Potentiometric Sensor for Determination of Clomiphene

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In this work, construction and analytical application of a new potentiometric PVC membrane sensor for the determination of Clomiphene are studied. The sensor respond based on ion-exchange mechanism between the organic layer of the membrane and aqueous phase. The proposed sensor showed a linear dynamic range between 8.0×10^{-6} and 1.0×10^{-2} mol L^{-1} of Clomiphene with a Nernstian slope of (57.6 ± 0.6) mV decade^{-1} and a detection limit of 6.3×10^{-6} mol L^{-1}. The best PVC membrane sensor response was obtained by a membrane composition of 30% PVC, 62% DBP, 6% ion-pair and 2% ionic liquid. The potentiometric response was independent to the solution pH in the range of 4.0 to 6.0. The proposed electrode displayed fast response time about 15 s, and it can be used for a period of six weeks without any considerable change in its performance. Application of this potentiometric sensor for the Clomiphene determination in some pharmaceutical formulations was satisfactory results.

1. INTRODUCTION

Clomiphene or Clomifene, 2-[4-(2-Chloro–1,2–diphenylethenyl)phenoxy]-N,N-diethylethanamine (Fig. 1), is a selective estrogen receptor modulator that increases production of gonadotropins by inhibiting negative feedback on the hypothalamus [1]. It is used mostly in female infertility, as ovulation induction to reverse oligoovulation or anovulation such as in infertility in polycystic ovary syndrome, and being used for ovarian hyperstimulation, such as part of an in vitro fertilization procedure [1].

Common side effects of clomiphene may include breast pain, enlarged ovaries, and hot flashes. There are also a number of less common but more serious side effects, including changes in vision, severe abdominal pain, or allergic reactions.

Different methods were reported for its determination, including spectrophotometric method [2,3], array-type DNA glass slide [4], high performance liquid chromatography (HPLC) [5-7], capillary electrophoresis [8], and NMR method [9].
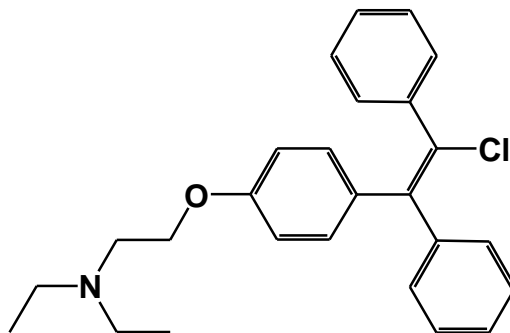

Figure 1. Chemical structure of clomiphene

Different electrochemical measurement techniques were used for drug analysis during recent year but potentiometric using indicator electrodes have advantages of rapid and ease of preparation and procedures, fast response time, reasonable selectivity, wide linear dynamic range, 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 [10-21].

PVC membrane electrodes are one of the subdivisions of potentiometric sensors which are widely used and have different application in analysis of ionic species [22-32].

In this work, electrode works based on ion-pair mechanism which was made from the interaction between Clomiphene and sodium tetraphenyl borate and they respond according to the ion-exchange mechanism. PVC membrane electrode was made after series of experiments.

2. EXPERIMENTAL SECTION

2.1. Apparatus

The glass cell where the Clomiphene indicator PVC membrane electrode 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), room temperature ionic liquid (1-n-butyl-3-

methylimidazolium tetrafluoroborate ([bmim]BF$_4$), dibutyl phthalate (DBP), nitrobenzene (NB), benzyl acetate (BA), *o*-nitrophenyloctylether (*o*-NPOE) and tetrahydrofuran (THF) (Merck Co., Germany). All materials were of the highest available purity without further modification. Clomiphene hydrochloride and its pharmaceutical formulations were obtained from a local pharmaceutical manufacturer (Tehran, Iran) as gift samples.

2.3. Preparation of the ion-pair complex

Sensing element used in the PVC membrane electrode was an ion-pair compound made from the interaction of Clomiphene and sodium tetraphenyl borate. It was prepared by mixing about 20 mL of 0.01 mol L^{-1} acidic solution of Clomiphene hydrochloride with 20 mL tetraphenyl borate solution. The resulting precipitate was then filtered, washed with distilled water and dried in the room temperature [21,23].

2.4. Preparation of PVC Membrane Electrodes

General procedure to prepare PVC membrane was as follow: different amounts of ion-pair along with appropriate amounts of PVC, plasticizer and additive (RTIL) 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} mol L^{-1} of Clomiphene hydrochloride solution). The electrode was finally conditioned for 20 h by soaking in the same solution [18-23].

2.5. Standard Clomiphene Solutions

A stock solution of 0.02 mol L^{-1} Clomiphene hydrochloride solution was prepared. The working standard solutions (1×10^{-7} to 1×10^{-2} mol L^{-1}) 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} mol L^{-1} Clomiphene hydrochloride solution | PVC membrane | sample solution ‖ Ag-AgCl, KCl (satd.)

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

solutions.

3. RESULTS AND DISCUSSION

3.1. PVC Membrane Composition Selection

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 [39-46]. 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 (mol L^{-1})*	DL (mol L^{-1})*	R^2
1	30	DBP,68	2	-	19.8±0.8	5.0×10^{-3}-1.0×10^{-3}	2.5×10^{-3}	0.850
2	30	DBP,66	4	-	38.2±0.7	1.0×10^{-3}-5.0×10^{-2}	9.5×10^{-4}	0.920
3	30	DBP,64	6	-	50.8±0.7	5.0×10^{-5}-1.0×10^{-2}	1.5×10^{-5}	0.934
4	30	DBP,62	8	-	47.7±0.5	1.0×10^{-4}-1.0×10^{-2}	6.5×10^{-6}	0.919
5	30	NB,64	6	-	22.6±0.9	7.0×10^{-4}-5.0×10^{-2}	5.0×10^{-4}	0.910
6	30	BA,64	6	-	33.9±0.6	1.0×10^{-4}-3.0×10^{-2}	1.0×10^{-4}	0.926
7	30	NPOE,64	6	-	25.7±0.7	7.0×10^{-4}-1.0×10^{-2}	5.0×10^{-4}	0.945
8	30	DBP,63	6	1	55.7±0.5	1.0×10^{-5}-1.0×10^{-2}	1.0×10^{-5}	0.959
9	30	DBP,62	6	2	57.6±0.6	8.0×10^{-6}-1.0×10^{-2}	6.3×10^{-6}	0.997
10	30	DBP,61	6	3	56.9±0.7	8.0×10^{-6}-1.0×10^{-2}	8.0×10^{-6}	0.995
11	30	DBP,68	0	2	3.6±0.7	4.0×10^{-3}-1.0×10^{-3}	4.0×10^{-3}	0.896

*The results based on triplicate measurements.

Plasticizer which mainly acts as a membrane solvent allowing homogeneous dissolution and diffusional mobility of the ion-pair inside the membrane [47-52]. The plasticizer should be water-immiscible liquid with low vapor-pressure, compatible with PVC, no functional groups which can undergo protonation reactions. The selectivity of such electrode can be drastically influenced by the choice of the membrane solvent [45-55]. Nature of the plasticizer has a marked effect on analytical responses e.g. slope, linear domain and selectivity of PVC membrane electrodes. Here, four plasticizers with different polarity (dielectric constant) were tested, dibutyl phthalate (DBP with DC of 6.4), nitrobenzene (NB with DC of 35.7), nitrophenyloctyl ether (NPOE with DC of 24), and benzylacetate (BA with DC of about 5.7), as listed in Table 1. The electrode responses showed that membrane had DBP better respond. DBP among the used plasticizers provided an effective linear range and a lower detection limit due to the better extraction of Clomiphene hydrochloride ions in the organic layer of the membrane. Using room-temperature ionic liquids (RTILs) in the composition of the membrane increases the extraction of Clomiphene ions and

improve 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. As a conclusion, 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

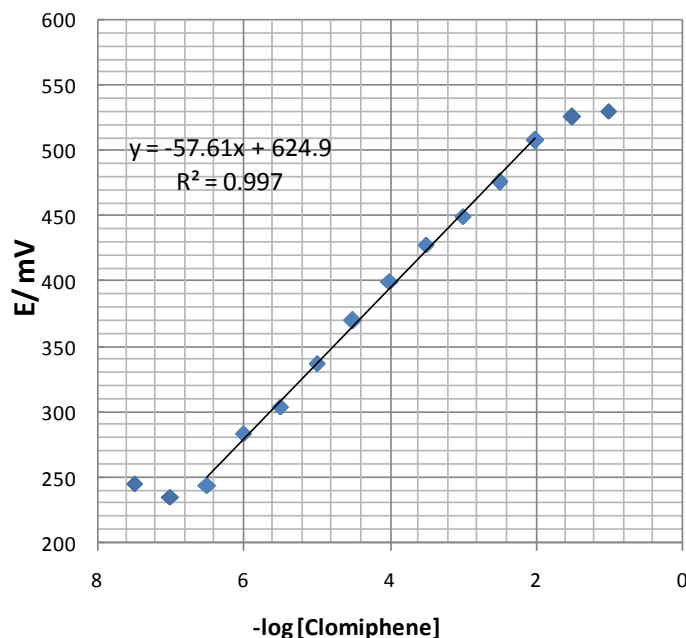The measuring range of a potentiometric sensor is the linear part of the calibration graph as shown in Figure 2.

Figure 2. Calibration curve of PVC membrane electrode, the results are based on 3 replicate measurements.

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 [48-55]. Calibration graph slope for PVC membrane electrode is 57.6 mV per decade of the Clomiphene concentration and a standard deviation of ±0.6 mV after 3 replicate measurements. A linear response towards the Clomiphene concentration was from 8.0×10^{-6}-1.0×10^{-2} mol L^{-1}. In this work, detection limit of the PVC membrane sensor was 6.3×10^{-6} mol L^{-1} which was calculated by extrapolating the two segments of the calibration curves.

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 [46-55]. Its calculation involved the variation and the recording of the Clomiphene concentration in a series of solutions from 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1}. 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 Clomiphene solution (1.0×10^{-4} mol L^{-1}) from the pH value of 1.0 up to 10.0 (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 4.0 to 6.0 which indicates the applicability of this electrode in the specified pH range [56].

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 6.0 might be justified by removing the positive charge on the drug molecule. Fluctuations below the pH value of 4.0 were caused by removal of the membrane ingredients or analyte in the solution. In both electrodes the same trend were observed [10,16,21].

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.
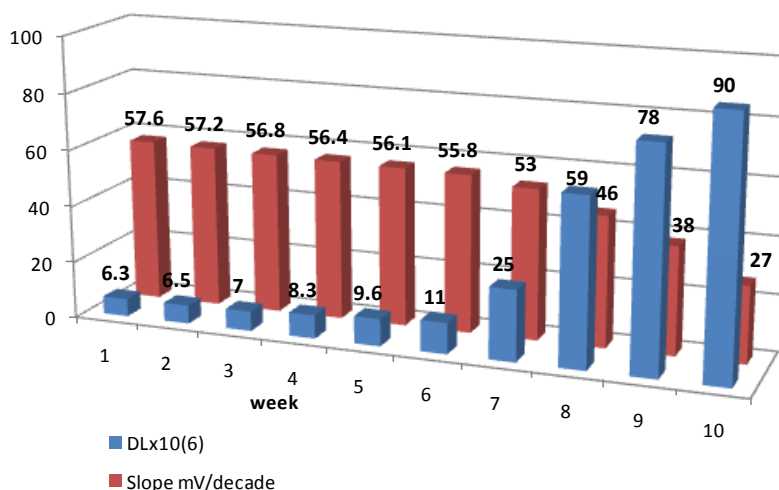

Figure 3. Behavior of the Clomiphene electrode in term of DL and Slope during ten weeks

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

3.6.1. Recovery Test from Tablet

The proposed sensor was evaluated by measuring the drug concentration in some pharmaceutical formulations (Table 2). The drug concentration was determined using calibration method. The results are in satisfactory agreement with the labeled amounts.

Table 2. Potentiometric determination of Clomiphene in pharmaceutical formulations

Sample	Labeled amount	Found by the electrode*
Sample 1	50 mg/tab	53.5± 0.7 mg/tab
Sample 2	50 mg/tab	55.1± 0.8 mg/tab
Sample 3	50 mg/tab	49.3±1.2 mg/tab

* The results are based on five replicate measurements.

3.6.2. Selectivity

Table 3. Selectivity coefficients of various interfering compounds for Clomiphene sensor

Interfering ion	Log (K_{MPM})
Na^+	-3.1
K^+	-3.8
NH_4^+	-3.2
Ca^{2+}	-3.5
Mg^{2+}	-3.7
Cl^-	-4.5
NO_3^-	-4.9
Lactose	-4.9
Glucose	-4.7

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 Clomiphene sensor were evaluated by the matched potential method (MPM) [56-62]. The resulting values of the selectivity coefficients are shown in Table 3. Note that

all selectivity coefficients are 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, 3,8, and 4.2%.

3.6.4. Ruggedness/Robustness

For ruggedness of the methods a comparison was performed between the intra- and inter-day assay results for Clomiphene 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 4.3%. On the other hand, the robustness was examined while the parameter values (pH of the solution and the laboratory temperature) changed slightly. Clomiphene 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 Clomiphene. The sensor demonstrated advanced performance with a fast response time, a lower detection limit of 6.3μM for PVC membrane electrode. The sensor enabled the Clomiphene 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% RTIL and 6% ion-pair. Using room-temperature ionic liquids (RTILs) in the composition of the membrane increases the extraction of Clomiphene ions, which is a hydrophobe ion, and improve the response of the sensor.

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