Full Paper

Novel All-solid-state (ASS) Polymeric-Membrane-Sensor (ASS-PME) for Diltiazem and Its Application

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Abstract- Diltiazem (DZ) is a common benzodiazepine family, which is a calcium channel blocker usually supplied and used as a hydrochloride salt. The widespread use of the pharmaceutical has naturally created an increasing need for its analysis. It is therefore the main objective of the present work to develop an all-solid-state (ASS) polymeric-membrane-electrode (PME) for the analysis of DZ hydrochloride in pharmaceutical formulations. The developed ASS-PME is based on the application of an ion-pair agent in its sensing element. Experiments showed that the optimal results could be achieved with a PME containing 10% wt. of the ion-pair agent (i.e. DZ-tetrakis (p-chlorophenyl) borate (TPClPB)), 56% wt. of dibutyl phthalate (DBP) as the membrane solvent, 30% wt. of polyvinyl chloride (PVC), and 4% wt. of a room temperature ionic liquid (RTIL). Next the polymeric membrane was coated on an ASS element made of a composite of an epoxy resin, graphite and multiwalled carbon nanotubes (MWCNTs) which was deposited on a copper wire, as the internal contact. The DZ-ASS-PME revealed a potential response of 56.8 ± 0.3 mV/decade over a wide concentration range of 2.0×10^{-7} to 1.0×10^{-3} M and was found to be suitable for applied to the analysis of DZ, as proved by the application of the ASS-PME in the measurement of DZ concentration in DZ tablets.

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

1. INTRODUCTION

As a calcium ion influx inhibitor, [(2S-*cis*)-3-(Acetyloxy)-5-[2-(dimethylamino)ethyl]-2,3-dihydro-2-(4-methoxyphenyl)-1,-5-benzolthiazepin-4(5H)-one) or diltiazem (DZ) (Fig. 1) [1] is commonly prescribed for conditions such as hypertension, angina pectoris and cardiac arrhythmias [2]. In the case of angina pectoris, which is the result of oxygen shortage in the muscular wall of the heart, the treatment requires increasing the blood flow, which is achieved either through increasing the oxygen supply of the blood or decreasing the oxygen demand by the target tissue [3].

Analysis of diltiazem in pharmaceutical and in biological fluids has been performed through various techniques ranging from high performance liquid chromatography (HPLC) [4-8], capillary electrophoresis [9,10], high performance thin layer chromatography (HPTLC) [11], spectrophotometry [12-14], and voltammetry [15],. All these techniques have various advantages like good sensitivity and detection limits, however, the potentiometric ion selective electrodes offer additional advantages including simplicity and rapidity of analysis over a wide range of concentration, very good selectivity and low limits of detection. In this light much concentration has been directed towards the development of potentiometric sensors for the determination pharmaceutical analytes [16-21].

Potentiometric ion-selective electrodes can be classified into different categories like PVC membrane electrodes (PMEs), coated wire electrodes (CWE), carbon paste electrodes (CPE), all solid state electrodes (ASS) and field effective transistors (FET) [22-24]. Another classification of these electrodes is dividing them into symmetrical and asymmetrical devices based on the similarity of difference of the physico-chemical environment on the two sides of the sensing element. Symmetrical devices, where the internal and external environments experienced by the sensing material are identical, reveal different behaviors as compared to the asymmetrical devices like CWEs, FETs, and ASSs, where the inner surface of the sensing element is commonly in contact with a solid contact, while the outside surface is in contact with the liquid sample .These differences include improved mechanical stability and limits of detection (i.e 10^{-5} to 10^{-7} M in the case of symmetrical devices, and about 10^{-8} M or lower in the case of the asymmetrical sensors) in the case of the asymmetrical devices.

Based on this definition ASS-PMEs are asymmetric electrodes [25-33], where a conductive composite deposited on a metal wire plays the role of the internal contact to transduce the chemical signal and the selectivity is introduced through the coating of the ASS elements with an outer layer of a selective PVC membrane. ASS-PMEs enjoy the classical advantages of asymmetrical devices including improved detection limits, better mechanical stabilities and simpler structures.

It is therefore the aim of the present work to introduce a novel ASS-PME for the selective determination of diltiazem. The information on a previously reported symmetrical sensor for diltiazem [21] was used as a basis of the development of the ASS-PME and the device was

used for the determination of the analyte in pharmaceutical formulations, to evaluate its applicability to real samples. The ASS-PME was based on an ion-pair compound, which was incorporated in the composition of the polymeric membrane coated on the solid contact element and the results proved the electrode to produce acceptable results in terms of selectivity, applicability range and detection limit as compared to the rivaling PME [21].
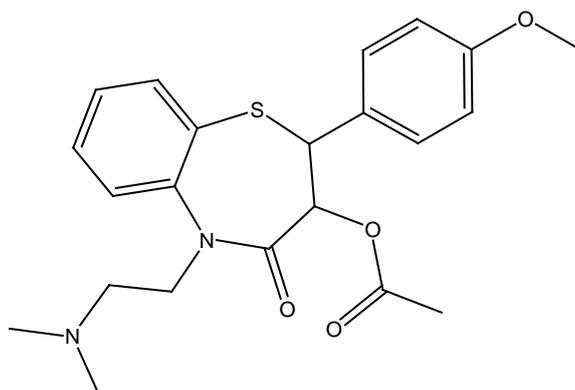
Fig. 1. Chemical structure of diltiazem (DZ)

2. EXPERIMENTAL SECTION

2.1. Apparatus and measurements

A cell arrangement of:

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

was used for all measurements. The ASS-PME is illustrated as Cu wire | ASS layer | PVC membrane in this arrangement. The ASS-PME indicator electrode was used to make the measurements as opposed to an Ag/AgCl reference electrode (Azar-Elelectrode Co., Iran) and the external contact of the two electrodes was through a 250 pH/mV meter (±0.1 mV).

2.2. Materials and Reagents

Analytical grade potassium tetrakis (*p*-chlorophenyl) borate (KTPClPB), acetophenon (AP), dibutyl phthalate (DBP), nitrobenzene (NB), benzyl acetate (BA), 1-octyl-3-methylimidazolium tetrafluoroborate; [C8mim] [BF4], tetrahydrofuran (THF) and graphite powder (1–2 μm) from Merck Co; high-molecular weight polyvinylchloride (PVC) from Fluka Co.; 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) from the Research Institute of the Petroleum Industry, Iran; Macroplast Su 2227 from Henkel Co.; and Desmodur RFE from Bayer Ag; Diltiazem hydrochloride (DZ-HCl) from

Sigma-Aldrich; and pharmaceutical formulations from a local pharmacy (Tehran, Iran), were used for the construction of the electrode and the tests. The DZ.HCl solutions ranging from 1×10^{-8} to 1×10^{-2} M in concentration were prepared using a 0.1 M solution of DZ.HCl in distilled water and were stored at 4 °C.

The real sample solutions were prepared in the following fashion. Twenty 20 mg diltiazem tablets were crushed and powdered and then the weight equivalent of 5 tablets was dissolved in distilled water in a 100-mL volumetric flask, and the pH of the resulting solution was adjusted to 4 using a 0.1 M acetate buffer (pH=4). The solutions were filtered using a Millipore filter (0.45 mm), prior to use.

2.3. Preparation of the DZ-TpClPB ion pair

The process of fabricating the ASS-PME started with the preparation of the DZ-TpClPB ion pair which acts as the active material of the sensor. The ion pair compound was prepared by mixing two solutions of DZ-HCl and potassium tetrakis(p-chlorophenyl) borate (KTPClPB). The choice of the salts is based on the presence of bulky hydrophobic anions in their structure. The KTpClPB and DZ.HCl solutions were prepared by dissolving 40 mg of KTpClPB and 40 mg of DZ.HCl in 5 and 15 mL of distilled water respectively. After thoroughly mixing and dissolving the species the two solutions were mixed and the ion-pair compound formed as a precipitate was filtered, washed with distilled water and dried at ambient conditions.

2.4. Fabrication of the DZ-TpClPB based ASS-PMEs

The all-solid state polymeric-membrane electrodes are composed of two main elements namely the solid contact and the selective membrane. The ASS solid contact was prepared through preparing a conductive polymeric composite (CPC) of various amounts of graphite powder, MWCNTs, an epoxy and a hardener. These ingredients were typically mixed in THF and then aged for about 20-30 minutes under ambient conditions to produce an oily mixture. Then a copper wire (0.5 mm i.d. and 15 cm in length) was repeatedly dipped into the mixture to be covered by the CPC and the system was left to dry for about 10 hours to form the ASS element. Experiments showed that the optimal CPC compositions is 32% wt. of the epoxy resin (Macroplast Su 2227) , 14% wt. of the hardener (Desmodur RFE) , 4% wt. of MWCNT and 50% wt. of graphite powder.

In the meantime PVC membrane mixture was prepared through mixing various amounts of DZ-TPClPB, PVC, a plasticizer and the RTIL ([C$_8$mim] [BF$_4$]), in tetrahydrofuran (THF) in a glass dish. This mixture was mildly warmed to accelerate the evaporation of THF, forming an oily mixture, which was then coated on the prepared ASS element by dipping it into the mixture [30-33]. The preparation of the ASS-PME was then completed through

letting the PME membrane dry in air for one day. Eventually the electrodes were treated in 10^{-3} M solutions of DZ.HCl for reaching equilibrium conditions prior to application.

3. RESULTS AND DISCUSSION

3.1. The Effect of the Composition of the Polymeric Membrane

The optimization of the composition of the polymeric membrane (PM), which can be regarded as the major element of any PME can be the most prominent step in the preparation of a PM based selective electrode [34-40]. As already mentioned the PM ingredients included the DZ-TpClPB ion-pair, the plasticizer, PVC and [C$_8$mim] [BF$_4$]. A summary of the PM compositions and results in terms of slope, linearity range and response time are given in Table 1. The PVC content of all tested PMs were 30% wt. and has not been included in the table for simplicity.

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

No.	Composition of the membrane (wt.%)			Characterization of PME		
	Plasticizer	Ion-pair	Ionic Additive	Slope (mV/decade)	LR (M)	Response time
1	DBP, 66	4	-	20.1±0.2*	1.0×10^{-4}-1.0×10^{-3}	55s
2	DBP, 64	6	-	32.4±0.3	1.0×10^{-4}-1.0×10^{-3}	56s
3	DBP, 62	8	-	37.2±0.4	5.0×10^{-5}-1.0×10^{-3}	52s
4	DBP, 60	10	-	40.4±0.2	5.0×10^{-5}-1.0×10^{-3}	50s
5	DBP,58	12	-	40.4±0.3	5.0×10^{-5}-1.0×10^{-3}	50s
6	DBP, 58	10	2[C$_8$mim] [BF$_4$]	53.2±0.2	3.0×10^{-7}-1.0×10^{-3}	33s
7	DBP, 57	10	3 [C$_8$mim] [BF$_4$]	54.9±0.3	3.0×10^{-7}-1.0×10^{-3}	29s
8	DBP, 56	10	4 [C$_8$mim] [BF$_4$]	56.8±0.3	2.0×10^{-7}-1.0×10^{-3}	22s
9	DBP, 55	10	5 [C$_8$mim] [BF$_4$]	56.8±0.4	2.0×10^{-7}-1.0×10^{-3}	22s
10	AP,56	10	4 [C$_8$mim] [BF$_4$]	50.5±0.2	3.0×10^{-7}-1.0×10^{-3}	24s
11	NB, 56	10	4 [C$_8$mim] [BF$_4$]	46.1±0.3	5.0×10^{-6}-3.0×10^{-3}	24s
12	BA, 56	10	4[C$_8$mim] [BF$_4$]	54.7±0.2	3.0×10^{-7}-1.0×10^{-3}	23s

*standard deviation of five repeated measurements

It has been very well established that the optimal PM behavior is observed at plasticizer/PVC ratios around 2 [37-45] and hence this was considered for the simplification

of the optimization procedure. On the other hand, the membrane plasticizer which is an inert low boiling point, water immiscible organic solvent with a suitable dielectric constant used so as to facilitate the mobility of the sensing material within the polymeric membrane, is a critical ingredient of any PM since it affects the nature and physical properties of the membrane, which in turn influence the responses of the sensors.

Given the required properties of membrane plasticizers, only a limited number of compounds qualify to be used for this purpose. For the purpose of the present work four commonly used plasticizers (i.e acetophenon (AP), dibutylphthalate (DBP) nitrobenzene (NB) and benzylacetate (BA)) were evaluated. The dielectric constants of the solvents ranged from 5.7 (BA), and 6.4 (DBP) to 17.3 (AP) and even 35.7 (NB) and this can be regarded as the basis of the differences in the experimental results in each case (Table 1). A quick overview of Table 1 reveals that membrane no. 8 containing 56% wt. of DPB, 10% wt. of DZ-TpClPB ion pair, 4% wt. of [C_8mim] [BF_4] produces the best results (i.e. a calibration curve slope of 56.8±0.3 mV/decade in the range of 2.0×10^{-7}-1.0×10^{-3} M), which is slightly better than those of membrane no. 9 (containing 55% wt. of DPB, 10% wt. of DZ-TpClPB ion pair, 5% wt. of [C_8mim] [BF_4]) in terms of the RSD. Plasticizers like AP and NB, which have higher dielectric constants, gave rise to weaker properties, most probably due to the hydrophobic nature of DZ, which prefers less polar environments with less dielectric constants. This is very well reflected by the decreased sensitivity of the NB-containing membranes (46.1±0.3 mV/decade) which is slightly modified in the membranes based on the medium polar AP (with a calibration curve slope of 50.5±0.2 mV/decade). It is noteworthy that BA, with the minimum dielectric constant still leads to a non-optimal sensitivity (of 54.7±0.2 mV/decade), which is although much improved as compared to NB and AP is less favorable as compared to DBP. This result can be held as proof that the dielectric constant of DBP is optimal.

The incorporation of small quantities of ionic compounds in the membrane compositions also leads to the reduced Ohmic resistance of the polymeric membranes. However this amount should not exceed certain limits since the excess of such compounds can cause interfering phenomena through the extraction of interfering species into the membrane phase, which decreases the selectivity of the responses. The application of proper amounts of room temperature ionic liquids (RTILs) as a new class of ionic additives has been found to lead to this end. So, the application of an RTIL namely [C_8mim] [BF_4] was evaluated in this work and found to lead to improved results. An evident example is the improvement in the sensitivity and linearity range of the sensor from 40.4±0.2 mV/decade and 5.0×10^{-5}-1.0×10^{-3} M in composition no. 4 to the optimal values in composition no. 8. The presence of the ionic liquids was also found to improve the response time of this membrane from 50 s to the optimal 22 s.

### 3.2. Calibration curve, response time and pH behavior of the ASS-PME

To plot the calibration curve of the sensor 1×10^{-8} to 1×10^{-2} M solutions of DZ.HCl were prepared and used and the E *vs.* –log [DZ] curves were drawn using the ASS-PME (Fig. 2). The results revealed that, as expected the ASS-PME shows improved results in terms of the linearity range as compared to the symmetric PME (which reportedly illustrated linearity ranges of 10^{-5} to 10^{-2} M [44-50]). Based on the experiments, the ASS-PME showed a wider linear response range from 1.0×10^{-7} to 1.0×10^{-3} M with a slope of 56.8 ± 0.3 mV per decade. Further the evaluation of the calibration curve proved the lower detection limit of the DZ-ASS-PME to be 8.0×10^{-8} M.
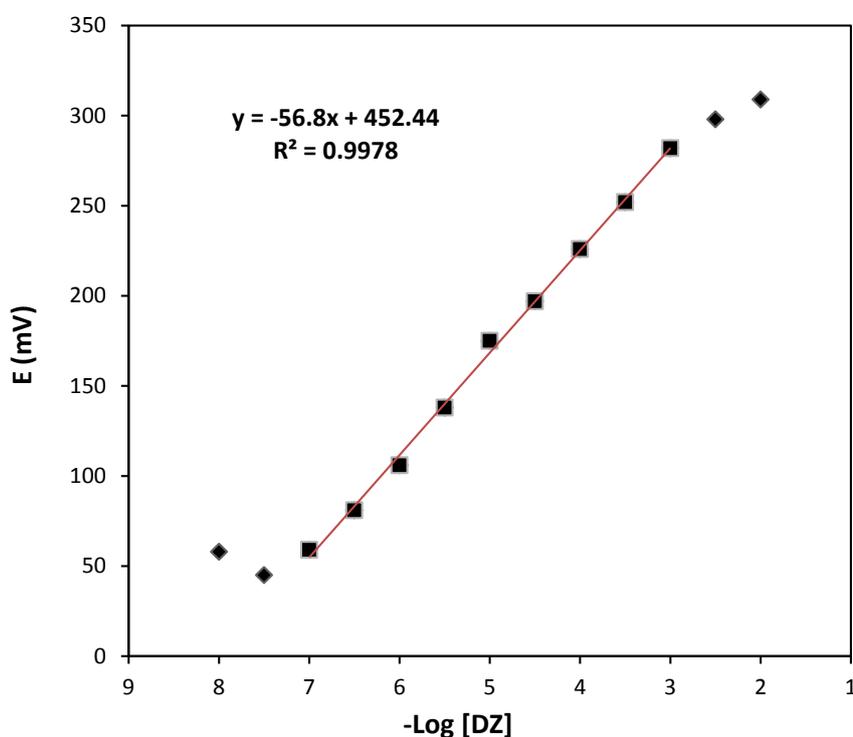
Fig. 2. The calibration curve of the DZ-ASS-PME from 1×10^{-8} to 1×10^{-2} M. (The potential value for each point represents the average of four replicate readings.)

The response time of the sensor, i.e. the time required to reach ± 1 mV of the equilibrium potential value by the device, after a 10 fold change in the concentration of the test solution, was also evaluated through the following fashion. The DZ-ASS-PME was successively immersed into DZ.HCl solutions with different concentrations. Each solution had a 10-fold concentration difference with the previous one and the measurement was performed in the concentration the range of 1.0×10^{-6} to 1.0×10^{-3} M, while recording the equilibrium time [43-48]. The results showed the response time of the sensor to be about 22 s.

The pH behavior of the sensor was also evaluated by monitoring the changes in te potential response of a 1.0×10^{-5} M DZ.HCl solution while varying the pH using concentrated acid or base solutions, so as to avoid considerable volume and hence concentration changes. The pH of the test solution was varied from 1.0 to 10.0 and the results are illustrated in Figure 3. At pH values between 3.0 and 6.0, the response of the ASS-PME was found to be independent from pH. In the pH values between 1.0 and 3.0, the response of the sensor decreased most probably due to the extraction of the membrane ingredients into the solution. The decrease from pH values in the rage of 6.0 to 10.0 was also attributed to the decreased concentration of the DZ^+ species, through the formation of neutral DZOH species in the solution.
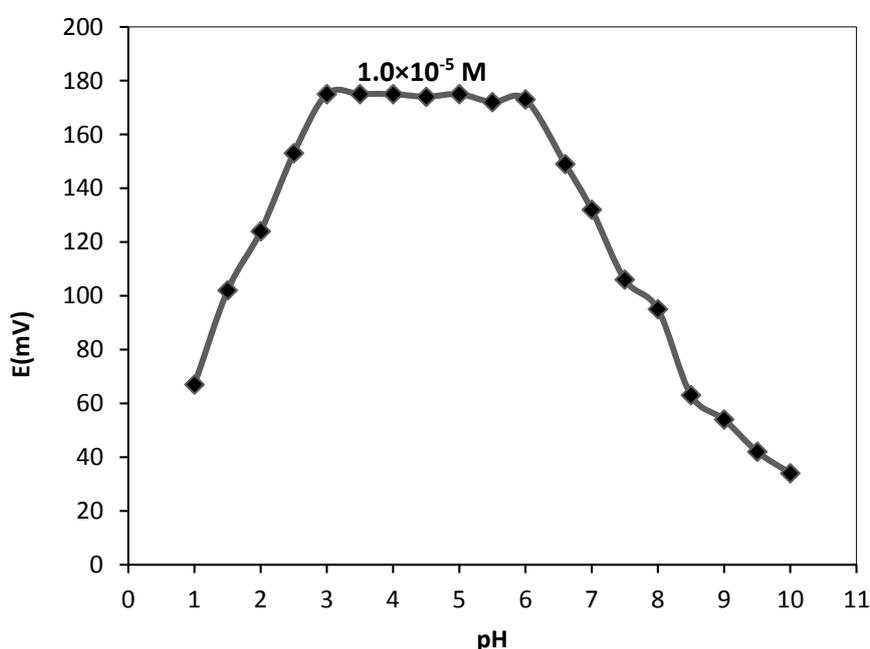
Fig. 3.pH-potential behavior of the ASS-PME in a 1.0×10^{-5} M DZ.HCl solution

3.3. Life-time and selectivity behavior of the ASS-PME

To evaluate the life time of the developed ASS-PME, i.e. average span of time during which it can be applied in analytical procedures without considerable changes in its sensitivity and linear range, 3 ASS-PMEs were chosen and used for 1 h every day for 10 weeks (which is typically the maximum life-time of ASS sensors [48-51]) and the responses were recorded (Table 3). Based on this data it is clear that after about 9 weeks the slope and linearity range of the chosen sensors revealed gradual decreases and hence 8 weeks was considered as the lifetime of the sensors.

Further the selectivity behavior of the devices were evaluated. The selectivity of a sensor can be defined as its tendency to produce a response in the presence of the target species in

the presence of other species of similar nature. This property is expressed in terms of the selectivity coefficients and can be evaluated through various methods. The method used in this study was the so-called matched potential method (MPM) [52-54]. The results of the selectivity evaluations presented in Table 4, are proof that no considerable interferences can be caused in the measurement of DZ concentration by the tested species (i.e. Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, Lactose, Glucose).

Table 3. Lifetime readings

Week	ASS-PME	
	Slope (mV per decade)	DL (M)
1	56.8±0.3	8.0×10^{-8}
2	56.7±0.3	9.0×10^{-8}
3	56.7±0.4	9.5×10^{-8}
4	56.5±0.3	9.5×10^{-8}
5	55.9±0.4	1.0×10^{-7}
6	55.4±0.2	1.0×10^{-7}
7	55.3±0.4	1.5×10^{-7}
8	55.3±0.3	2.5×10^{-7}
9	54.8±0.4	3.0×10^{-7}
10	47.3±0.2	6.0×10^{-7}

Table 4. Selectivity coefficients obtained for CP sensors

Interfering species	ASS-PME Log (K_{MPM})
Na^+	-5.2
K^+	-5.5
NH_4^+	-5.9
Ca^{2+}	-6.1
Mg^{2+}	-6.3
Cl^-	-5.5
NO_3^-	-5.4
Lactose	-6.4
Glucose	-6.3

3.4. Analytical Application

The devised sensors were used in the analysis of solutions of pure diltiazem in distilled water, as well as those of its tablets. During the measurements the linear range, detection limit, selectivity, precision, accuracy, and ruggedness/robustness of the devices were evaluated to assess the validation of their application.

The results achieved by the analysis of the concentration of diltiazem in 100 mg DZ tablets, using the calibration curve method are summarized in Table 5. The table further includes the results of the analysis of the same samples by HPLC and it can be clearly seen that the two sets of results are in accordance and compatible with the values declared on the tablet labels.

Table 5. Measurement of DZ.HCl in pharmaceutical formulations by the proposed sensors and standard methods

Sample	Labeled amount (mg/tab.)	Found by ASS-PME (mg/tab.)	Standard method (mg/tab.)
Sample 1	60	63.5±0.3*	64.1±0.3*
Sample 2	60	65.1±0.5	63.9±0.4
Sample 3	60	60.5±0.4	59.7±0.3

* Averages of five repeated measurements

The repeatability of the results was further evaluated through successive analysis of three standard synthetic samples. The RSD% of these measurements was calculated to be 2.6%. Also the ruggedness of the method based on using the devised sensors was assessed by comparing the results of intra- and inter-day experiments acquired by two different operators in the same laboratory. The RSD% of these data was also found to reach a maximum of 2.2%. Robustness was obtained while the important parameters (i.e. pH of the solution and the laboratory temperature) changed slightly. The recovery of DZ was also found to be good and did not change significantly when critical parameters were altered.

4. CONCLUSIONS

A new ASS-PME was constructed and used for the determination of the concentration of diltiazem. The polymeric membrane used in the device was found to give the best results when containing 10% wt. of DZ-TpClPB, 56% wt. of dibutylphthalate, 30% wt. of poly(vinyl chloride), and 4% wt. of $[C_8mim] [BF_4]$. The ASS element of the sensor was a conductive composite made of graphite, MWCNTs, and epoxy resin coated on a copper wire.

The ASS-PME revealed a Nernstian slope of 56.8±0.3 mV/decade over a wide concentration of 2.0×10^{-7} to 1.0×10^{-3} M and was found to have a lower detection limit of 8.0×10^{-8} M. The response time of the device was 23 s and its response was pH-independent in the pH range of 3.0 to 6.0. The method based on the application of the sensor was evaluated and validated and the results proved it to be effectively applicable to the analysis of diltiazem hydrochloride in synthetic and real pharmaceutical samples.

Acknowledgement

REFERENCES

[1] Budavari Susan, The Merck Index, 11th, Merck and Co., Inc, (1989) 505.

[2] M. M. T. Buckley, S. M. Grant, K. M. Goa, D. McTavish, and E. M. Sorkin, Drugs 39 (1990) 757.

[3] C. B. Cleveland, D. E. Francke, W. M. Heller, J. A. Kepler, G. P. Provost, and M. J. Reilly, American Hospital Formulary Service 98, Drug Information, American Society of Health-System Pharmacists, Bethesda, MD (1998).

[4] K. Li, X. Zhang, and F. Zhao, Biomed Chromatogr. 17 (2003) 522.

[5] V. A. Chatpalliwar, P. K. Porwal, and N. Upmanyu, J. Pharm. Anal. 2 (2012) 226.

[6] K. Ishii, K. Minato, H. Nakai, and T. Sato, Chromatographia 41 (1995) 450.

[7] B. Artalejo-Ortega, A. Bamio-Nuez, C. Fauli Trillo, and A. Pozo Carrascosa, Cienc. Pharm. 7 (1997) 20.

[8] M. Zhong, H. Wang, and J. Zhang, Zhongguo Yiyuan Yaoxue Zashi, 15 (1995) 355.

[9] Y. Kuwahara, and H. Nishi, Yakugaku Zasshi 118 (1998) 456.

[10] H. Nishi, T. Fukuyama, M. Matsuo, and S. Terabe, J. Chromatogr. 513 (1990) 279.

[11] P. V. Devarajan, and V. V. Dhavse, J. Chromatogr. B 706 (1998) 362.

[12] C. S. P. Sastry, K. Sreedhar, M. N. Reddy, and D. G. Sankar, Indian J. Pharm. Sci. 57 (1995) 170.

[13] B. V. Kamath, K. Shivram, and A. C. Shah, J. Pharm. Biomed. Anal. 11 (1993) 407.

[14] K. Sreedhar, C. S. P. Sastry, M. N. Reddy, and D. G. Sankar, Indian Drugs 32 (1995) 90.

[15] P. Norouzi, M. R. Ganjali, B. Larijani, A. Mirabi-Semnakolaii, F. S. Mirnaghi and A. Mohammadi, Pharmazie 63 (2008) 633.

[16] M. R. Ganjali, T. Razavi, F. Faridbod, S. Riahi, and P. Norouzi, Curr. Pharm. Anal. 5 (2009) 28.

[17] F. Faridbod, F. Mizani, M. R. Ganjali, and P. Norouzi, Int. J. Electrochem. Sci. 8 (2013) 10461.

[18] M. R. Ganjali, B. Larijani, F. Faridbod, and P. Norouzi, Int. J. Electrochem. Sci. 8 (2013) 10487.

[19] F. Faridbod, M. R. Ganjali, and P. Norouzi, Int. J. Electrochem. Sci. 8 (2013) 6107.

[20] F. Faridbod, M. R. Ganjali, R. Dinarvand, S. Riahi, P. Norouzi, and M. B. A. Olia, J. Food. Drug Anal. 17 (2009) 264.

[21] M. R. Ganjali, T. Razavi, R. Dinarvand, S. Riahi and P. Norouzi, Int. J. Electrochem. Sci. 3 (2008) 1543.

[22] M. R. Ganjali and B. Larijani, Anal. Bioanal. Electrochem. 7 (2015) 635.

[23] M. R. Ganjali, R. Rezapour, M. Pirali-Hamedani and H. Rashedi, Int. J. Electrochem. Sci. 10 (2015) 6924.

[24] M. R. Ganjali, F. Faridbod, N. Davarkhah, S. J. Shahtaheri, and P. Norouzi, Int. J. Environ. Res. 9 (2015) 333.

[25] I. Isildak, Turk. J. Chem. 24 (2000) 389.

[26] P. Kumar, D. Kim, M. H. Hyun, M. Won, and Y. Shim, Electroanalysis 25 (2013) 1864.

[27] I. Isildak, and A. Asan, Talanta 48 (1999) 967.

[28] B. Kemer, and M. Ozdemir, Turk. J. Chem. 32 (2008) 521.

[29] C. Z. Lai, M. M. Joyer, M. A. Fierke, N. D. Petkovich, A. Stein, and P. Bühlmann, J. Solid State Electrochem. Curr. Res. Dev. Sci. Technol. 13 (2009) 123.

[30] M. R. Ganjali, Z. Memari, F. Faridbod, and P. Norouzi, Int. J. Electrochem. Sci. 3 (2008) 1169.

[31] M. R. Ganjali, A. Daftari, P. Nourozi, and M. Salavati-Niasari, Anal. Lett. 36 (2003) 1511.

[32] F. Faridbod, N. Davarkhah, and S. Karamdoust, Int. J. Electrochem. Sci. 10 (2015) 8308.

[33] M. R. Ganjali, P. Norouzi, F. S. Mirnaghi, S. Riahi, and F. Faridbod, IEEE Sens. J. 7 (2007) 1138.

[34] H. A. Zamani, G. Rajabzadeh, M. R. Ganjali, and S. M. Khatami, Electroanalysis 17 (2005) 2260.

[35] M. R. Ganjali, H. A. Zamani, P. Norouzi, M. Adib, and M. Accedy, Acta Chim. Slov. 52 (2005) 309.

[36] M. Shamsipur, M. Yousefi, M. Hosseini, and M. R. Ganjali, Anal. Lett. 34 (2001) 2249.

[37] M. Shamsipur, S. Rouhani, H. Shaghi, M. R. Ganjali, and H. Eshghi, Anal. Chem. 71 (1999) 4938.

[38] H. A. Zamani, M. R. Ganjali, and M. Adib, Sensor Lett. 6 (2006) 345.

[39] H. A. Zamani, M. Rohani, A. Zangeneh-Asadabadi, M. S. Zabihi, M. R. Ganjali, and M. Salavati-Niasari, Mat. Sci. Eng. C 30 (2010) 917.

[40] M. R. Ganjali, M. Rezapour, M. R. Pourjavid, and S. Haghgoo, Anal. Sci. 20 (2004) 1007.

[41] F. Faridbod, M. R. Ganjali, B. Larijani, P. Norouzi, S. Riahi, and F. S. Mirnaghi, Sensors 7 (2007) 3119.

[42] V. K. Gupta, A. K. Singh, and L. K. Kumawat, Electrochim. Acta 95 (2013) 132.

[43] A. K. Jain, V. K. Gupta, L. P. Singh, P. Srivastava, and J. R. Raisoni, Talanta 65 (2005) 716.

[44] H. A. Zamani, M. Nekoei, M. Mohammadhosseini, and M. R. Ganjali, Mater. Sci. Eng. C 30 (2010) 480.

[45] M. R. Ganjali, P. Norouzi, M. Adib, and A. Ahmadalinezhad, Anal. Lett. 39 (2006) 1075.

[46] V. K. Gupta, A. K. Singh, M. Al Khayat, and B. Gupta, Anal. Chim. Acta 590 (2007) 81.

[47] M. R. Ganjali, P. Norouzi, A. Atrian, F. Faridbod, S. Meghdadi, and M. Giahi, Mater. Sci. Eng. C 29 (2009) 205.

[48] M. R. Ganjali, I. Alahdadi, M. Aghazadeh, and E. Pourbasheer, Int. J. Electrochem. Sci. 10 (2015) 6913.

[49] S. K. Srivastava, V. K. Gupta, and S. Jain, Electroanalysis 8 (1996) 938.

[50] V. K. Gupta, A. K. Jain, Shiva Agarwal, and G. Maheshwari, Talanta 71 (2007) 1964.

[51] A. K. Singh, V. K. Gupta, and B. Gupta, Anal. Chim. Acta 1 (2007) 171.

[52] H. A. Zamani, M. R. Ganjali, P. Norouzi, and S. Meghdadi, Anal. Lett. 41 (2008) 902.

[53] H. A. Zamani, M. R. Ganjali, P. Norouzi, and M. Adib, Sensor Lett. 5 (2007) 522.

[54] H. A. Zamani, J. Abedini-Torghabeh, and M. R. Ganjali, Electroanalysis 18 (2006) 888.