Determination of Ondansetron Hydrochloride by a Liquid Membrane Potentiometric Sensor Based on Room Temperature Ionic Liquids

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A new potentiometric sensor is introduced for simple and fast determination of Ondansetron hydrochloride in its formulations. Liquid membrane electrode in connection with Ag-Ag/Cl reference electrode was set-up and used for the potentiometric measurements. The membrane of the indicator electrode composed of a suitable ion-pair complex, dibutyl phthalate as the solvent mediator, PVC as a polymeric matrix and a room temperature ionic liquid (RTIL). RTIL helps the membrane to plasticize the media better and extract the drug ions from the aqueous solution to the organic phase of the membrane effectively. Different room temperature ionic liquids were tested. Using room temperature ionic liquids also decrease the Ohmic resistance of the membrane. The proposed sensor can applied in the concentration range of 5.0×10^{-6}-1.0×10^{-2} mol L^{-1} of Ondansetron with a detection limit of 4.5×10^{-6} mol L^{-1}. The potentiometric measurement can be done in pH range of 3.5 to 5.5. The proposed electrode displayed fast response time about 18 s and can be used for a period of seven weeks without any considerable change in its performance.

1. INTRODUCTION

Ondansetron (or Zofran, or Demitron), (RS)-9-methyl-3-[(2-methyl-1H-imidazol-1-yl)methyl]-2,3-dihydro-1H-carbazol-4(9H)-one (Fig. 1), is a highly selective and potent 5-hydroxytryptamine type

3 (5-HT3) receptor antagonist. It is effective in the treatment of nausea and vomiting during cancer chemotherapy and radiotherapy, and has reported anxiolytic and neuroleptic properties [1-3].

5HT released by chemotherapy, radiotherapy and surgery also activates the 5HT3 receptors that are found in the CTZ in the brain, causing further messages to be sent to the vomiting centre. Ondansetron works by blocking the 5HT3 receptors that are found in the brain and gut. This prevents the nausea messages being sent from these areas to the vomiting centre. Therefore it prevents nausea, retching and vomiting that can otherwise happen following surgery or due to cancer treatments.

Very few analytical methods have been reported for the determination of Ondansetron which include high performance liquid chromatography (HPLC) [4-7], high performance thin layer chromatography (HPTLC) [8] and visible spectrophotometric method [9].
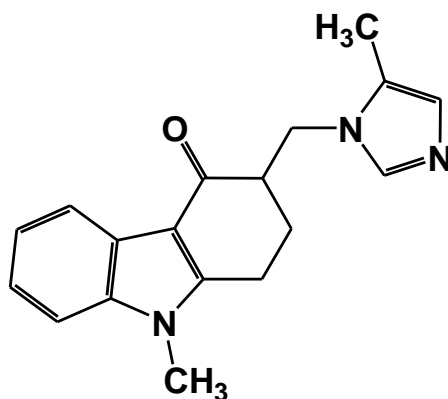

Figure 1. Chemical structure of Ondansetron

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 [10-19]. PVC membrane electrodes are one of the subdivisions of potentiometric sensors which are widely used and have different application in analysis of ionic species [20-33].

In this work, the proposed electrode works based on ion-pair complex which it was made from the interaction between Ondansetron and sodium tetraphenyl borate and they respond according to the ion-exchange mechanism. PVC membrane electrode was made after series of experiments. Also, different room temperature ionic liquids (RTILs), 1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4), 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6), and 1-octyl-3-methylimidazolium tetrafluoroborate ([omim]BF_4) was used in the composition of the liquid membrane sensor to improve the performance of the device.

2. EXPERIMENTAL SECTION

2.1. Apparatus

The glass cell where the Ondansetron indicator electrode (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), and tetrahydrofuran (THF) (Merck Co., Germany). Room temperature ionic liquids, 1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF$_4$), 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF$_6$), and 1-octyl-3-methylimidazolium tetrafluoroborate ([omim]BF$_4$) were taken from Iran Petroleum Industry Institute. All materials were of the highest available purity without further modification. Ondansetron hydrochloride and its pharmaceutical formulation 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 membrane of the sensor was an ion-pair compound made from the interaction of Ondansetron hydrochloride and sodium tetraphenylborate. Sodium tetraphenylborate (NaTPB) is the organic compound with the formula of NaB(C$_6$H$_5$)$_4$, Fig. 2. It is a salt, wherein the anion consists of four phenyl rings bonded to boron. This white crystalline solid is water soluble and can be used to prepare other tetraphenylborate salts, which are often highly soluble in organic solvents. The compound is used in inorganic and organometallic chemistry as a precipitating agent.
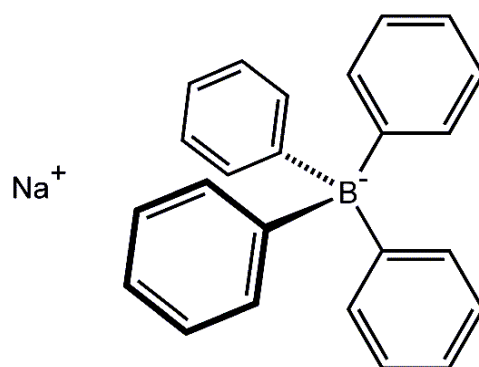

Figure 2. Chemical structure of sodium tetraphenylborate

Ion-pair compound was prepared by mixing about 20 mL of 0.01 mol L^{-1} acidic solution of Ondansetron hydrochloride with 20 mL tetraphenyl borate solution. The resulting precipitate was then filtered, washed with distilled water and dried in room temperature for further usage [16].

2.4. Preparation of the liquid membrane

General procedure to prepare the membrane of the sensor 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 4 h. Afterwards, the tube was filled with an internal filling solution (1.0×10^{-3} mol L^{-1} of Ondansetron hydrochloride solution). The electrode was at last conditioned for 15 h by soaking in the same solution [14-19].

2.5. Ondansetron standard solutions

Ondansetron hydrochloride is a white crystalline solid with m.p. 178.5° to 179.5°. It is soluble in aqueous solutions but solubility decreases with pH>5.7. A solution of 0.02 mol L^{-1} Ondansetron hydrochloride was prepared as stock solution. The working standard solutions (1×10^{-7} to 1×10^{-2} mol L^{-1}) were then prepared by appropriately dilution of the stock solution with distilled water.

2.6. Potentiometric measurement cell assembly

Following cell assembly for measurements were used:

Ag-AgCl ‖ internal solution, 1×10^{-3} mol L^{-1} Ondansetron hydrochloride solution | PVC membrane | sample solution ‖ Ag-AgCl, KC1 (satd.)

These measurements were done using calibration method with several standard solutions.

2.7. Sample preparation for the real assay

Twenty tablets of Ondansetron hydrochloride finely powdered. Portions equivalent to the weight of one, two and three tablets (each tablet contain 4 mg Ondansetron) were weighed and transferred into a 100-mL volumetric flask. 50 mL of distilled deionized water was then added. The contents were shaken thoroughly to dissolve the compound, then made up to volume and adjust the pH to 4 with acetate buffer (0.1 mol L^{-1}). Suitable aliquots of this solution were filtered through a Millipore filter (0.45 mm).

3. RESULTS AND DISCUSSION

PVC membrane electrodes are also called liquid membrane sensors. Although over plasticized solvent polymeric membrane electrodes provide a nearly liquid membrane interior, it is a dry and robust membrane to the touch. Using room temperature ionic liquids in the composition of the membrane maybe is another reason for applying this name.

3.1. PVC Membrane Composition Selection

Membrane composition effect on the potential responses of the liquid membrane sensor was tested. The operating characteristics of PVC membrane sensor can be significantly modified by changing the relative amount of the membrane components. 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 the sensor response. Previous studies shows that the membrane prepared with a plasticizer/PVC ratio about 2.2 can show the best performance [34-40].

Table 1. Selection of the liquid membrane components

No.	PVC	Plasticizer	Ion-pair	RTIL	Slope* (mV/decade)	LR (mol L^{-1})*	DL (mol L^{-1})*	Response time	R^2
1	30	DBP,67	3	-	15.7±0.8	5.0×10^{-4}-1.0×10^{-3}	5.0×10^{-4}	1 min	0.844
2	30	DBP,65	5	-	32.1±0.6	1.0×10^{-4}-1.0×10^{-3}	8.0×10^{-5}	55 s	0.921
3	30	DBP,63	7	-	47.9±0.5	5.0×10^{-5}-5.0×10^{-3}	4.5×10^{-5}	48 s	0.953
4	30	DBP,61	9	-	43.8±0.5	5.0×10^{-5}-5.0×10^{-3}	5.0×10^{-5}	52 s	0.941
5	30	NB,63	7	-	19.9±0.8	1.0×10^{-4}-1.0×10^{-3}	1.0×10^{-4}	1 min	0.876
6	30	NPOE,63	7	-	33.6±0.7	10×10^{-4}-5.0×10^{-3}	1.0×10^{-4}	1 min	0.910
7	30	BA,63	7	-	36.2±0.8	1.0×10^{-4}-1.0×10^{-2}	5.0×10^{-5}	58 s	0.922
8	30	DBP,62	7	1[bmim]BF$_4$	51.7±0.5	5.0×10^{-5}-8.0×10^{-3}	5.0×10^{-5}	42 s	0.962
9	30	DBP,61	7	2 [bmim]BF$_4$	54.4±0.5	1.0×10^{-5}-1.0×10^{-2}	5.0×10^{-6}	34 s	0.978
10	30	DBP,60	7	3 [bmim]BF$_4$	56.5±0.4	9.0×10^{-6}-1.0×10^{-2}	8.5×10^{-6}	26 s	0.985
11	30	DBP,59	7	4 [bmim]BF$_4$	55.7±0.4	1.0×10^{-5}-1.0×10^{-2}	9.0×10^{-6}	31 s	0.980
12	30	DBP,60	7	3 [omim]BF$_4$	53.8±0.4	8.0×10^{-6}-1.0×10^{-2}	8.0×10^{-6}	38 s	0.973
13	30	DBP,60	7	3 [bmim]PF$_6$	58.2±0.3	5.0×10^{-6}-1.0×10^{-2}	4.5×10^{-6}	18 s	0.997
14	30	DBP,67	0	3	3.7±0.9	5.0×10^{-4}-1.0×10^{-3}	5.0×10^{-4}	2 min	0.779

*The results are based on five replicate measurements.

Table 1 summarizes the most important prepared membranes. As it can be seen, the optimum

amount of PVC was selected 30 mg and the best amount of plasticizer was 60 mg. Plasticizer should be a water-immiscible organic liquid which provide a homogeneous dissolution and diffusional mobility of the ion-pair complex inside the membrane [41-43]. The plasticizer should be an organic liquid with low vapor-pressure, compatible with PVC, no functional groups which can undergo protonation reactions. The type of the used plasticizer can affect the analytical responses e.g. slope, linear domain and selectivity of the sensor. Four general plasticizers with different dielectric constants were used, including dibutyl phthalate (DBP with DC of 6.4), nitrophenyloctyl ether (NPOE with DC of 24), nitrobenzene (NB with DC of 35.7) and benzylacetate (BA with DC of about 5.7). The responses showed that the membrane had DBP better responds. DBP among the used plasticizers provided an effective linear range and a lower detection limit due to the better extraction of Ondansetron ions in the organic layer of the membrane.

As seen in Table 1, three room temperature ionic liquids were also used in the composition of the membrane no. 8 to no. 13. Results shows that using [bmim]PF_6 helps the Ondansetron ions better exchange from the aqueous solution to the organic phase of the membrane. RTILs can be act as an ionic additive and beside the mentioned effect; they can also decrease the membrane Ohmic resistance.

Miscibility of RTILs with water is often understood by their hydrophobicities. The hydrophobicity mainly depends on the composition of ILs. Thus, ILs can be water-immiscible or hydrophobic ILs, such as 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and hydrophilic ILs such as [bmim][BF_4] [44]. The first group is a better candidate for using in construction of electrochemical sensors or biosensors because these electrochemical devices contact with water during their operations. The miscibility of ILs in water is strongly dependent on their anions. Cl^-, Br^-, I^-, NO_3^-, CH_3COO^- and CF_3COO^- are anions that make the ILs miscible with water. ILs composed of anions such as PF_6^- and Tf_2N^- are in immiscible with water. Miscibility of anions such as BF_4^- is dependent on the structure of the cations. Although in general they are miscible with water, the miscibility will decrease with the increase in the cation chain length which is due to the increased surface activity of the longer chain cations. Here, [bmim][PF_6] has a hydrophobe anion and a hydrophil cation which can exchange with cationic drug Ondansetron.

As it can be seen from Table 1, absence of the ion-pair complex in the membrane causes a very poor response (membrane no. 14), which confirm the significance of the ion-pair complex. The best Nernstian slope was obtained 58.2±0.3 mV per decade with the membrane no. 13. This membrane composition was selected for the next experiments.

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 3. 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 [45-54]. Calibration graph slope for liquid membrane sensor is 58.2 mV per decade of the Ondansetron concentration and a standard deviation of ±0.3 mV after five replicate measurements. A linear response

towards the Ondansetron concentration was from 5.0×10^{-6}-1.0×10^{-2} mol L^{-1}. In this work, detection limit of the liquid membrane sensor was 4.5×10^{-6} mol L^{-1} which was calculated by extrapolating the two segments of the calibration curves.
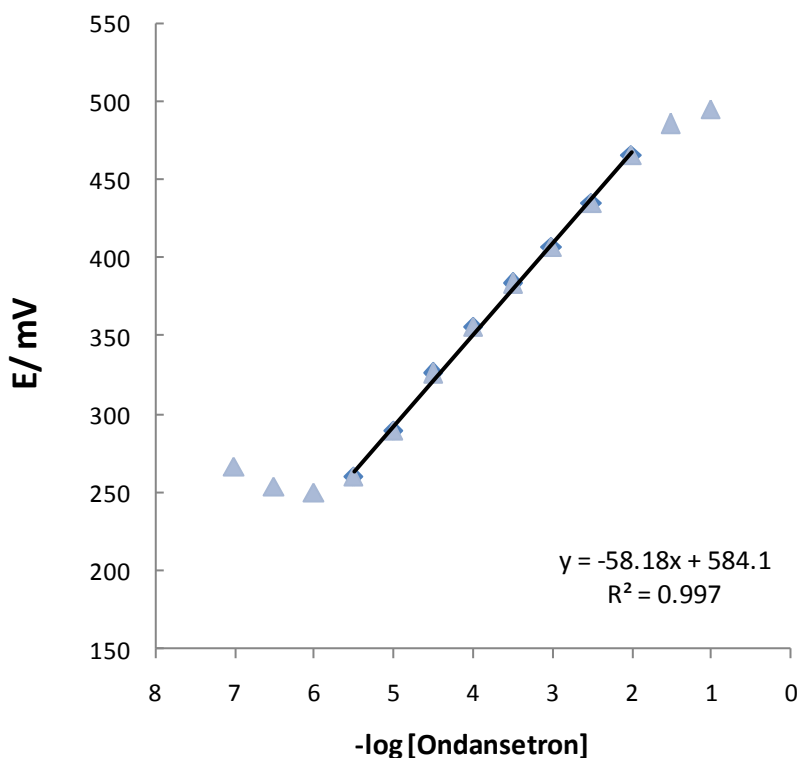

Figure 3. Calibration curve of liquid membrane sensor, the results are based on 5 replicate measurements

3.3. Dynamic Response Time

Dynamic response time is the required time for the sensor to achieve values within ±1 mV of the final equilibrium potential, after successive immersions in the sample solutions [54,55]. Its calculation involved the variation and the recording of the Ondansetron concentration in a series of solutions from 1.0×10^{-5} 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 the liquid membrane sensor was about 18 s in the concentrated solutions.

3.4. pH Effect on the Response

To examine the effect of pH on the electrode responses, the potential was measured at specific concentration of the Ondansetron 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 3.5 to 5.5, 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 5.5 might be justified by removing the positive charge on the drug molecule and decrease the solubility of the drug in aqueous solution. Fluctuations below the pH value of 3.5 were caused by removal of the membrane ingredients or analyte in the solution.
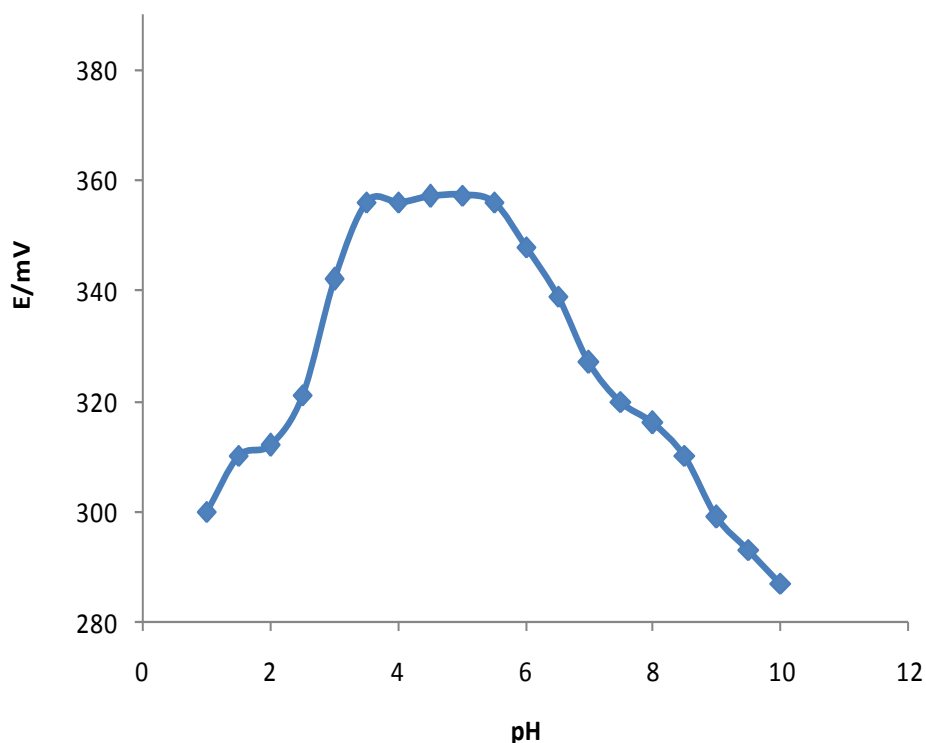

Figure 4. Applicable pH of the electrodes in the test solution of 1.0×10^{-4} mol L^{-1}

3.5. Life-time Study

The average lifetime for most of the reported potentiometric sensors is in the range of 4–10 weeks [37-40]. Sensor lifetime was estimated by the calibration curve, periodical test of a standard solution and calculation of its response slope. For this estimation, three electrodes were employed extensively (1 hour per day) for 10 weeks.

After 7 weeks utilization of the liquid membrane sensor, two changes were observed: a slight gradual decrease in the slope and an increase in the detection limit. It is well known that the loss of plasticizer, sensing element, or ionic site from the polymeric film due to leaching into the sample solution after several times of usage, is a primary reason for limited lifetimes of the sensors. Using RTILs in the composition of the membrane causes a longer lifetime of the sensor.

Table 3. Lifetime of PVC membrane electrode

Week	Slope (mV per decade)	DL (mol L^{-1})
First	58.2±0.3	4.5×10^{-6}
Second	57.8±0.2	5.0×10^{-6}
Third	57.4±0.3	6.5×10^{-6}
Fourth	57.1±0.4	8.5×10^{-6}
Fifth	56.7±0.3	1.0×10^{-5}
Sixth	55.9±0.4	2.5×10^{-5}
Seventh	55.2±0.5	4.0×10^{-5}
Eighth	41.0±0.7	7.5×10^{-5}
Ninth	28.3±0.7	1.5×10^{-4}
Tenth	18.7±0.8	5.0×10^{-3}

3.6. Analytical Applications

Table 4. Potentiometric determination of Ondansetron hydrochloride in pharmaceutical formulations

Sample	Labeled amount (mg/tab.)	Found by the sensor* (mg/tab.)
Sample 1	4	3.89±0.06
Sample 2	4	4.10±0.08
Sample 3	4	3.90±0.11

* The results are based on five replicate measurements.

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

Interfering ion	Log (K_{MPM})
Na$^+$	-3.5
K$^+$	-3.1
NH$_4^+$	-3.0
Ca^{2+}	-3.3
Mg^{2+}	-3.4
Cl$^-$	-3.7
NO$_3^-$	-
Lactose	-
Glucose	-

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

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.

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 Ondansetron sensor were evaluated by the matched potential method (MPM) [56-58]. The resulting values of the selectivity coefficients are shown in Table 5. Note that all selectivity coefficients shows that the interferences negligible in the performance of the electrode assembly.

For repeatability monitoring, 3 standard samples were measured. The RSD values by PVC membrane were 2.43, 3.12 and 2.78%. For ruggedness of the methods a comparison was performed between the intra- and inter-day assay results for Ondansetron 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 4.7%. On the other hand, the robustness was examined while the parameter values (pH of the solution and the laboratory temperature) changed slightly. Ondansetron 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, a potentiometric liquid membrane sensor was constructed for determination of Ondansetron hydrochloride in its pharmaceutical formulation. The sensor demonstrated advanced performance with a fast response time, a lower detection limit of 4.5×10^{-6} mol L^{-1} for PVC membrane electrode and potential responses across the range of 5.0×10^{-6}-1.0×10^{-2} mol L^{-1}. Sensor respond based on ion-exchange mechanism. The best membrane sensor performance was achieved by a membrane composition of 30% PVC, 60% DBP, 3% RTIL and 7% ion-pair complex.

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