Anal. Bioanal. Electrochem., Vol. 8, No. 1, 2016, 92-103

Analytical & Bioanalytical Electrochemistry

www.abechem.com

Full Paper

Verapamil All-Solid-State Sensor and its Application for the Analysis of Pharmaceutical Formulations

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Received: 28 October 2015 / Received in revised form: 26 December 2015 / Accepted: 10 January 2016 / Published online: 15 February 2016

Abstract- An all-solid-state polymeric membrane electrode (ASS-PME) has been constructed for the analysis of Verapamil (VP) which is a calcium channel blocker used in the management of angina, arrhythmia and hypertension. The PME element of the ASS-PME has been based on the application of an ion-pair sensing reagent and the results revealed the best sensing behavior to occur in the case of compositions of 6%wt VP-tetraphenyl borate (the sensing element), 62%wt dioctyl phthalate as the solvent mediator, 30%wt poly(vinyl chloride) and 2%wt of an ionic liquid. The ASS element, on the other hand, is made of a composite of graphite, multiwall carbon nanotubes (MWCNTs), and epoxy resin coated on a Cu wire. The response behavior of the ASS-PME device was found to be linear from 1.0×10^{-7} to 1.0×10^{-3} M, with a slope of 55.3±0.2 mV/decade and a detection limit of 7.0×10^{-8} M was reached under the optimal conditions. The device was also successfully used in the real sample analysis.

Keywords- Verapamil, Sensor, All solid state, Potentiometry, Pharmaceutical formulation

1. INTRODUCTION

Medications containing 5-[N-(3,4-dimethoxyphenylethyl)methylamino]-2-(3,4-dimethoxyphenyl)-2-isopropylvaleronitrile hydrochloride or verapamil (Fig. 1) are used for the treatment of various heart and blood pressure conditions and the fast acting formulations

of this compound, i.e. Verapamil hydrochloride and Isoptin are prescribed for angina, arrhythmia and hypertension.

Verapamil-based medicines appear in the form of 40 mg to maximum 180 mg tablets, or slow release forms where the dosage ranges from 120 to 240 mg. Pharmacological studies have revealed that of the 90% of verapamil which is absorbed through the digestive tract, only 10–20% of the compound finds its way to the blood intact, through penetration [1], and the rest undergoes a so-called first-pass effect in the liver. When administered to humans, the compound converts to over 6 metabolites [2].

The analysis of the verapamil hydrochloride content of biological and pharmaceutical samples has been carried out through some methods ranging from the chromatography-fluorimetry [3] or chromatography-UV [4] procedures applied to biological fluids, as well as gas–liquid chromatography [5], capillary gas chromatography [6], potentiometry–conductometry [7], stripping voltammetry [8], atomic emission spectrometry [9], and mass spectrometry [10].

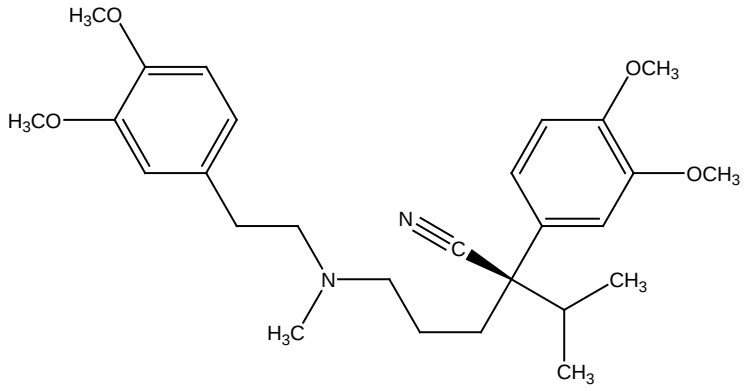

Fig. 1. Chemical structure of Verapamil

Ion-selective electrodes (ISEs), which are among the simple and facile tools used for the analysis of a wide range of chemical compounds, fall into various categories, such as PVC membrane electrodes (PME) [11-23], coated wire electrodes (CWE) [24-26], carbon paste electrodes (CPE) [27], all solid state electrodes (ASS) [28-33] and field effective transistors (FET) based sensors.

From a structural point of view, the sensors are also divided to symmetric and asymmetric groups based on the physico-chemical environment experienced by the PVC element. By definition, symmetric devices can be described as those in which, the PVC membrane is an internal and an external solution, while in asymmetric configurations, only the outer surface of PVC element comes in contact with the test solution, while its other side touches a solid state transducer. A symmetric membrane electrodes can easily remove during the long time

treatments. One major difference between symmetric and asymmetric devices is that the former suffer comparatively higher detection limits, usually in the order of 10^{-5} to 10^{-7} M. The asymmetric electrodes, on the other hand, are improved in this regard and typically reach detection limits of 10^{-8} M or less.

A category of asymmetric devices are the all-solid-state polymeric membrane electrodes (ASS-PMEs), in which a solid state element like a polymeric composite of graphite mixed with epoxy resin, which is used as the internal contact, is further coated with an ISE PVC membrane. These devices have been found to present improved detection limits, mechanical stability and structural simplicity [28-33].

Based on our teams experience in the development of symmetric ISEs for different compounds, including verapamil [34], this work was focused on evaluating the possibility of developing a verapamil ASS-PME, based on an ion-exchange mechanism. The device was practically optimized and evaluated for the analysis of verapamil in pharmaceutical samples.

2. EXPERIMENTAL SECTION

2.1. Measurements

The ASS-PME was used as the indicator electrode in the following cell assembly:

Cu wire | ASS layer | PVC membrane | sample solution || Ag-AgCl, KC1 (satd.)

In which the Ag/AgCl electrode (Azar-Elelectrode Co., Iran), used as the reference electrode, was linked to the ASS-PME device through an ion analyzer (with a 250 pH/mV meter with ±0.1 mV precision). The calibration methods using different standard solutions, was used for the measurements.

2.2. Materials and Reagents

Sodium tetraphenyl borate (NaTPB), potassium tetrakis (p-chlorophenyl) borate (KTPClPB), dioctyl phthalate (DOP), nitrobenzene (NB), dibutyl sebacate (DBS), benzyl acetate (BA), *o*-nitrophenyloctylether (NPOE), 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6), tetrahydrofuran (THF), the other solvents, salts and graphite powder (1–2 μm)) were of analytical reagent grade and were procured from Merck Co. High-molecular weight PVC was from Fluka Co and the MWCNTs (10-40 nm diameters, 1-25 μm length, core diameter: 5-10 nm, BET: 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, Tehran, Iran. The Epoxy (macroplast Su 2227) and the hardener (desmodur RFE) were obtained from Henkel and Bayer Ag (Germany), respectively. VP hydrochloride was obtained from Sigma-Aldrich and the pharmaceutical

formulations were received from a local pharmacy (Tehran, Iran).

To obtain VP.HCl solutions, a 0.1 M verapamil solution in water was prepared and diluted to prepare the rest of the solutions in the range of 1×10^{-8} to 1×10^{-2} M. All solutions were kept at 4 °C.

The real samples solutions were prepared in the following fashion. Twenty 40 mg VP.HCl tablets were crushed and powdered, and then an exact weight equivalent of 5 tablets was transferred into a 100-mL volumetric flask and dissolved in distilled. Then the solution was diluted with an acetate buffer (0.1 M; pH=4) and filtered using a Millipore filter (0.45 mm) and used as the stock solution.

2.3. Synthesis of the ion-pair

The ion-pair complex to be used in the PME was prepared by mixing solutions of VP-HCl (40 mg in 5 mL distilled water) and a solution of suitable an organic salt with hydrophobic large anions and small inorganic cations (e.g. sodium tetraphenyl borate (NaTPB) or potassium tetrakis (p-chlorophenyl) borate). The resulting precipitate was filtered, and rinsed with distilled water, then dried in room temperature.

2.4. Preparing the ASS-PMEs

The PME element was prepared by mixing various weights of the ion-pair sensing compound, PVC, a plasticizer and an ionic additive in tetrahydrofuran, and aging the resulting solution under mild heating to evaporate the solvent, so as to form a viscous solution [11-15]. In parallel the conductive polymeric composite (CPC) was prepared by mixing known quantities of the graphite powder, MWCNTs, epoxy, and hardener in tetrahydrofuran (THF). The resulting CPC paste was then quoted on a copper wire (0.5 mm diameter and 15 cm length) to form the ASS element, after evaporating its solvent content for 20-30 min. The coated paste was left to dry for 10 h and next polished.

The evaluations showed that the best results were achieved with an ASS element containing 30% wt. of the epoxy resin, 15% wt. of the hardener, 5% wt. of MWCNTs and 50% wt. of graphite powder. Finally the viscose PME solution was coated on this element by immersing it into the mixture 3 times. Then, the whole ASS-PME system was let to dry for one day and conditioned in a 10^{-3} M solution of VP.HCl before use.

3. RESULTS AND DISCUSSION

3.1. The Composition of the Polymeric Membrane

The various compositions of the PME solutions prepared so as to optimize the ASS-PME are given in Table 1. It has been established that the plasticizer/PVC ratio should be around 2

[34-40] to yield the optimal response. To ease the calculations 30%wt of PVC was used in all compositions.

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

No.	Composition of the membrane			Characterization of PME		
	Plasticizer	**Ion-pair**	**Ionic Additive**	**Slope mV/decade**	**LR (M)**	**Response time**
1	DOP, 66	4	-	28.2±0.2*	1.0×10^{-4}-1.0×10^{-3}	48 s
2	DOP, 65	5	-	37.1±0.3	1.0×10^{-4}-1.0×10^{-3}	47 s
3	DOP, 64	6	-	46.3±0.4	5.0×10^{-5}-1.0×10^{-3}	43 s
4	DOP, 63	7	-	46.1±0.3	5.0×10^{-5}-1.0×10^{-3}	41 s
5	DOP, 63	6	1 NaTPB	53.1±0.4	5.0×10^{-6}-1.0×10^{-3}	33 s
6	DOP, 62	6	2 NaTPB	54.3±0.2	2.0×10^{-7}-1.0×10^{-3}	29 s
7	DOP, 61	6	3 NaTPB	54.3±0.3	2.0×10^{-7}-1.0×10^{-3}	28 s
8	DOP, 62	6	2 KpClTPB	54.2±0.2	2.0×10^{-7}-1.0×10^{-3}	28 s
9	DOP, 62	6	2 $[bmim]PF_6$	55.3±0.2	1.0×10^{-7}-1.0×10^{-3}	22 s
10	DBS, 62	6	2 $[bmim]PF_6$	55.2±0.3	1.0×10^{-7}-5.0×10^{-3}	22 s
11	NB, 62	6	2 $[bmim]PF_6$	51.4±0.4	3.0×10^{-7}-1.0×10^{-3}	24 s
12	BA, 62	6	2 $[bmim]PF_6$	53.5±0.3	2.0×10^{-7}-1.0×10^{-3}	22 s
13	NPOE, 62	6	2 $[bmim]PF_6$	51.3±0.2	3.0×10^{-7}-1.0×10^{-3}	25 s

*standard deviation of five repeated measurements

Various solvent mediators (plasticizers) were tested in the PME composition. Plasticizers are non-volatile water-immiscible solvents, which facilitate the movement of the sensing material throughout the PME [41-45]. From the different plasticizers used, i.e. dibutyl sebacate (DBS) with a dielectric constant (DC) of 4.5, dibutyl phthalate (DOP) with a DC of 6.4, ortho-nitrophenyloctyl ether (NPOE) with a DC of 24, nitrobenzene (NB) with a DC of 35.7 and benzylacetate (BA) with a DC of 5.7 (Table 1), DOP showed the optimal results (no. 9) and the resulting ASS-PME showed the best performance. The behavior can be attributed to the hydrophobicity of the VP cation, which naturally tends to favor being extracted into a plasticizer with a low dielectric constant.

Another element of the PME is its ionic additive content. These compounds are incorporated in the PME composition so as to reduce its Ohmic resistance. Ionic additives are used in relatively small amounts to avoid any interference in the ion-exchange phenomena on their part, which can damage the selectivity of the device. The ASS-PME of the present work was incorporated with a room temperature ionic liquid (RTIL) $[bmim]PF_6$, as a novel family of ionic additives, as well as Sodium tetraphenyl borate (NaTPB), potassium tetrakis (p-

chlorophenyl) borate (KTPClPB). The results showed that from among the additives evaluated [bmim]PF_6 led to the optimal sensing behavior (no. 9).

From the results illustrated in Table 1, one can evidently see that membrane composition no. 9 (i.e. 6%wt of ion-pair, 62%wt of DOP, 30%wt of PVC, and 2%wt of [bmim]PF_6) leads to a near Nernstian slope of 55.3±0.2 mV/decade. Consequently all evaluations were made using an ASS-PME with the optimal ASS and PME compositions.

3.2. Calibration curves

To perform the measurements of VP.HCl by the developed ASS-PME a calibration curve (E *vs.* –log [VP]) was depicted (Fig. 2) and the curve was found to follow the Nernst equation in the range of 1.0×10^{-7} to 1.0×10^{-3} M and resulted in a semi-Nernstian slope of 55.3±0.2 mV per decade.

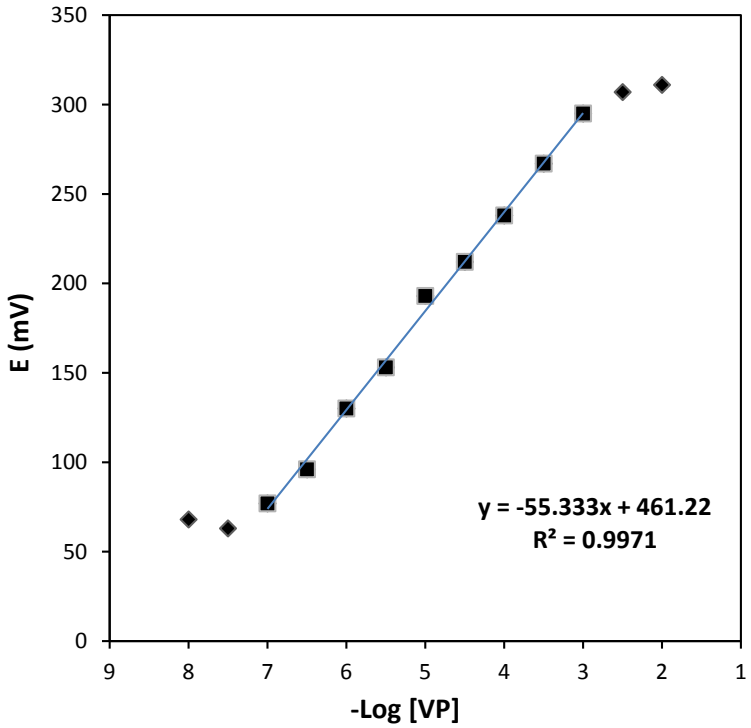

Fig. 2. The calibration curve of ASS-PME response to solutions of VP (each point is the average of 5 replicate measurements)

As already mentioned in the case of most of the PME sensors, which are symmetrical devices, used for the analysis of pharmaceuticals [34,35], the response is linear in the range of 10^{-5} to 10^{-2} M. This is a proof of the improvement of the response range in the asymmetric ASS-PME, which as described, produces a linear response from 1.0×10^{-7} to 1.0×10^{-3} M. The

extrapolation of the linear segments of the calibration at low concentrations helped evaluate the lower detection limit of the sensor as being 7.0×10^{-8} M.

3.3. Response Time, pH-Potential behavior and the life-time of the ASS-PME

The response time of the ASS-PME, which similar to other potentiometric devices, can be defined as the period required for reaching the final equilibrium response ±1 mV, upon inducing a 10 fold concentration increase in the test solution was also evaluated for the developed sensor through successive immersions of the sensors in the analyte solution each with a 10 fold concentration difference [36-41]. The results for the measurements using VP solutions in the range of 1.0×10^{-7} to 1.0×10^{-3} M, revealed the response time of the sensor to be 22 s.

To monitor the pH-potential behavior of the ASS-PME, the pH of a 1.0×10^{-5} M VP test solution was altered from 1.0 to 10.0 by adding concentrated sodium hydroxide and hydrochloric acid solutions, and the recorded results were depicted in Fig. 3. These results revealed that with a pH window of 3.0 to 6.0 the potential readings were independent from the pH of the solution while beyond the two extremes of this range the potential response dropped. The drop at the higher pH values was attributed to the masking of the positive charge the VP cations, while this behavior at more acidic media was attributed to the reduced solubility of VP, as well as the leaching out of the PME ingredients at pH < 3.

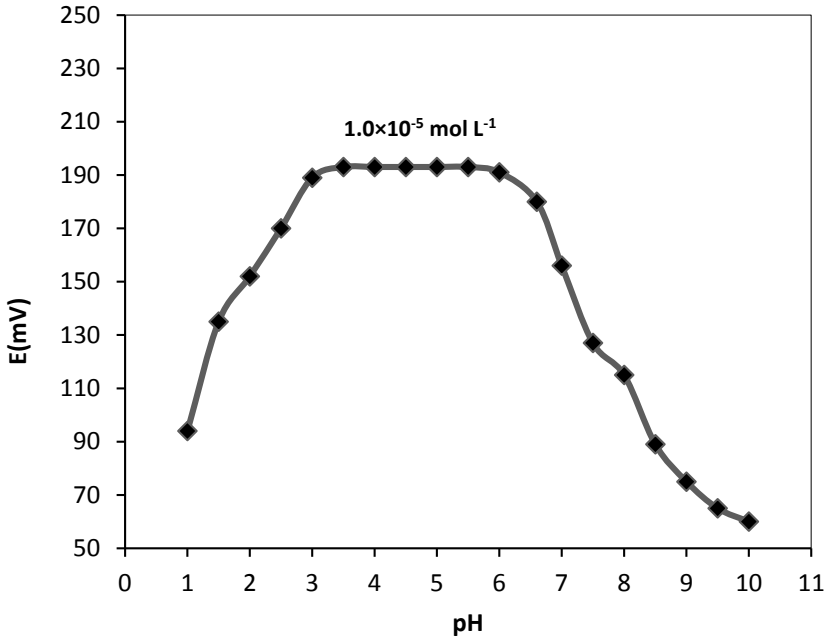

Fig. 3. pH *vs*. potential behavior of the ASS-PME in a 1.0×10^{-5} M VP solution with varying pH.

To assess the lifetime of the developed device the changes in changes in the potential slope and detection limit of the device over time were recorded. To this end, 3 ASS-PMEs were chosen and daily used for 1 hour/day in a period of 10 weeks and the readings were recorded (Table 2). The results illustrated that after a period of 8 weeks of using the devices under the explained conditions the potential slopes gradually decreased while the and lower detection limits increased. It is well-known that ASS-PMEs are known to possess improved life-times as opposed to symmetrical PMEs as a result of their improved properties and mechanical stability, however the mentioned deterioration in the slope and detection limits are inevitable due to the leaching out of the PME ingredients as a result of chronic use.

Table 2. Lifetime of ASS-PME

Week	ASS-PME	
	Slope (mV per decade)	DL (M)
First	55.3±0.2	7.0×10^{-8}
Second	55.2±0.3	7.2×10^{-8}
Third	55.0±0.4	7.3×10^{-8}
Fourth	54.8±0.3	7.5×10^{-8}
Fifth	54.6±0.2	7.6×10^{-8}
Sixth	54.5±0.3	7.8×10^{-7}
Seventh	54.4±0.4	7.0×10^{-7}
Eighth	54.3±0.4	6.8×10^{-7}
Ninth	54.2±0.3	6.5×10^{-7}
Tenth	33.5±0.6	1.0×10^{-5}

3.4. Validation of the ASS-PMEs

The applicability of the devices to real-time analyses was evaluated through using them in the determination of VP in pure solutions and in pharmaceutical tablets. The validation of the sensors was carried out through the evaluation of their linear range and detection limit, selectivity, precision, accuracy, and ruggedness/robustness.

To this end the developed ASS-PMEs were used to analyze the VP content tablets using the calibration method (Table 3), and the results were compared against those produced by HPLC standard method. The comparisons did not indicate any significant differences

between the two sets of data acquired.

To assess the selectivity of the ASS-PMEs, which can be described as their tendency to respond to the analyte in mixed solutions further containing interfering species different approaches exist, among which the matched potential method (MPM) was chosen [46-49], and the data acquired through the method are summarized in Table 4. The results indicated that the interferences to the response of the sensor from the ionic and non-ionic species tested did not leave considerable effects, and hence the response in the presence of the interfering species is valid.

Table 3. Measurement of VP.HCl in pharmaceutical formulations by the proposed sensors and standard methods

Sample	Labeled amount (mg/tab.)	Found by the ASS-PME* (mg/tab.) n=5	Standard method n=5
Sample 1	40	39.66±0.33	39.08±0.16
Sample 2	40	40.45±0.31	40.77±0.15
Sample 3	40	41.60±0.24	41.34±0.19

* Averages of five repeated measurements

Table 4. Selectivity coefficients obtained for VP ASS polymeric membrane sensor

Interfering species	ASS-PME Log (K_{MPM})
Na^+	-6.6
K^+	-6.3
NH_4^+	-6.0
Ca^{2+}	-6.8
Mg^{2+}	-6.9
Cl^-	-6.7
NO_3^-	-6.8
Lactose	-6.9
Glucose	-6.8

To evaluate the repeatability of the results, 3 standard synthetic samples were prepared and used for repeated measurements. The RSD% of the results obtained was calculated to be 3.3%. Further the ruggedness of the device was assessed through comparing the results and RSD% values obtained through the intra- and inter-day analyses, in the same laboratory and the difference in the results did not exceed 3.8%. Finally the robustness of the ASS-PME was obtained by slightly changing important parameters like the pH of the solution and the laboratory temperature, during the measurement of the VP recovery values, which were found to be good under most conditions and not significantly change by alerting these critical parameters.

4. CONCLUSIONS

The new verapamil selective ASS-PME which was developed, was successfully used to the analysis of verapamil in different samples. The study revealed the best ion-pair based ASS-PME to have a PME containing 6%wt of VP-tetraphenyl borate, 62%wt dioctyl phthalate, 30%wt of poly(vinyl chloride), and 2%wt of an ionic liquid. The ASS element was composed of a conductive composite of graphite, MWCNTs, and epoxy resin coated on a copper wire. The optimized ASS element was coated with the optimal PME to yield the ASS-PME and the resulting sensor showed a near Nernstian slope of 55.3±0.2 mV/decade over a wide concentration range of 1.0×10^{-7} to 1.0×10^{-3} M. The validity evaluations of the selectivity, pH behavior, response time, ruggedness and robustness of the device revealed that the developed ASS-PME is applicable in the quality control measurements of verapamil in pharmaceutical formulations.

Acknowledgement

The financial support of this work by research council of University of Tehran is gratefully acknowledged.

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