

N-phenylaza-15-crown-5 as Ionophore in PVC-Matrix for Fe²⁺ - Selective Sensor

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ABSTRACT

The preparation of polymer membrane selective to Iron(II) ion and its application to ion-selective electrode is reported here. PVC membrane contains Iron-selective N-phenylaza-15-crown-5 as ionophore. The membrane electrode is highly selective to Iron(II) ion and exhibit good linear response over a wide concentration range of 1.0×10^{-2} to 1.0×10^{-6} M with Nernstian slope of 29.2 ± 0.6 mV per decade. The detection limit of electrode is 2.5×10^{-6} M. It has a response time of <15 s and can be used for more than 2 months without any measurable divergence in potential. The proposed sensor shows fairly a good discriminating ability towards Fe²⁺ ion in comparison to some hard and soft metals. The electrode was applied to the determination of Fe²⁺ ions in the ferrous sulfate syrup.

Keywords: Fe⁺²-selective electrode; PVC membrane; Temperature coefficient; Potentiometry

INTRODUCTION

Amongst the various analytical techniques available, the use of ion-selective membrane electrodes is well establishing routine analytical technique. Good ion-selective electrodes (ISEs) possess many advantages over the traditional methods of analysis as they provide accurate, reproducible, fast and often selective determination of various ionic species. Not only this, the ion-selective electrodes (ISEs) allow non-destructive, on line monitoring of particular ion in small volume of sample without any pretreatment. Because of these merits, the use of ISEs is increasing day by day in medicinal, environmental, agricultural and industrial field. During last four decades, a number of ion-selective electrodes with polymeric membranes have been reported [1-10].

The various sensors applying sensing polymers can be used for physical measurements such as temperature, mechanical properties (touch switch devices, deformation sensors, pressure sensors, etc.), acoustic properties (microphones, ultrasonic sensors, etc.), infra-red radiation, relative humidity and physical gas sensing. Polymers can be used as membranes that are sensitive and specific to the detection of ion concentrations, also in special sensors for medical and biology, e.g. enzyme and immunosensors [11]. In this work, results on the PVC matrix membrane sensor incorporating (N-phenylaza-15-crown-5) ionophore for the determination of Iron(II) in aqueous solutions have been presented and discussed.

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EXPERIMENTAL

1. Reagents and materials

Reagent grade dibutyl phthalate (DBP), oleic acid (OA), tetrahydrofuran (THF), high relative molecular and N-phenylaza-15-crown-5 (all from Merck) were used as received. Nitrate and chloride salts of all cations used were of the highest purity available (all from Merck or Fluka) and used without any further purification. Double distilled deionized water used throughout.

2. Electrode preparation

The general procedure to prepare the PVC membrane was to mix thoroughly 30mg of powdered PVC, 62 mg of plasticizer DBP and 3 mg of additive oleic acid in 3 ml of THF. To this mixture was added 5 mg of ionophore NPA15C5 and the solution was mixed well. The solvent was allowed to evaporate at room temperature. After 24h, transparent membrane of 10 mm diameter was cut, attached to a pyrex glass tube. The tube was then filled with internal filling solution (1.0×10^{-3} M Fe^{2+}). The electrode was finally conditioned for 8 h by soaking in a 1.0×10^{-2} M solution of Fe^{2+} .

3. Emf measurements

All emf measurements were carried out with the following assembly:

$\text{Hg}-\text{Hg}_2\text{Cl}_2, \text{KCl (sat'd)} / \text{internal solution}(1.0 \times 10^{-3} \text{ M } \text{Fe}^{2+}) / \text{PVC membrane} / \text{test solution} / \text{Hg}-\text{Hg}_2\text{Cl}_2, \text{KCl (sat'd)}$.

The potentiometric measurements were performed with a Metrohm pH meter E516 at 25.0 ± 0.1 °C. Activities were calculated according to the Debye–Huckel procedure [12].

RESULTS AND DISCUSSION

1. Effect of membrane composition

It is well known that the sensitivity and selectivity obtained for a given ionophore depend significantly on the membrane composition and the nature of solvent mediator and additives used [13]. Thus, the influences of the membrane composition, nature and amount of plasticizer and amount of oleic acid as a lipophilic additive on the potential response of the Fe(II) sensor were investigated and the results are summarized in Table 1. It is seen that, the use of 62% DBP in the presence of 30% PVC, 5% ionophore and 3% oleic acid (NO. 5, Table 1) results in the best sensitivity, with a Nernstian slope of 29.2 ± 0.6 mV/decade over a wide dynamic range.

Table 1. Optimization of the membrane ingredients

No	Composition (%)				Slope (mV/decade)	Linear range [M]	Regression coefficient
	Ionophore	PVC	Plasticizer	Additive(OA)			
1	4	33	60(DBP)	3	16.8	$1.0 \times 10^{-6}-1.0 \times 10^{-2}$	0.9945
2	3	30	62(DBP)	5	22.2	$1.0 \times 10^{-6}-1.0 \times 10^{-2}$	0.9959
3	3	32	62(DBP)	3	18.2	$1.0 \times 10^{-6}-1.0 \times 10^{-2}$	0.9807
4	5	30	62(AP)	3	11.2	$1.0 \times 10^{-5}-1.0 \times 10^{-2}$	0.9962
5	5	30	62(DBP)	3	29.2	$1.0 \times 10^{-6}-1.0 \times 10^{-2}$	0.9961
6	5	30	60(AP)	5	9.5	$1.0 \times 10^{-5}-1.0 \times 10^{-2}$	0.9831
7	5	30	60(DBP)	5	31.2	$4.0 \times 10^{-6}-1.0 \times 10^{-2}$	0.9919
8	8	30	59(DBP)	3	18.1	$1.0 \times 10^{-6}-1.0 \times 10^{-2}$	0.9968

2. Response time

The critical response characteristic of the electrode was assessed according to IUPAC recommendations [14]. Fig. 1. illustrates the static response time of the membrane electrode. As it is seen, the static response time is less than 15s for Fe^{2+} concentration $\leq 1.0 \times 10^{-4}$ M and the response of the electrode was remained constant for more than 5 min, after which only a very slow divergence was recorded (± 1 mV).

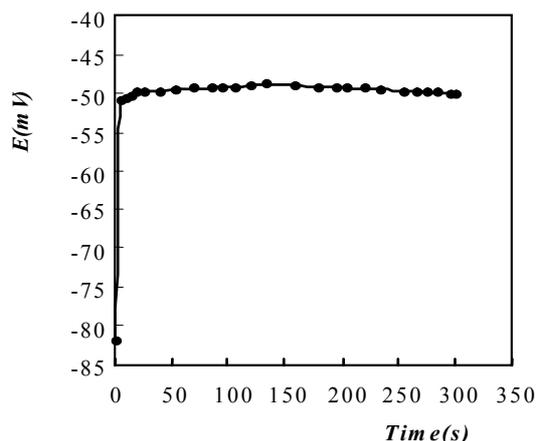


Fig. 1. Static response time of the proposed electrode by changing the Fe^{2+} concentration from 1.0×10^{-5} to 1.0×10^{-4} M.

3. Calibration curve and statistical data

The potential responses of different ion – Selective electrodes based on NPA15C5 are shown in Fig. 2. As it is seen, among different cations tested, the largest sensitivity was obtained for Fe^{2+} ion. The e.m.f. vs. $-\log a(\text{Fe}^{2+})$ of the PVC membrane

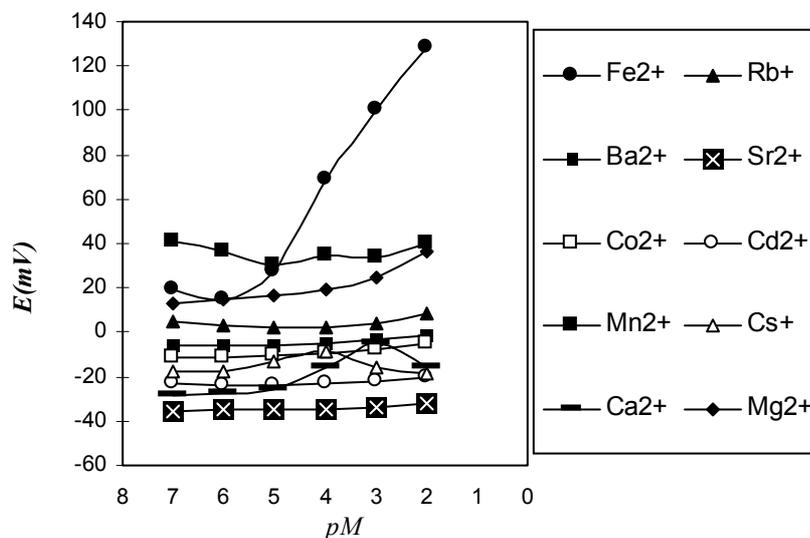


Fig. 2. Potential response of various metal ion-selective electrodes based on NPA15C5.

based on NPA15C5, prepared under optimal composition, indicated a rectilinear range from 1.0×10^{-6} to 1.0×10^{-2} M. The slope of the calibrations curve was 29.2 ± 0.6 mV per decade of Fe^{2+} concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 2.5×10^{-6} M. The standard deviation of ten replicate measurements is ± 0.6 mV. The membrane electrodes prepared could be used for more than 2 months without any measurable change in potential.

4. Potentiometric selectivity

The selectivity behavior is obviously one of the most important characteristics of an ion-selective electrode, determining whether a reliable measurement in the target sample is possible [15,16]. The selectivity coefficients of the proposed membrane selective electrode were determined against a number of interfering ions by using the matched potential method (MPM) [16–18]. This is a recently recommended procedure by IUPAC, which gets rid of the limitations of the corresponding methods based on the Nicolski–Eisenman equation for the determination of potentiometric selectivity coefficients. These limitations include non–Nernstian behavior of interfering ions and inequality of charges of primary interfering ions. The obtained results for the $K_{\text{Fe},\text{M}}^{\text{pot}}$ of Fe^{2+} ion-selective electrode are summarized in Table 2.

Table 2. Selectivity coefficients of various interfering ions (M^{n+})

M^{n+}	$K_{Fe,M}^{pot}$	M^{n+}	$K_{Fe,M}^{pot}$
Rb ⁺	4.04×10^{-3}	Mn ²⁺	2.11×10^{-2}
Li ⁺	5.04×10^{-3}	Co ²⁺	2.80×10^{-2}
Cs ⁺	5.64×10^{-3}	Ba ²⁺	3.15×10^{-2}
Cd ²⁺	9.95×10^{-3}	Mg ²⁺	5.40×10^{-2}
Ag ⁺	1.82×10^{-2}	Sr ²⁺	4.96×10^{-2}
Ca ²⁺	1.40×10^{-2}	Hg ²⁺	2.84×10^{-1}
Zn ²⁺	1.60×10^{-2}	Al ³⁺	2.00×10^{-2}

As is seen, the selectivity coefficients obtained are relatively small, indicating that the diverse ions used do not disturb the functioning of the Fe²⁺ ion-selective electrode significantly. In order to realize the level of interference caused by these ions in the performance of electrode, mixed run studies were carried out [19–21].

Fig. 3. shows the variation of potentials with Fe²⁺ ion concentration in presence of different concentration of Hg²⁺. It is observed that the increasing of the concentration of Hg²⁺ ion would cause decreasing of the linear range and increasing of the detection limit.

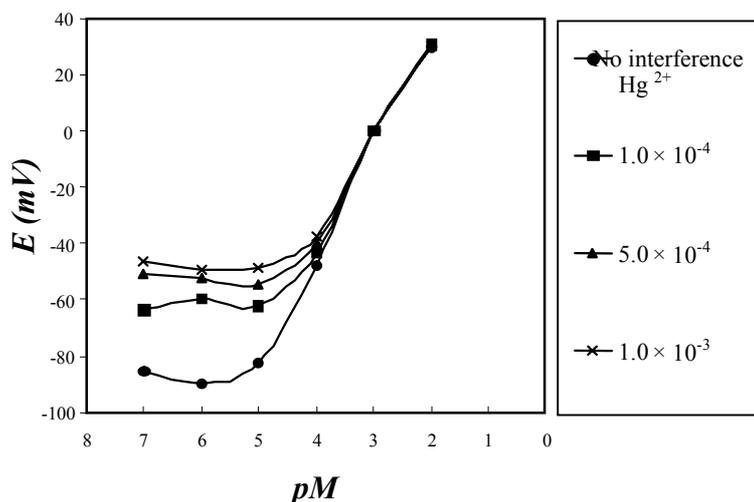


Fig. 3. Effect of different concentrations of Hg²⁺ ions on the variation of potential.

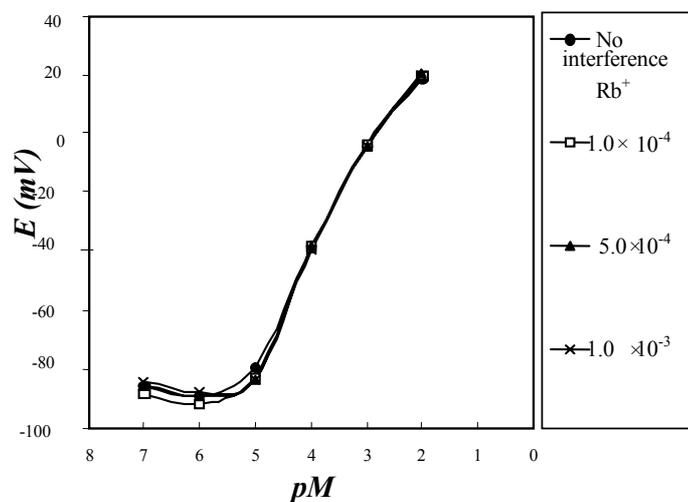


Fig. 4. Effect of different concentrations of Rb⁺ ions on the variation of potential.

Mixed run studies were also carried out for a noninterference ion such as Rb^+ ion and result was shown in Fig. 4. It is shown that the presence of Rb^+ ions don't overly contribute on membrane potentials.

5. Effect of temperature

The trend of changes of electrode performance with temperature, at test solution temperatures 20,25,30,35,40,45 and 50 °C for the Fe^{2+} -electrode are represented in Table 3.

The electrode exhibits good Nernstian behavior in the temperature range (20–50°C). The standard cell potentials, (E_{cell}°), were determined at different temperatures from the

respective calibration plots as the intercepts of these plots at $\text{pFe}^{2+}=0$, and were used to determine the isothermal temperature coefficient (dE°/dt) of the cell with the aid of the following equation [22]:

$$E_{\text{cell}}^{\circ} = E_{\text{cell}(25^{\circ}\text{C})}^{\circ} + (dE^{\circ}/dt)_{\text{cell}} (t - 25) \quad (1)$$

Plot of E_{cell}° vs. $(t-25)$ produced a straight line, as shown in Fig. 5.

The slope of this line was taken as the isothermal temperature coefficient of the cell. It amounts to $0.00081 \text{ V}/^{\circ}\text{C}$. The standard potentials to the ($\text{Hg}/\text{Hg}_2 \text{Cl}_2; \text{KCl}(\text{sat'd})$) reference electrode were calculated using the following equation:

$$E_{\text{Hg}/\text{Hg}_2 \text{Cl}_2}^{\circ} = 0.241 - 6.6 \times 10^{-4} (t - 25) \quad (2)$$

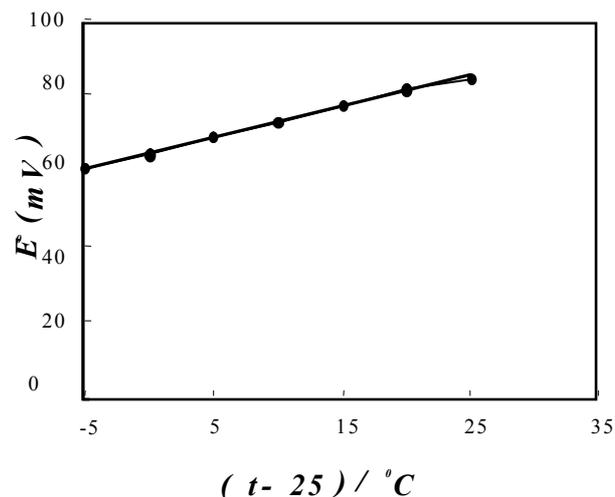


Fig. 5. Variation of standard potential of the cell with changes of test solution temperatures.

The values of the standard potentials of Fe (II)-electrode was calculated at the different temperatures from the following relation:

$$E_{\text{cell}}^{\circ} + E_{\text{reference}}^{\circ} = E_{\text{electrode}}^{\circ} \quad (3)$$

Plot of $E_{\text{electrode}}^{\circ}$ vs. $(t-25)$ gave a straight line, as shown in Fig. 6.

Table 3. Trend of changes of electrode performance with temperature

Temperature (°C)	Slope (mV/decade)	E° (mV)	Linear range (M)
20	26.6	60.58	$1.0 \times 10^{-2} - 1.0 \times 10^{-6}$
25	28.0	63.90	$1.0 \times 10^{-2} - 1.0 \times 10^{-6}$
30	29.8	68.38	$1.0 \times 10^{-2} - 1.0 \times 10^{-6}$
35	31.1	72.64	$1.0 \times 10^{-2} - 1.0 \times 10^{-6}$
40	32.0	76.86	$1.0 \times 10^{-2} - 1.0 \times 10^{-6}$
45	33.5	81.18	$1.0 \times 10^{-2} - 1.0 \times 10^{-6}$
50	84.1	84.08	$1.0 \times 10^{-2} - 1.0 \times 10^{-6}$

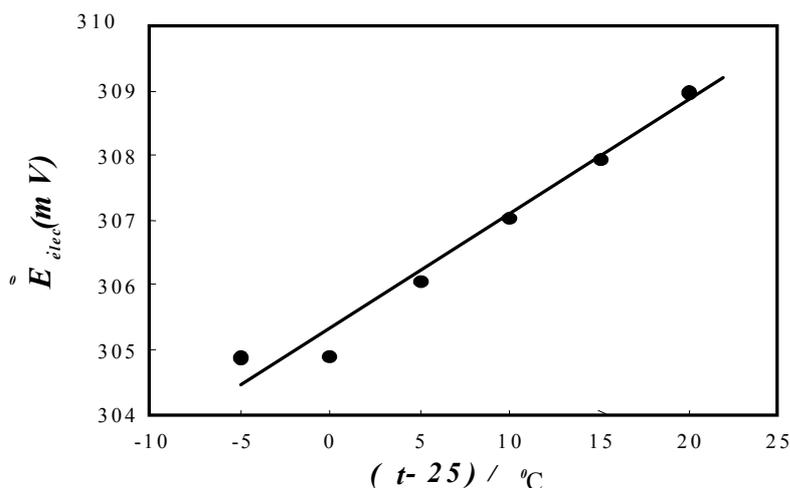


Fig. 6. Variation of standard potential of the electrode with changes of test solution temperatures.

The slope of the line was taken as the isothermal temperature coefficient of the Fe (II)–electrode. It amounts to $0.00017 \text{ V}/^\circ\text{C}$. The small values of $(dE^\circ/dt)_{\text{cell}}$ and $(dE^\circ/dt)_{\text{electrode}}$ reveal the high thermal stability of the electrode within the investigated temperature range.

6. Application

The proposed electrode was successfully applied to the determination of iron (II) ions in the ferrous sulfate syrup by standard addition method. An electrode was immersed into a sample of 10 cm^3 with unknown concentration (C_x) and the equilibrium potential of E_1 was recorded. Then 0.1 cm^3 of $1.0 \times 10^{-2} \text{ M}$ of Fe (II) 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:

$$C_x = \frac{C_s V_s}{(V_x + V_s) 10^{-\frac{\Delta E}{S}} - V_x} \quad (4)$$

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 [23]. The concentration of Fe^{2+} in the initial sample (C_x) was found to be $1.468 \times 10^{-3} \text{ M}$. The result thus obtained was found to be in good agreement with that obtained (C_x) by standard addition method $1.431 \times 10^{-3} \text{ M}$.

CONCLUSION

The main advantage of the potentiometric sensor is its simplicity of preparation, short conditioning time, fast response time, Nernstian behavior and improved good selectivity. The electrode has a life time of more than two months. The electrode also was successfully applied to the direct determination of Fe(II) in the ferrous sulfate syrup.

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