

PVC membrane and All-Solid-State Sensor for the Potentiometric Analysis of Trimipramine

Maryam Sharifi-Sistani¹, Farnoush Faridbod^{2,3,*}, Hamid Rashedi^{1,4}, Nazila Davarkhah²

¹ Alborz Campus, University of Tehran, Tehran, Iran

² Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran

³ Biosensor Research Center, Endocrinology & Metabolism Molecular-Cellular Sciences Institute, Tehran University of Medical Sciences, Tehran, Iran

⁴ Department of Chemical Engineering, Faculty of Engineering, University of Tehran, Tehran, Iran

*E-mail: faridbodf@khayam.ut.ac.ir

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Two symmetrical and asymmetrical potentiometric membrane electrodes were developed and evaluated for the analysis of Trimipramine (TMP). The symmetrical electrode was a poly(vinyl chloride) (PVC) membrane electrode (PME), a similar membrane of which was further used on an all-solid-state (ASS) electrode to make the asymmetrical ASS-PME. Both instruments function based on the ion-exchange between aqueous solutions of TMP and an organic phase (i.e. the PVC membrane) optimally composed of 6% of an ion-pair of TMP-TPB, 63% of dibutyl phthalate, 30% of PVC and 1% of NaTPB. The optimal electrodes revealed a Nernstian behavior. The ASS electrode was prepared using a conductive composite of graphite, MWCNTs, and epoxy resin which was coated on a copper wire. The ASS-PME, on the other hand, was prepared by covering the ASS electrode with a thin layer of the optimal PVC membrane. The PME and ASS-PME revealed Nernstian slopes of 57.1 ± 0.3 and 58.2 ± 0.4 mV/decade over the concentration ranges of 1.0×10^{-6} - 1.0×10^{-2} and 1.0×10^{-7} - 1.0×10^{-4} M. The method of using the instruments was validated and the applicability of sensors for quality control analyses of TMP in pharmaceutical formulations, was also evaluated.

Keywords: Trimipramine, PVC membrane sensors, All solid state electrodes, Ion-pair complex

1. INTRODUCTION

Trimipramine (TMP), (\pm)-3-(10, 11-dihydro-5H-dibenzo [b,f]azepin-5-yl)-N, N,2-trimethylpropan-1-amine (Fig. 1), is a tricyclic antidepressant, which is used to restore the balance of the neurotransmitters of the brain [1]. The side effects of TMP include dry mouth, blurred vision, mydriasis, decreased lacrimation, constipation, urinary hesitancy or retention, reduced GI motility,

tachycardia (high heart rate), anticholinergic delirium (particularly in the elderly and in Parkinson's disease), weight gain, orthostatic hypotension, impotence, loss of libido, tremor, dizziness, sweating, anxiety, insomnia and agitation [2].

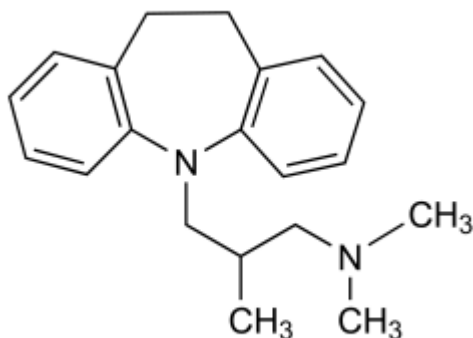
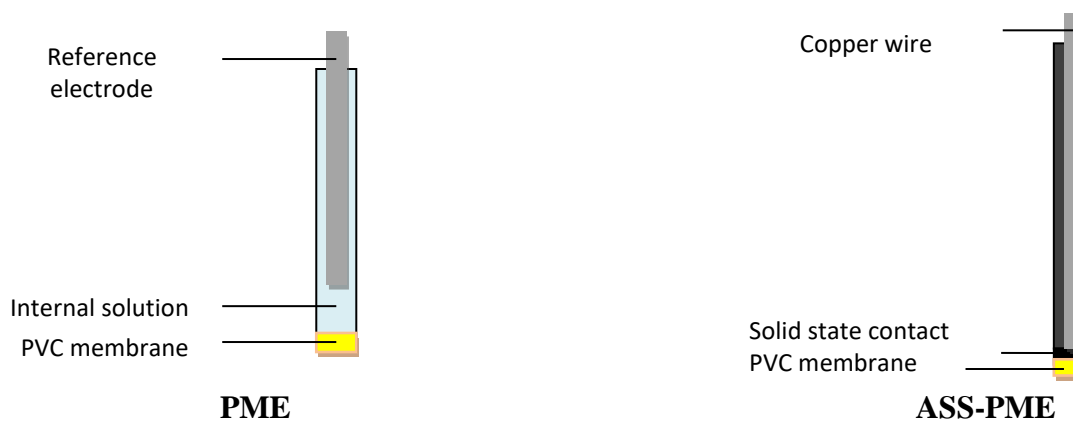


Figure 1. Structure of TMP



Scheme 1. Schematic illustrations of the PME and ASS-PME

Generally high performance liquid chromatography (HPLC) is used for the analysis of TMP in pharmaceutical or biological samples [3]. Given that drug sensors can usually compete with such analytical instrument, they can offer facile, inexpensive and fast solutions for the analysis of active ingredients in various medicinal and biological samples. These instruments enjoy further advantages in terms of wide linear response ranges, no need to sample pre-treatments and good selectivity [4-14].

PVC membrane sensors can be constructed as symmetric and asymmetric sensors instruments (Scheme 1). Symmetrical instruments, like PVC membrane sensors, are based on fixing a selective membrane between an internal and an external solution, while in the case of the asymmetrical instruments only the outer surface of the membrane is in contact with the sample solution and the inner surface is in contact with a solid element acting as the transducer. The former class of sensors have short

life times due to the mechanical instability of the membranes. The asymmetrical instruments also excel the symmetrical ones in terms of the lower detection limits which are reportedly in the range of 10^{-5} to 10^{-6} M for the symmetrical and 10^{-8} M for the asymmetrical instruments.

All-solid-state polymeric membrane electrodes (ASS-PME) constitute a family of asymmetric sensors [15-23], in which a conductive element composed of a conducting polymer or a polymeric composite of graphite and epoxy resins, is coated with a selective PVC membrane. Consequently the internal standard solution, which in the case of symmetrical instrument restricts the lower detection limits due to the possibility of its loss, can be eliminated. Such devices further are simpler to optimize since they do not require an inner filling solution.

Accordingly, the present work was focused on preparing a TMP-selective PME and an ASS-PME and evaluation of its application in the analysis of some pharmaceutical formulations. Both electrodes were based on using an ion-exchanging (TMP-TPB) compound in a polymeric matrix. The function of the sensors was further validated and the instruments were also used in analysis of the TMP content of pharmaceutical samples.

2. EXPERIMENTAL SECTION

2.1. Devices

One of the PME and ASS-PME electrodes was used as an indicator electrode in each experiment, together with a reference electrode (Ag/AgCl; Azar-Electrode Co., Iran). The setup was connected to an ion analyzer (a 250 pH/mV meter with ± 0.1 mV precision), to form the following cell assemblies:

For PME:

Ag-AgCl || inner solution, 1×10^{-3} M TMP solution | PVC membrane | sample solution || Ag-AgCl, KCl (satd.)

For ASS-PME:

Copper wire | ASS layer | PVC membrane | sample solution || Ag-AgCl, KCl (satd.)

The measurements were then performed using the calibration method using a series of standards.

2.2. Chemicals

Dibutyl phthalate (DBP), nitrobenzene (NB), benzyl acetate (BA), sodium tetraphenyl borate (NaTPB) and tetrahydrofuran (THF) (Merck Co., Germany) and high-molecular weight polyvinylchloride (PVC) (Fluka Co., USA) were of the highest purities available and were used as received from the supplier. Trimipramine maleate and the pharmaceutical formulations were from a local manufacturer. The epoxy and hardener (macroplast Su 2227, desmodur RFE) were from Henkel and Bayer Ag (Germany). The multi-walled carbon nanotubes (MWCNTs) (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 obtained from the Research Institute of the Petroleum Industry (RIPI), (Tehran, Iran).

2.3. Preparing the ion-pair sensing agent

The sensing agent used in the PME and OME-ASS was the ion-pair of trimipramine maleate and sodium tetraphenyl borate (TMP-TPB). This agent was prepared through mixing about 10 mL of an acidic 0.01 M solution of TMP, with a similar volume of a TPB solution, to form a precipitate (Fig. 2), which was then filtered, washed with water and desiccated in the ambient temperature [6,7]. NaTPB is a salt with a large hydrophobic anion. Such salts are usually used as precipitating reagents in inorganic or organometallic experiments [6,7].

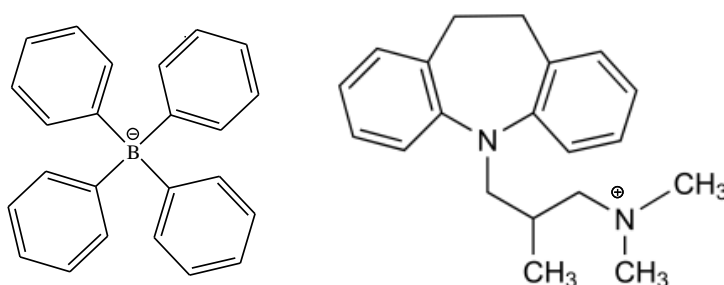


Figure 2. Chemical structure of ion pair

2.4. Preparing the PME and ASS-PME

Two types of sensors were prepared using a polymeric membrane, which was composed of the TMP-TPB ion-pair, PVC, a suitable plasticizer and an ionic additive. The ingredients were admixed in a 5-mL beaker containing tetrahydrofuran (THF), and the mixture was heated to slowly evaporate its THF content and form an oily concentrated solution.

For making the PME, the tip of a plastic tube (~3 mm o.d.) was inserted into the above-described oily mixture for 10 s. This way a ~0.3 mm transparent membrane was formed on the tip of the tube, which was then stored under room temperature for about 5 hours, to lose its THF content. The so-prepared electrode was next filled with a 1.0×10^{-3} M solution of TMP and conditioned in the same for 15 hours [24-28].

In the case of the ASS-PME, instead of the above mentioned tubes, conductive composite of MWCNTs-epoxy resin deposited on a copper wire, was used as the internal contact and transducer and inserted into the oily mixture for being coated. The composite was composed of 0.50 g (50% w/w) of graphite powder, 0.05 g (5% w/w) of MWCNTs, 0.30 g (30% w/w) of the epoxy, and 0.15 (15% w/w) of the hardener. To prepare the transuding element the ingredients were mixed in THF and then allowed to lose its solvent content by resting in the air for about 20-30 min. Next the resulting paste was coated on the polished surface of a shielded copper wire (0.5 mm diameter and 15 cm length).

The coating was performed by inserting the wire into the paste for about 10 times allowing the resulting assembly to dry for about 10 h. The ASS contact was then dipped into the solution of the optimal polymeric membrane solution for 3 times and then allowed to dry in air for one day and then conditioned in a 10^{-3} M solution.

2.5. The TMP solutions

Since TMP maleate is water soluble, a 0.1 M solution of the compound was prepared in distilled water and as the stock solution. The rest of the solutions in the concentration range of 1×10^{-9} - 1×10^{-2} M were prepared by diluting the stock solution and all solutions were stored in a refrigerator at 4°C before use.

The real sample solutions were prepared by milling 20 tablets of TMP wand taking the weight equivalent of 5 tablets (each tablet ~ 25 mg of TMP) were carefully weighed and transferred to a 100-mL flask and dissolved in an acetate buffer (0.1 M; pH=4). The solutions were next taken filtered using a Millipore filter (0.45 mm) and used as the stock solution for real samples.

3. RESULTS AND DISCUSSION

The application of potentiometric sensors offers advantages of low cost, simplicity and high speed for the analysis of different ingredients of pharmaceutical samples. Although the instruments cannot fully compete with advanced analytical instruments they can produce accurate results in the analysis of pharmaceutical formulations. Since the most important section of PME is the polymeric membrane, the composition of this membrane directly affect the performance of such instruments.

3.1. Composition of the Polymeric Membrane

The effects of the membrane composition on the responses of the electrodes were evaluated. The ingredients present in the membranes are the polymeric matrix (PVC), the plasticizer and the selectophore (ion-pair), each of which plays a specific role in the function and response of the electrode based on the membrane. As established by numerous reports membranes with a plasticizer/PVC ratio of around 2.2 produce optimal responses [25-30]. To keep the experiments easier to follow 30 mg of PVC was used in all optimization experiments (Table 1).

Table 1. Compositions of the membranes used in preparation of TMP sensor

Entry	PVC (%wt.)	Plasticizer (%wt.)	Ion-pair (%wt.)	additive (NaTPB) (%wt.)	Slope* (mV/decade)	R ²
1	30	DBP,70	0	0	1.9±0.3	0.870
2	30	DBP,64	6	0	49.4±0.3	0.981
3	30	DBP,63	7	0	32.2±0.3	0.985
4	30	DBP,65	5	0	39.2±0.3	0.990
5	30	DBP,64	6	0	49.4±0.3	0.989

6	30	DBP,63	6	1	57.1±0.3	0.997
7	30	DBP,62	6	2	47.6±0.3	0.997
8	30	NB,63	6	1	34.8±0.3	0.985
9	30	BA,63	6	1	27.9±0.3	0.973

*standard deviation of five repeated measurements

The plasticizer, on the other hand acts as a solvent, which allows for the homogeneous dissolution and diffusional mobility of the selectophore through the membrane [27-32]. This liquid ingredient of the membrane should be water-immiscible, have low vapor-pressures, be chemically inert and compatible with PVC. The selectivity of polymeric membrane electrodes is greatly influenced by the choice of the solvents. As it can be seen in Table 1, in this work, three solvents with different polarities (i.e. dielectric constants (DCs)) were evaluated. These were dibutyl phthalate (DBP, DC=6.4), nitrobenzene (NB, DC=35.7) and benzylacetate (BA, DC=~5.7). The experiments revealed the membranes containing DBP produced better responses in terms of linear response and sensitivity, which can be attributed to the better extraction of Trimipramine maleate into the membrane phase in their presence. Table 1 further shows that membranes containing 6 mg of the ion-pair have responses closer to a Nernstian behavior. Further BA and NB led to poorer responses as compared to DBP. Based on the results in Table 1, membrane no. 6 containing 30% wt. of PVC, 6% wt. of the ion-pair, 1% wt. of NaTPB and 63% wt. of DBP produces the optimal results, and was hence used for building the ASS-PMEs.

3.2. Calibration Curve and the Statistical Data

The calibration curve (potential vs. $-\log [\text{TMP}]$) was plotted through recording the potential responses of the electrodes to a series of standard solutions each with a 10 fold difference in concentration with the previous one (Fig. 3). The linear section of the calibration curve shows the measuring range of the sensor. As mentioned earlier, PME sensors for pharmaceutical compounds have been found to produce linear results between 10^{-5} to 10^{-2} M [24-31]. The PME developed in this work was found to have a linear response from 1.0×10^{-6} to 1.0×10^{-2} M. According to Fig. 3, the potential response of the PME was 57.1 ± 0.3 mV per decade was found. In the case of the ASS-PME, the response was linear over a wider range of 1.0×10^{-7} to 1.0×10^{-4} M and a slope of 58.2 ± 0.4 mV per decade was observed. The lower detection limits of the PME and ASS-PME were also found to be as low as 6.3×10^{-7} and 1.0×10^{-7} M.

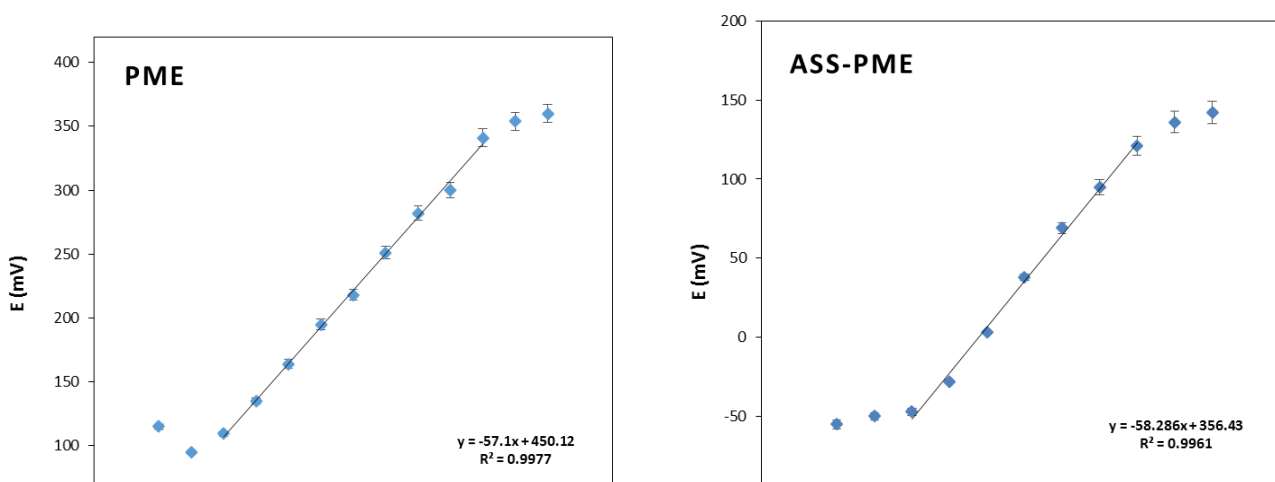


Figure 3. Calibration curves of the PME and ASS-PME; each point represents the average of five replicate measurements.

3.3. Response Time

The response time (RT) of a sensor shows the time required for the sensor to reach a stable response within ± 1 mV of the final potential, upon a tenfold change in the concentration of the test solution. RT can be determined through the successive immersions of a sensors into a series of analyte solutions with tenfold concentration differences [29-32]. In this case solutions in the concentration range of 1.0×10^{-6} to 1.0×10^{-2} M were used for the tests and the RT values for the PME and ASS-PME were determined to be 15 and 11 s, respectively.

3.4. The effect of pH on the potential response

The electrodes was evaluated using 1.0×10^{-3} , and 1.0×10^{-5} M TMP solutions and varying the pH in the range of 1.0 to 10.0. The pH changes were induced using concentrated NaOH or HCl, and the results are shown in Fig. 4, according to which the potential response of both electrodes was pH-independent in the range of 3.5 to 7.0.

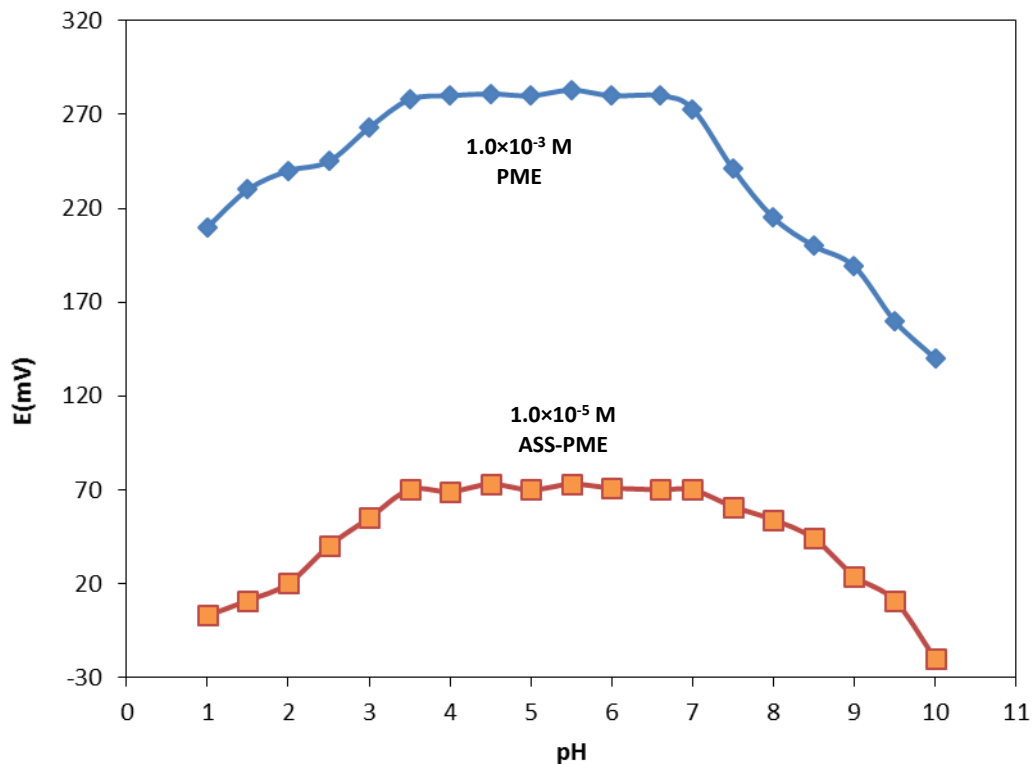


Figure 4. Potential/pH behavior of the electrodes in 1.0×10^{-3} and 1.0×10^{-5} M solutions of TMP, for the PME and ASS-PME

Below 3.5 and above 7.0, the potential response of the electrodes changed with pH, which could be attributed to the removal of the positively charged TMP cations, as well as decrease in the solubility of the drug in the high and low pH values, respectively.

3.5. Life-times of the electrodes

Potentiometric sensors are known to have lifetimes of around 4 to 10 weeks [28-32]. To evaluate the lifetime of potentiometric sensors, which is an important factor for evaluating a sensor the changes in the slopes and detection limits of sensors are evaluated over time. During the experiments three PMEs and three ASS-PMEs were chosen and used for 1 hour/day for 10 weeks and the results were recorded (Table 2). According to these experiments after 7 weeks of use, the potential slope of the PMEs decreased, while their lower detection limits slowly increased. The ASS-PMEs, on the other hand, had a longer lifetime and the changes were observed after 9 weeks. The alterations in the response behaviors of the sensors are attributed to the leaching of the membrane ingredients into the solution after repeated usage.

Table 2. Lifetime of PME and ASS-PME

Week	PME		ASS-PME	
	Slope (mV per decade)	DL (M)	Slope (mV per decade)	DL (M)

First	57.1±0.3	6.3×10 ⁻⁷	58.2±0.4	1.0×10 ⁻⁷
Second	57.0±0.4	9.0×10 ⁻⁷	58.1±0.3	5.2×10 ⁻⁷
Third	56.8±0.5	1.5×10 ⁻⁶	58.0±0.4	6.5×10 ⁻⁷
Fourth	56.6±0.5	5.5×10 ⁻⁶	57.8±0.3	8.0×10 ⁻⁷
Fifth	55.7±0.3	8.0×10 ⁻⁶	57.6±0.4	9.5×10 ⁻⁷
Sixth	55.5±0.4	9.0×10 ⁻⁵	57.5±0.5	1.5×10 ⁻⁶
Seventh	55.2±0.4	1.5×10 ⁻⁵	57.4±0.6	3.0×10 ⁻⁶
Eighth	37.3±0.5	1.0×10 ⁻⁴	57.2±0.5	4.0×10 ⁻⁶
Ninth	22.6±0.7	2.5×10 ⁻⁴	57.0±0.4	7.5×10 ⁻⁶
Tenth	17.2±0.8	5.0×10 ⁻⁴	40.7±0.7	1.0×10 ⁻⁵

3.6. Analytical validation

The sensors were used for the analysis of TMP in pure solutions and in pharmaceutical tablets, to validate their applicability. To this end the linear range, detection limit, selectivity, precision, accuracy, and ruggedness/robustness of the sensors should be assessed. The evaluations were started by measuring the concentration TMP in pharmaceutical formulations using the calibration method and the results are presented in Tables 3-5. The results were found to be in good agreement with the values expressed on the labels.

Table 3. Potentiometric determination of TMP in 25 mg/tab pharmaceutical formulations

Sample	labeled amount (mg/tablet)	find by the electrode*	Recovery	RSD
1	25	24.2	97%	1.05%
2	25	23.7	95%	
3	25	24	96%	

Table 4. Potentiometric determination of TMP in 100 mg/tab pharmaceutical formulations

sample	labeled amount (mg/tablet)	find by the electrode*	Recovery	RSD
1	100	97.1	97.1%	0.67%
2	100	97.8	97.8%	
3	100	96.5	96.5%	

Table 5. Potentiometric determination of TMP in 4% Drop pharmaceutical formulations

sample	labeled amount (Drop 4%)	find by the electrode*	Recovery	RSD
1	4	3.6	90%	3.15%
2	4	3.8	95%	
3	4	3.6	90%	

The selectivity of the PME and ASS-PMEs were also studied, using samples further containing some interfering species, and the results were expressed as the selectivity coefficient. In this work the matched potential method (MPM) was used for determining the selectivity coefficients [35-38] and the selectivity coefficients are summarized in Table 6. The obtained results indicate that the interferences in the TMP response from the ionic and non-ionic species are not significant.

Table 6. Selectivity coefficients obtained for TMP sensors

Interfering species	PME	ASS-PME
	Log (K_{MPM})	Log (K_{MPM})
Na⁺	-3.6	-3.7
K⁺	-3.2	-3.0
NH₄⁺	-2.7	-2.8
Ca²⁺	-3.6	-3.5
Mg²⁺	-3.5	-3.6
Cl⁻	-3.7	-3.6
NO₃⁻	-4.0	-4.3
Lactose	-4.6	-4.4
Glucose	-4.5	-4.4

To evaluate the repeatability of the results obtained using the sensors, initially three standard synthetic samples were prepared and analyzed five times using the electrodes. The RSD% values 3.73 and 3.33% of the PME and ASS-PME. The reproducibility of the results was determined in the following fashion. 3 PMEs and 3 ASS-PMEs were used for the analysis of a standard solution. The RSD% values obtained this way were 3.62 and 3.57% for the symmetrical and asymmetrical electrodes.

The ruggedness of the the analyses performed using the electrodes was also evaluated through comparing the results of the experiments performed by two analysts in intra- and inter-day regimes in the same laboratory. None of the RSD% values for the PMEs exceeded 4.5%, and the values obtained for the ASS-PME did not exceed 3.7%. Eventually, the robustness of the methods was evaluated while important parameters, i.e. pH of the solution and the laboratory temperature, were slightly changed. Under these conditions the TMP recovery values in percent were less than 4.35%.

According to the literature survey, there is no reports on potentiometric sensors for TMP determination. However, Table 7 shows the comparison of the proposed sensors with another electrochemical electrodes reported for TMP determination. Although voltammetric method has a lower detection limit, suffer from limited linear range. Potentiometric sensor offers a wide linear range of determination and simple preparation and operator. Also, theses sensors are a good choice for determination of active ingredient in pharmaceutical formulations.

Table 7. Comparison of the proposed sensors with a previous report on TMP electrochemical determination

Electrode	Technique	DL	[Ref.]
Carbon paste electrode (CPE) modified with some fatty acids	Voltammetry	1.0×10^{-9} M	[39]
PME ASS-PME	Potentiometry	6.3×10^{-7} M 1.0×10^{-7} M	This work

4. CONCLUSIONS

A PVC membrane electrode (PME), and all solid state polymeric membrane electrode (ASS-PME) capable of determining Trimipramine were developed using an ion-pair selectophore. The polymeric membrane used in the electrodes was found to produce the best results when containing 6% wt. of TMP-TPB (the selectophore), 63% wt. of dibutyl phthalate, 30% wt. of PVC, and 1% wt. of an ionic liquid. The ASS element used in the ASS-PME was composed of a conductive composite of graphite, MWCNTs, and an epoxy resin coated on a copper wire. This ASS element was next coated with a thin layer of the PVC membrane. The sensors showed a Nernstian behavior (slope of 57.1 ± 0.3 mV/decade for the PME, and 58.2 ± 0.4 mV/decade for the ASS-PME) were observed in the concentration ranges of 1.0×10^{-6} to 1.0×10^{-2} M and 1.0×10^{-7} to 1.0×10^{-4} M respectively. Validation of the analytical methods based on using the electrodes proved they were applicable to the analysis of Trimipramine in pharmaceutical formulation.

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