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Fe (II) Ion-Selective Membrane Electrode based onTetra-Phenyl Porphyrin in PVC Matrix

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ABSTRACT

Fe2+ ion-selective membrane sensor has been fabricated from polyvinyl chloride (PVC) matrix membrane containing neutral carrier tetra phenyl porphyrin (TPP) ionophore. The addition of sodium tetraphenylborate (NaTPB) and the plasticizer DBP has been found to substantially improve the performance of the sensor. The best performance was obtained with the sensor having a membrane of composition of TPP: NaTPB: DBP: PVC in the ratio 6:3:61:30 respectively. The sensor shows a linear response over a wide concentration range of 1.0 × 10-6 to 1.0 × 10-2 M with a Nernstian slope of 29.4 ± 0.6 mV decade-1 and a detection limit of 9.6 × 10-7 M. It has a response time of <12 s and can be used for more than seven weeks without any measurable divergences in its potentials. The proposed sensor could be used in a pH range of 3.0-5.0. Potentiometric selectivity coefficients determined by matched potential method (MPM) indicate excellent selectivity for Fe2+ ion.

Keywords: Fe^{2+} ion; Selective electrode; Membrane; Porphyrins; Nernstian slope

INTRODUCTION

Porphyrins (which come from the Greek for "purple") are a ubiquitous class of naturally occurring molecules involved in a wide variety of important biological processes ranging from oxygen transport to photosynthesis, from catalysis to pigmentation changes [1]. The common feature of all these molecules is the basic structure of the porphine macrocycle, which consists of a 16-atoms ring containing four nitrogen atoms, obtained by linking four tetrapyrrolic subunits with four methine bridges, as shown in Figure 1.

Iron (II) is a constituent of hemoglobin which is essential for the normal transportation of oxygen to the tissues. There is approximately 10-15 mg of iron (II) in the foods ingested during a day. Studies indicate that normal subjects absorb ten per cent of iron in the food [2]. The absence of iron in the organism causes anemia, the result is a decrease in red blood cell content. This deficiency is treated with iron salts via oral or intramuscular administration [3]. The excess of iron during treatment with iron salts may produce severe poisoning, causing symptoms of gastric irritation, vomiting,

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pallor and circulatory collapse [4]. Liquid membrane ion-selective electrodes (LMISE) in particular have much importance for the analysis of pharmaceutical products. The relatively low cost, high simplicity, selectivity and low analysis time are advantages of using LMISE compared with tedious procedures suggested in the pharmacopeias [5, 6].

Ion Selective Electrodes are being widely used in the fields of environmental, industrial, agricultural and medicinal fields of as they offer several advantages over other methods of analysis. The most attractive features of this technique are the speed with which samples can be analyzed portability of the device, sample non-destruction, online monitoring, cost effectiveness and large measuring range. Some commercialized sensors for alkali and alkaline earth metals, halides, etc. are available; however more efforts are required to develop ion-selective electrodes of commercial standards for heavy metal ions, which are toxic beyond a certain concentration level.

Ion selective electrodes provide analytical procedures for such situations as they are fast, convenient and require minimum sample pre-treatment of sample and may also be suitable for online analysis. Efforts in this direction are on using of the different materials for preparation of the membranes. The main requirement to impart selectivity to the ion sensor is to use membranes of a material which shows strong affinity for a particular metal ion and poor to others. The main problem in the development of a good sensor is that such materials are not easily available. Thus, newer materials synthesized are continuously being examined for such roles. Recently, a number of selective membrane electrodes for some transitional and heavy-metal ions have been reported [7-18].

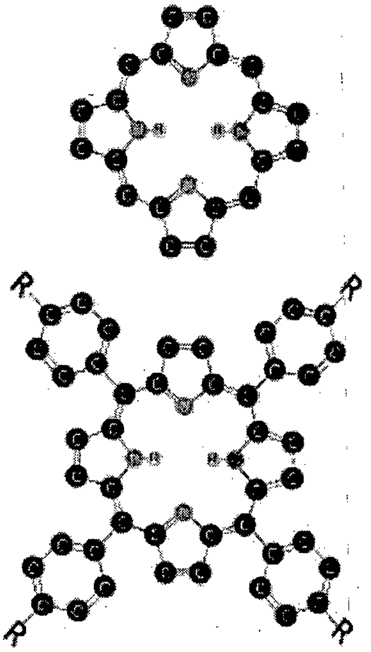

Figure 1. Structure of the porphyrin macrocycle (top) and of Tetraphenyl-porphyrin (bottom). The hydrogen atoms saturating the carbon bonds are not shown. The R-groups in TPP are H atoms.

EXPERIMENTAL

Reagents and materials

Reagent grade acetophenone (AP), dibutyl phthalate (DBP), sodium tetraphenylborate (NaTPB), oleic acid (OA), high relative molecular weight poly vinyl chloride (PVC), tetrahydrofuran (THF) were purchased from Merck and Aldrich and used as received. The nitrate and chloride salts of all cations used (all from Merck and Aldrich) were of the highest available purity and used without any further purification. Double distilled deionized water was used throughout. Tetraphenyl porphyrine (TPP) (Fig.1) was synthesized as described in J. Org. Chem., (1967) [19].

Preparation of membrane

The PVC-based membranes were prepared by dissolving appropriate amounts of porphyrine, anion excluder NaTPB, solvent mediators, dibutyl phetalate (DBP) and appropriate amounts of PVC in THF (5 ml) after complete dissolution of all the components and thorough mixing, the resulting mixture was transferred into a glass dish of 2 cm in diameter. The THF content of the mixture was evaporated slowly, until oily concentrated mixture is obtained. A Pyrex tube (3-5 mm o.d.) was dipped into the mixture for about 10 s, so that a transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 12 h. the tube was then filled with the internal filling solution 1.0×10-3 M Fe(II). The electrode was finally conditioned for 24 h by soaking in a 1.0×10-2 M solution of Fe(II).

EMF measurement

The potential measurements were carried out at 25±0.1 °C with a digital milivoltmeter (RANGE Model RE68) by setting up the following cell assembly, employing a saturated calomel electrode (SCE) as a reference electrode. Activities were calculated according to the Debye-Huckel procedure [20]. A cell assembly comprises:

SCE / internal solution (1.0×10-3 M Fe2+) / membrane / test solutions / SCE

RESULT AND DISCUSSION

Effect of membrane composition on the electrode response

The potential of the cell set-up with membranes of tetraphenyl porphyrin was determined as a function of Fe2+ activity and the results obtained are shown in Fig.2. Sodium tetra phenyl borate was added to all the prepared membranes to reduce the interference from sample anions (Donnan exclusion), optimize sensing selectivity and to reduce bulk membrane impedance [21]. The improvement in the performance was attempted by the addition of plasticizers to the membranes.

The addition of plasticizers not only improves the workability of the membranes, but also contributes significantly towards the improvement in the working concentration range, stability and shelf life of the sensor [22, 23]. However, the selectivity usually remains unaffected and mainly depends on the metal-ionophore interaction. The plasticizer to be used in membranes should exhibit high lipophilicity, high molecular weight, low tendency for exudation from the polymer matrix, low vapor pressure and high capacity to dissolve the substrate and other additives present in the membrane. Additionally, its viscosity and dielectric constant should be adequate [24]. Thus, three plasticizer namely, NB, AP and DBP were added in order to improving of the sensors performance. All performance characteristics of the sensors are compiled in table 1. The results show that in this case, the use of 61% DBP in the presence of 30% PVC, 6% ionophore and 3% NaTPB (No. 4, Table1) which shows the widest working concentration range (1.0 × 10-6 to 1.0 × 10-2 M) and a Nernstian slope of 29.4 ± 0.6 mV decade-1 of activity. Repeated monitoring of potentials (10 measurements) at the same concentration (1.0 × 10-3 M) gave a standard deviation of ±0.6 mV. The potential responses of different ion-selective electrodes based on TPP are shown in Fig. 2.

Table 1. Optimization of the membrane ingredients

No.	Composition (%)					
	Ionophore	PVC	Plasticizer	Additive	Slope	Working activity range (M)
1	5	30	62(NB)	3(NaTPB)	12.2	1.0×10^{4}- 1.0×10^{2}
2	5	30	62(AP)	3(NaTPB)	25.6	1.0×10^{6}- 1.0×10^{2}
3	5	30	62(DBP)	3(NaTPB)	28.4	1.0×10^{5}- 1.0×10^{2}
4	6	30	61(DBP)	3(NaTPB)	29.4	1.0×10^{6}- 1.0×10^{2}
5	6	30	57(DBP)	7(NaTPB)	26.8	1.0×10^{5}- 1.0×10^{2}
6	5	30	59(AP)	6(OA)	17.4	1.0×10^{6}- 1.0×10^{2}
7	5	30	59(DBP)	6(OA)	25.4	1.0×10^{6}- 1.0×10^{2}
8	7	30	60(DBP)	3(NaTPB)	31.7	1.0×10^{6}- 1.0×10^{2}
9	8	30	58(AP)	4(NaTPB)	22.8	1.0×10^{5}- 1.0×10^{2}

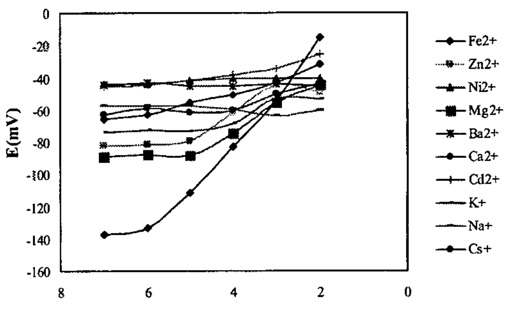

Fig. 2. Potential response of various metal ion-selective electrodes based on TPP.

Calibration curve and statistical data

The potential electrode response to varying concentrations of Fe2+ ions displays a linear response to the Fe2+ ion concentration in the range of 1.0 × 10-6 to 1.0 × 10-2 M (Fig. 3). The slope of the calibration graph was 29.4 ± 0.6 mV decade-1 of the Fe(II) ion concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 9.6 × 10-7 M. The standard deviation of 10 replicate measurements is ±0.6 mV.

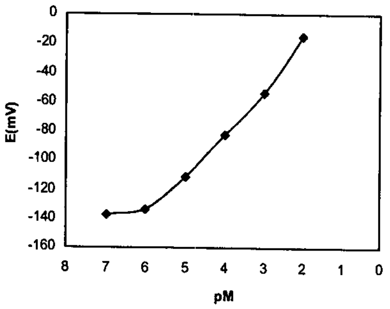

Fig. 3. Calibration curve of the Fe(II) membrane sensor based on TPP (with membrane 4).

Effect of pH

The effect of pH on the performance of the membrane sensor for a solution containing 1.0 × 10-3 and 1.0 × 10-4 M Fe2+ was considered in the pH range of 3.0-5.0 and the results are shown in Fig. 4. The deviation in potential at pH below 3.0 appears due to H+ ion interference and above 5.0 complex hydrolyze.

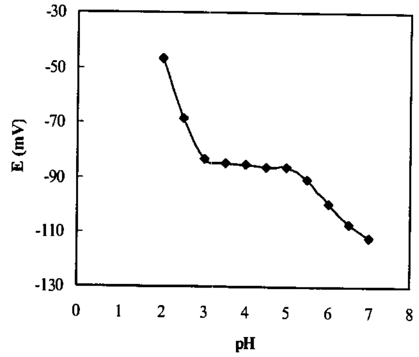

Fig. 4. Effect of the pH of test solution (1.0 × 10-4 M) on the potential response of the Fe2+ ion-selective electrode.

Potentiometric selectivity

The selectivity is the most important characteristics, as it determines the extent of utility of a sensor in real sample measurement. The selectivity coefficient values were determined by matched potential method (MPM), which was proposed by Gadzekpo and Christian [25] to overcome difficulties in obtaining selectivity coefficient values when ions of unequal charges are involved. In this procedure, the selectivity coefficient $K^{Pot}_{Fe^{2+},B}$ is calculated by the expression:

$$K^{Pot}_{Fe^{2+},B} = \frac{a'_{Fe^{2+}} - a_{Fe^{2+}}}{a_B} = \frac{\Delta a_{Fe^{2+}}}{a_B} \qquad (1)$$

and is therefore determined by measuring the change in potential upon increasing by a definite amount the primary ion activity from an initial values of $a_{Fe^{2+}}$ to $a'_{Fe^{2+}}$ and a_B represents the activity of interfering ion (B) added to the same reference solution of activity $a_{Fe^{2+}}$ which causes the same potential change. The values of $a_{Fe^{2+}}$ and $a'_{Fe^{2+}}$ were taken to be 1×10^{-3} M and 5×10^{-3} M, where as the values of a_B were experimentally determined. The values determined by MPM are given in table 2.

Table 2. Selectivity coefficient $K^{Pot}_{Fe^{2+},B}$ values for Fe^{2+} selective sensors by the matched potential method

$K^{pot}_{Fe,M}$	M^{n+}	$K^{pot}_{Fe,M}$	M^{n+}	
	Zn^{2+}	1.34×10^{-3}	Ni^{2+}	1.74×10^{-3}
	Cu^{2+}	2.96×10^{-1}	Ba^{2+}	3.45×10^{-3}
	Mg^{2+}	5.71×10^{-2}	Li^{+}	2.84×10^{-3}

Response and lifetime

The span of time between the instant of the ISE insertion and a reference electrode, and their consequent contact in a sample solution (or the instant when a change is induced in the concentration of the target ion), and the first instant at which the E slope fluctuations against the time curve become equal to ± 0.1 mV min^{-1}, is regarded as the response time of that electrode.

The response time of the sensor has been determined by measuring the time required to achieve a steady potential for 1.0×10^{-4} M solution, when Fe^{2+} ion activity was rapidly increased 10-fold from 1.0×10^{-5} to 1.0×10^{-4} M. The results are depicted in Fig. 5. As it can be seen from Fig. 5, the electrode reaches to its equilibrium response in a very short time (12 s). The main factor responsible for limited lifetime of a sensor is believed to be the loss of one or more of its components while contacting with aqueous solution. Sufficient lipophilicity of ionophores and plasticizers ensures stable potentials and long lifetimes [24, 26-27]. The lifetime of the membrane sensor prepared could be used for 2 months without any measurable change in potential. However, it is important to emphasize that the membrane was stored in a 1.0×10^{-2} M, Fe^{2+} solution when it wasn't in use.

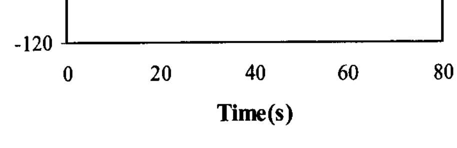

Fig. 5. Static response time of the proposed electrode by changing the Fe^{2+} concentration from 1.0×10^{-5} to 1.0×10^{-4} M

Application

The proposed electrode was successfully applied to the determination of Fe (II) ions in the sample water by standard addition and atomic absorption methods. The potential of 10 ml above solution was measured as testing sample (E_1). Then 0.1 ml of 1.0×10^{-2} M of Fe^{2+} standard was added into the testing solution and the equilibrium potential of E_2 was obtained. From the potential change of ΔE (E_2 - E_1) one can determine the concentration of the testing sample using the equation given below:

$$C_x = \frac{C_s C_s}{(V_x + V_s)10^{-\Delta E/S} - V_x} \qquad (2)$$

Here C_x is the Fe(II) concentration of testing sample, C_s is the concentration of the standard, V_x and V_s are the corresponding volumes, S is the slope of the electrode response, and ΔE is the change in potential [32]. The concentration of Fe^{2+} in the initial sample (C_x) was found to be 7.32×10^{-3} M. the result thus obtained was found to be in good agreement with that obtained (C_x) by standard addition method 7.47×10^{-3} M.

CONCLUSION

The plasticized PVC-based membrane incorporating TPP as an ionophore, DBP as solvent mediator and NaTPB as anion excluder in a PVC matrix in the ratio of 6:3:61:30 (Ionophore:NaTPB:DBP:PVC) could be used to determine Fe^{2+} in the concentration range 1×10^{-6} to 1×10^{-2} M with a slope of 29.4 ± 0.6 mV $decade^{-1}$ of activity and a fast response time of <12 s. The sensor displays a Nernstian response over a large range of concentration with a detection limit close to 9.6×10^{-7} M. The selectivity of the electrode towards Fe^{2+} is quite good over other cations and the lifetime of the assembly is more than seven weeks in aqueous.

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