99.63	1.205
	5.00×10^{-4}	4.89×10^{-4}	97.8	0.53	1.00×10^{-4}	9.89×10^{-5}	98.9	0.951	1.00×10^{-4}	1.004×10^{-4}	100.40	0.748
	1.00×10^{-3}	9.66×10^{-4}	96.6	2.85	—	—	—	—	1.00×10^{-3}	1.004×10^{-3}	100.40	1.468
(Sibutramine) ₃ -PT	5.00×10^{-5}	4.87×10^{-5}	97.4	3.31	5.00×10^{-5}	4.99×10^{-5}	99.8	0.934	5.00×10^{-5}	5.00×10^{-5}	100.00	1.582
	1.00×10^{-4}	9.82×10^{-5}	98.2	0.87	8.00×10^{-5}	8.00×10^{-5}	100.0	1.105	8.00×10^{-5}	7.95×10^{-5}	99.38	0.809
	5.00×10^{-4}	4.98×10^{-4}	99.6	0.69	1.00×10^{-4}	9.62×10^{-5}	96.2	1.600	1.00×10^{-4}	9.94×10^{-5}	99.40	1.394
	1.00×10^{-3}	9.70×10^{-4}	97.0	1.53	—	—	—	—	1.00×10^{-3}	9.91×10^{-4}	99.10	1.184

Table 6 Statistical comparison between results of determination of Regitrim capsules on applying the proposed and reference methods

Parameter	Sibu-TPB	(Sibu) ₃ -PT
Standard addition		
Mean recovery, %	99.43	98.67
SD, %	0.962	1.192
RSD, %	0.967	1.208
<i>F</i> -ratio (9.28) ^a	1.787	1.164
<i>t</i> -test (2.447) ^b	0.996	1.802
FI		
Mean recovery, %	99.81	99.47
SD, %	1.106	1.236
RSD, %	1.108	1.243
<i>F</i> -ratio (9.28) ^a	1.352	1.083
<i>t</i> -test (2.447) ^b	0.531	0.920
Reference method ⁹		
Mean recovery, %	100.27	
SD, %	1.286	
RSD, %	1.283	

Average of four determinations for the proposed and reference methods.

a. Tabulated *F*-values at 95% confidence level.

b. Tabulated *t*-values at 95% confidence level and 6 degrees of freedom.

method. The results were statistically evaluated using *t*- and *F*-tests²⁵ (at 95% confidence level). The results indicate that the calculated *t*- and *F*-values did not exceed the theoretical values.

Conclusions

Experimental comparison of two ion associate complexes of Sibu for use as electroactive compounds using different plasticizers in potentiometric sensors revealed that, in most cases, the Sibu membrane sensor displayed good analytical performance characteristics. The proposed electrodes offer the advantage of fast response, good selectivity, long time stability, simple operation, low cost and direct application over a wide pH range without prior sample treatment. The proposed sensors might be useful detectors in batch and flow injection conditions for determination of Sibu in its pharmaceutical preparation.

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