Int. J. Electrochem. Sci., 8 **(2013)** 6107 - 6117

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Potentiometric PVC membrane Sensor for the Determination of Terbinafine

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Received: 5 January 2013 / *Accepted:* 2 February 2013 / *Published:* 1 May 2013

In this work, potentiometry was used for the determination of Terbinafine which is one of the antifungal drugs. The indicator electrode used in the potentiometric method was a kind of PVC membrane sensor. The sensing element of the PVC membrane was made from the interaction of Terbinafine hydrochloride and sodium tetraphenyl borate. The electrode respond based on the ion-exchange mechanism. The best PVC membrane sensor was composed of 30% PVC, 62% DBP, 6% ion-pair and 2% ionic liquid. The response of the sensor was about 15 s and the Nernstian slope of the calibration curve was 57.8±0.4 mV per decade. The lifetime of the sensor was obtained 6 weeks. The proposed method was successfully applied in the determination of Terbinafine in the pharmaceutical formulations.

Keywords: Terbinafine, Potentiometric Sensor, PVC membrane, Ion-Pair, Ionic liquids

1. INTRODUCTION

Terbinafine (Fig. 1), chemically (E)-N-(6,6-dimethyl-2-hepten-4-inyl)-N-methyl-1-naphtalenemethanamine is an antifungal agent of the allylamine class that selectively inhibits fungal *squalene epoxidase* [1].

In other words, Terbinafine inhibits fungal and bacterial cell wall growth, causing the contents of the cell to be unprotected and finally die. Thus, it is applied to the skin in the incidence of dermatophytoses, pityriasis versicolor, and cutaneous candidiasis occurrence or superficial fungal infections like seborrheic dermatitis, tinea capitis, and onychomycosis especially for its short duration therapy [2]. Terbinafine is used for treatment of dermal affections in the form of creams, gels, tablets and solutions. It may cause some side effects such as an allergic reaction, a rash, and changes in vision or blood problems [3].

Some techniques have been reported for the determination of Terbinafine in pharmaceutical formulations including capillary zone electrophoresis [4], HPLC [5], UV−spectrophotometric method [6], polarography [7], voltammetric [8] and non-aqueous methods [9].

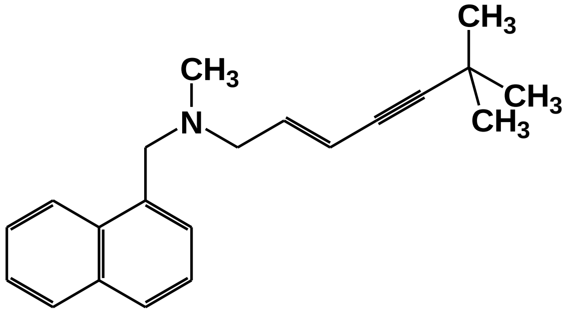

Figure 1. Chemical structure of Terbinafine

Many various measurement methods were used for drug analysis during the recent years but potentiometric using indicator electrodes have advantages of rapid and ease of preparation and procedures, fast response time, reasonable selectivity, wide linear dynamic range, portability and low cost. These characteristics have certainly led to the preparation of numerous sensors for several ionic species, and the list of available electrodes has grown largely over the past years [10-19].

PVC membrane electrodes are one of the subdivisions of potentiometric sensors which are widely used and have different application in analysis of ionic species [20-30].

In this work, potentiometric method was used for the determination of Terbinafine. The indicator electrode used in the potentiometric measurement was a PVC membrane electrode. The active element of the membrane is a kind of ion-pair which was synthesized by the interaction of Terbinafine hydrochloride and tetraphenyl borate. The electrode responds based on the ion-exchange mechanism. Different membrane compositions were tested to find the best sensory response. An immiscible room temperature ionic liquid (RTIL) was also added to the composition of the membrane. The structure of the ionic liquid (IL) and its interaction with the environment is very important for selecting a suitable IL for special application. Transport properties play an important role in chemical reactions, electrochemistry, and liquid–liquid extraction.

2. EXPERIMENTAL SECTION

2.1. Apparatus

The glass cell where the Terbinafine PVC membrane sensor was placed; consisted of two Ag/AgCl double junction reference electrodes (Azar-Elelectrode Co., Iran) as internal and external reference electrodes. Both electrodes were connected to a Corning ion analyzer with a 250 pH/mV meter with ±0.1 mV precision.

2.2. Materials and Reagents

Chemicals (of analytical reagent grade) were: high-molecular weight polyvinylchloride (PVC) (Fluka Co., USA), sodium tetraphenyl borate (NaTPB), dibutyl phthalate (DBP), nitrobenzene (NB), benzyl acetate (BA), nitrophenyloctylether (NPOE), room temperature ionic liquid (1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) and tetrahydrofuran (THF) (Merck Co., Germany). All materials were of the highest available purity without further modification. Terbinafine hydrochloride and its pharmaceutical formulation were obtained from a local pharmaceutical manufacturer (Tehran, Iran) as gift samples.

2.3. Synthesis of the Sensing Element

Sensing element used in the construction of the PVC membrane sensors was an ion-pair compound which is made from the interaction of Terbinafine hydrochloride and sodium tetraphenyl borate. It was prepared by mixing about 20 mL of 0.01 M solution of Terbinafine hydrochloride with 20 mL sodium tetraphenyl borate solution. The resulting precipitate was then filtered, washed with distilled water and dried in room temperature [10,11]. This compound is the ion-pair which behave as an ion-exchange in the membrane layer.

2.4. Preparation of the sensor

General procedure to prepare the PVC membrane was as follow: different amounts of ion-pair along with appropriate amounts of PVC, plasticizer and additive were dissolved in tetrahydrofuran (THF), and the solution was mixed well into a glass dish of 2 cm diameter. Then, THF was evaporated slowly until an oily concentrated mixture was obtained. A plastic tube (about 3 mm o.d.) was dipped into the mixture for about 10 s so a transparent membrane of about 0.3 mm in thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 5 h. Afterwards, the tube was filled with an internal filling solution (1.0×10^{-3} M of Terbinafin hydrochloride solution). The electrode was finally conditioned for 20 h by soaking in the same solution [14-19].

2.5. Standard Terbinafine Solutions

A stock solution of 0.02 M Terbinafine hydrochloride solution was prepared. The working standard solutions (1×10^{-7} to 1×10^{-2} M) were prepared by appropriately dilution of the stock solution with distilled water.

2.6. The emf Measurements

Following cell assembly for the conduction of emf (electromotive force) measurements were used:

Ag-AgCl || internal solution, 1×10^{-3} M Terbinafin hydrochloride solution | PVC membrane | sample solution || Ag-AgCl, KC1 (satd.)

These measurements were done using calibration of the electrodes with several standard solutions.

3. RESULTS AND DISCUSSION

3.1. Membrane Composition

Membrane composition effect on the potential responses of the electrode was tested. The operating characteristics of PVC membrane sensor can be significantly modified by changing the relative amount of the membrane components of the electrode. The main components of a membrane are PVC matrix, plasticizer and the ion-pair as a sensing material. Each membrane component plays a special role in the membrane function and electrode response. Previous studies shows that the membrane prepared with a plasticizer/PVC ratio about 2.2 can show the best performance [14-19]. As it can be seen in Table 1, the optimum amount of PVC was selected 30 mg.

Table 1. Optimization of PVC membrane ingredients

Entry	**PVC**	**Plasticizer**	**Ion-pair**	**RTIL**	**Slope* (mV/decade)**	**LR (M)***	**DL (M)***	**R^2**
1	30	DBP,68	2	-	16.6±0.6	5.0×10^{-3}-1.0×10^{-2}	2.5×10^{-3}	0.877
2	30	DBP,66	4	-	38.2±0.7	1.0×10^{-3}-1.0×10^{-2}	9.5×10^{-4}	0.927
3	30	DBP,64	6	-	51.4±0.6	5.0×10^{-5}-1.0×10^{-2}	1.5×10^{-5}	0.952
4	30	DBP,62	8	-	50.8±0.7	8.0×10^{-5}-1.0×10^{-2}	6.5×10^{-5}	0.943
5	30	NB,64	6	-	25.3±0.5	5.0×10^{-4}-5.0×10^{-2}	5.0×10^{-4}	0.896
6	30	BA,64	6	-	26.9±0.6	4.0×10^{-4}-5.0×10^{-2}	2.5×10^{-4}	0.912
7	30	NPOE,64	6	-	34.2±0.5	5.0×10^{-4}-1.0×10^{-2}	5.0×10^{-4}	0.932
8	30	DBP,63	6	1	53.6±0.5	1.0×10^{-5}-1.0×10^{-2}	1.0×10^{-5}	0.966
9	30	DBP,62	6	2	57.8±0.4	7.0×10^{-6}-1.0×10^{-2}	6.5×10^{-6}	0.997
10	30	DBP,61	6	3	55.7±0.5	7.5×10^{-6}-1.0×10^{-2}	7.0×10^{-6}	0.993
11	30	DBP,68	0	2	5.1±0.7	5.0×10^{-3}-1.0×10^{-3}	4.5×10^{-3}	0.876

Nature of the plasticizer has a noticeable effect on the analytical responses such as slope, linear domain and selectivity of PVC membrane electrodes. Here, four plasticizers with different polarity (dielectric constant) were tested, benzylacetate (BA with DC of about 5.7), dibutyl phthalate

(DBP with DC of 6.4), nitrophenyloctyl ether (NPOE with DC of 24), and nitrobenzene (NB with DC of 35.7), as listed in Table 1. The electrode responses showed that membrane with DBP responds better. DBP among the used plasticizers provided an effective linear range and a lower detection limit due to the better extraction of Terbinafine ions, which is a hydrophone ion, in the organic layer of the membrane.

Using room-temperature ionic liquids (RTILs) in the composition of the membrane increases the extraction of Terbinafine ions and improves the response of the sensor.

As it can be seen from Table 1, absence of ion-pair in the membrane causes a very poor response (membrane no. 11), which confirm significance of the ion-pair.

The electrodes behavior show that the best Nernstian slope is 57.8±0.4 mV per decade. Finally, membrane no. 9 with the composition of 30% PVC, 6% ion-pair, 2% RTIL and 62% DBP was the optimum one for the sensor design.

3.2. Calibration Graph and Statistical Data

The measuring range of a potentiometric sensor is the linear part of the calibration graph as shown in Figure 2. Measurements could be performed in this lower range, but noted that more closely spaced calibration points are required for more precise determinations. For many electrodes the measuring range can extend from 1 molar to 10^{-6} or even 10^{-7} molar concentrations [31-44]. Calibration graph slope for PVC membrane electrode is 57.8 mV per decade of the Terbinafine concentration and a standard deviation of ±0.4 mV after five replicate measurements. A linear response towards the Terbinafine concentration was 7.0×10^{-6}-1.0×10^{-2} M. In this work, detection limit of the PVC membrane sensor was 6.5×10^{-6} M which was calculated by extrapolating the two segments of the calibration curves.

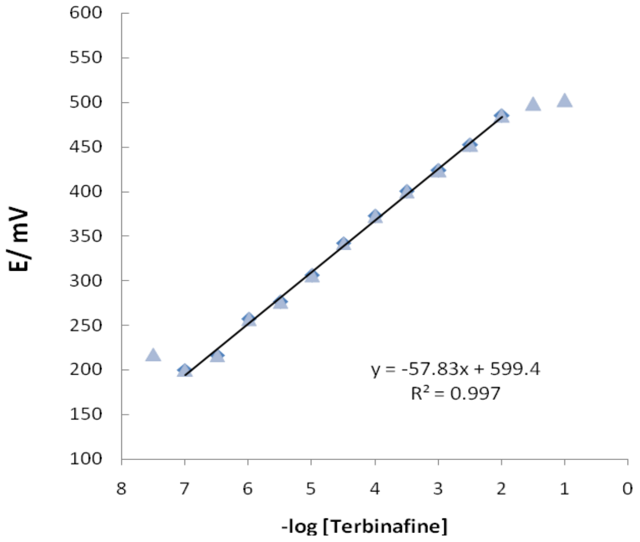

Figure 2. Calibration curve of PVC membrane sensor (no. 9), the results are based on 5 replicate measurements.

3.3. Dynamic Response Time

Dynamic response time is the required time for the electrode to achieve values within ±1 mV of the final equilibrium potential, after successive immersions in the sample solutions [45-59]. Its calculation involved the variation and the recording of the Terbinafine concentration in a series of solutions from 7.0×10^{-6} to 1.0×10^{-2} M. Sensor was able to quickly reach its equilibrium response in the whole concentration range. This time for PVC membrane electrode was about 15 s in the concentrated solutions.

3.4. pH Effect on the Electrodes Response

To examine the effect of pH on the electrode responses, the potential was measured at specific concentration of the Terbinafine solution (1.0×10^{-4} M) from the pH value of 1.0 up to 9.0 (concentrated NaOH or HCl solutions were employed for the pH adjustment) by PVC membrane electrode. The results showed that the potential remained constant despite the pH change in the range of 3 to 6, which indicates the applicability of this electrode in the specified pH range.

Relatively noteworthy fluctuations in the potential *vs.* pH behavior took place below and above the formerly stated pH limits. In detail, the fluctuations above the pH value of 6 might be justified by removing the positive charge on the drug molecule. Fluctuations below the pH value of 3 were caused by removal of the membrane ingredients or analyte in the solution. In both electrodes the same trend were observed.

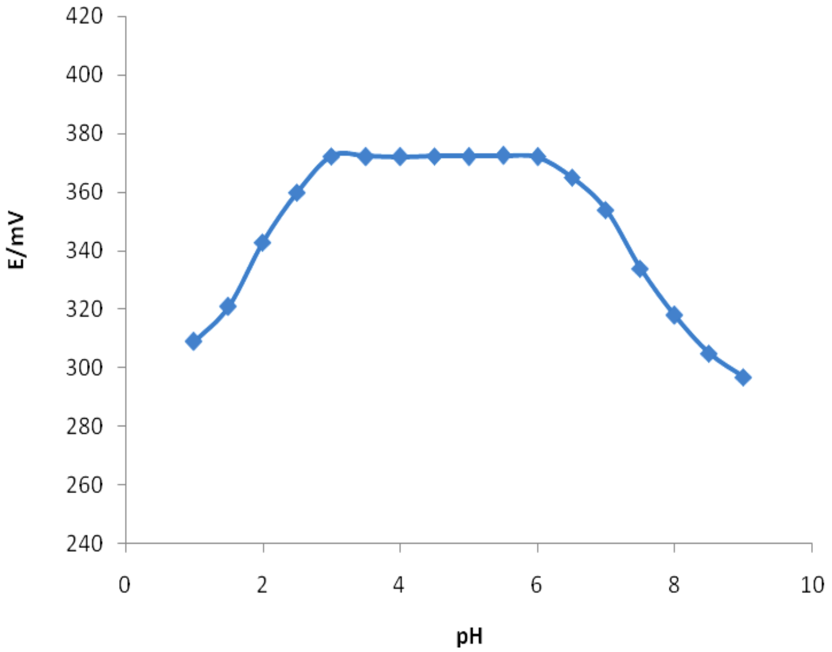

Figure 3. Applicable pH of the electrodes in the test solution of 1.0×10^{-4} M

3.5. Life-time Study

Electrode lifetime was estimated by the calibration curve, periodical test of a standard solution and calculation of its response slope.

Table 3. Lifetime of PVC membrane electrode

Week	Slope (mV per decade)	DL (M)
First	57.8	6.5×10^{-6}
Second	57.7	7.0×10^{-6}
Third	57.5	8.5×10^{-6}
Fourth	57.4	1.0×10^{-5}
Fifth	57.1	2.5×10^{-5}
Sixth	57.0	3.0×10^{-5}
Seventh	50.5	7.5×10^{-5}
Eighth	43.1	2.5×10^{-4}
Ninth	33.6	6.0×10^{-4}
Tenth	21.2	1.0×10^{-3}

For this estimation, three electrodes were employed extensively (1 hour per day) for 10 weeks. After 6 weeks utilization of PVC membrane electrode, two changes were observed: a slight gradual decrease in the slope and an increase in the detection limit.

In PVC membrane electrodes after several time of usage, the membrane ingredients leak from the organic layer and affect the membrane response.

3.6. Analytical Applications

Linearity, limit of detection, recovery test, selectivity, precision, accuracy, and ruggedness/robustness were the parameters used for the method validation.

3.6.1. Recovery Test from pharmaceutical formulations

The proposed sensor was evaluated by measuring the drug concentration in some pharmaceutical formulations (Table 4). The drug concentration was determined using calibration method. The results are in satisfactory agreement with the labeled amounts. The corresponding recovery percentage value varied from 94.3-105.4%.

Table 4. Potentiometric determination of Terbinafine in pharmaceutical formulations

Sample	Labeled amount	Found by the electrode*
Terbinafine Tablet	250 mg/tab	
Sample 1		255.2±1.4
Sample 2		246.7±1.2
Sample 3		253.7±1.1
Terbinafine Hydrochloride Solution	1%	
Sample 1		1.2±0.3%
Sample 2		1.3±0.4%
Sample 3		1.3±0.5%

* The results are based on five replicate measurements.

3.6.2. Selectivity

Table 5. Selectivity coefficients of various interfering compounds for Terbinafine sensor

Interfering ion	Log (K_{MPM})
Na^+	-3.2
K^+	-3.1
NH_4^+	-3.0
Ca^{2+}	-3.5
Mg^{2+}	-4.0
Cl^-	-4.2
NO_3^-	-3.8
Lactose	-4.2
Glucose	-4.2

Selectivity, which describes an ion-selective electrode’s specificity toward the target ion in the presence of interfering ions, is the most important characteristic of these devices. The potentiometric selectivity coefficients of the terbinafin sensor were evaluated by the matched potential method (MPM) [60-62]. The resulting values of the selectivity coefficients are shown in Table 5. Note that all selectivity coefficients suggest that interferences were negligible in the performance of the electrode assembly.

3.6.3. Precision and accuracy

For repeatability monitoring, 3 standard samples were measured. The RSD values by PVC membrane were 3.5, 4.3 and 2.7%.

3.6.4. Ruggedness/Robustness

For ruggedness of the methods a comparison was performed between the intra- and inter-day assay results for Terbinafine obtained by two analysts.

The RSD values for the intra- and inter-day assays in the cited formulations performed in the same laboratory by the two analysts did not exceed 4.6%. On the other hand, the robustness was examined while the parameter values (pH of the solution and the laboratory temperature) changed slightly. Terbinafine recovery percentages were good under most conditions, and not showing any significant change when the critical parameters were modified.

4. CONCLUSIONS

In the present work, potentiometric electrode was constructed for determination of Terbinafine. The sensor demonstrated advanced performance with a fast response time, a lower detection limit of 6.5×10^{-6} M for PVC membrane electrode and potential responses across the range of 7.0×10^{-6} to 1.0×10^{-2} M. The sensor enabled the Terbinafine determination in pharmaceutical formulations. Sensor respond based on ion-exchange mechanism. The best PVC membrane electrode performance was achieved by a membrane composition of 30% PVC, 62% DBP, 2% IL and 6% ion-pair.

ACKNOWLEDGEMENT
The authors are grateful to the Research Council of University of Tehran for the financial support of this work.

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