A Novel Iron(III) Potentiometric Sensor Based on (E)-N’-((2-hydroxynaphthalen-3-yl)methylene)benzohydrazide

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Here, we report the design and application of a new PVC membrane electrode, based on (E)-N’-((2-hydroxynaphthalen-3-yl)methylene)benzohydrazide as a reliable complexing agent, for determination of iron(III) ion. The electrode illustrates an excellent Nernstian slope of 19.9±0.3 mV/decade over a wide linear range of concentration from 5.0×10$^{-9}$ to 1.0×10$^{-2}$ M with a detection limit of 1.0×10$^{-9}$ M of Fe$^{3+}$ in solution. The tolerable pH range of 2.4 to 4.0, response time of 10 s and measurement stability for 3 months is valuable characteristics of the sensor. The analytical application of the sensor was successfully tested by potentiometric titration of a Fe(III) solution with EDTA in some water samples. The accuracy of given measuring data was tested by determination of Fe$^{3+}$ in some water solutions from different resources with both the sensor and an atomic absorption spectrometer, as a standard method. The results were well comparable. We inform a reliable device that provides a simple method to determine Fe$^{3+}$ ion in a fast manner with high accuracy.

Keywords: Benzohydrazide; Iron(III); Potentiometric sensor; PVC membrane

1. INTRODUCTION

Iron is one of the most important elements in the world, which plays essential roles in environmental and biological systems. It has a significant role in electron and oxygen transfer [1, 2]. Several forms of iron such as inorganic Fe$^{3+}$, Fe$^{2+}$ and organic complexes can be found as colloids of oxides, oxyhydroxides or mixed with organic materials. Indeed, the life is impossible without this element for most organisms. Excess of iron in our body causes some diseases such as cancer and heart diseases but some others, hemochromatosis and anemia are the result of iron deficiency [3–9]. Because of the role of iron in the nature, the development of any analysis technique for iron determination in different clinical, medical, environmental and industrial samples is vital.
Today, different methods are used to measure iron ions, for example, inductively coupled plasma–mass spectrometry, neutron activation analysis, atomic absorption spectrometry (AAS), high-performance liquid chromatography (HPLC), flow injection and fluorimetry [10–15]. Most these methods require several time-consuming manipulation steps, expensive devices and specialists to operate or data processing.

Ion-selective electrodes (ISEs) based on polyvinyl chloride (PVC) membrane are wildly used in determining of various metal ions in industrial and environmental samples. ISEs have many advantages including simplicity, fast and easy preparation procedures, low cost, fast response times, wide concentration ranges, low detection limits, stable responses and renewability [16–25]. In these years, there are many reports on PVC-membrane ion selective electrodes for Fe$^{3+}$ ion determination in various samples [26–30]. In this work, we investigated the properties of a new ISE based on (E)-N'-(2-hydroxynaphthalen-3-yl)methylene)benzohydrazide (HNBH) as a novel ion carrier for determination of trace amount of Fe$^{3+}$ ion in real samples.

2. EXPERIMENTAL

2.1 Reagents and materials

All nitrate salts of cations were purchased from Merck (Germany). The nitrate and chloride salts used in all measurements were purchased from Fluka (Switzerland). Aqueous solutions were prepared with distilled-deionized water. The high molecular weight PVC powder, sodium tetraphenyl borate (NaTPB), bis(2-ethylhexyl)sebacate (BEHS), bis(2-ethylhexyl)phosphate (BEHP), tris(2-ethylhexyl)phosphate (TEHP), nitrobenzene (NB) and tetrahydrofuran (THF) were obtained from Aldrich and Merck. (E)-N'-(2-hydroxynaphthalen-3-yl)methylene) benzohydrazide (HNMB) was synthesized and purified in Inorganic Chemistry Research Laboratory of Kerman University, Iran [31].

2.2 Apparatus

Potentiometric measurements were carried out with a pH/mV-meter (Zagshimi, Iran), at 25.0±0.1 °C. The reference electrodes were Hg/Hg$_2$Cl$_2$ and Ag/AgCl (Azar electrode, Iran). A digital pH-meter (Jenway 3020, UK) was used for pH measurements. A UV/Vis spectrophotometer (UV-2100, JENUS, China) was used to record electronic spectra. An atomic absorption spectrometer (AAS, Shimadzu AA 760, Japan) was used to determine metal ions under the recommended conditions ordered in the instrument manual.

2.3 Preparation of the Iron(III)-selective electrode

30 mg of powdered PVC; 64 mg of NB (as a plasticizer), 3 mg of the ionophore (HNMB) and 3 mg of additive NaTPB was dissolved in 3 mL of fresh THF as the composition of the optimized membrane. This mixture was kept at room temperature to allow extra solvent to evaporate. Then, a
glass tube (3–5 mm id. on top) was dipped into the mixture for 10 s to form a thin and transparent membrane (about 0.3 mm thickness) on the tip of the tube. The prepared tube was kept at room temperature for about 1 h and then was filled with an internal filling solution of $1.0 \times 10^{-3}$ M of Fe(NO$_3$)$_3$. Finally, the purposed electrode was soaked in a $1.0 \times 10^{-3}$ M ferric nitrate solution for 24 h. A silver/silver chloride electrode was used as internal electrode. In order to optimize the supply membranes, the various ingredient ratios and conditioning time were tested.

2.4 EMF measurements

The measurements were done with the following cell assembly:

$\text{Ag–AgCl} | \text{internal solution (1.0} \times 10^{-3} \text{ M Fe(NO}_3)_3 \text{)} | \text{PVC membrane} | \text{test solution} | \text{Hg–Hg}_2\text{Cl}_2, \text{ KCl (sat’d)}$.

All measurements were carried out in a 100 ml glass cell at a constant magnetic stirring of the desired solution. The activities of ions were calculated according to the Debye–Huckel procedure [32].

3. RESULTS AND DISCUSSION

The HNMB structure (L, Fig. 1) contains nitrogen and oxygen donor atoms, which is an appropriate metal ion carrier. According the report from our co-workers, this structure is best suitable to complex Fe(III) according the general formula $[\text{Fe(L)}_2\text{NO}_3]^{-}[31]$, as shown in Fig. 2.

![Figure 1. The chemical structure of HNMB](image)

![Figure 2. The chemical structure of the complexed Fe(III) ion by HNMB.](image)

In order to find a clue about the interaction of the ionophore toward the Fe(III) in an organic
phase, in a preliminary spectrophotometrical experiment, we did titration of a proper amount of HNMB with a standard solution of Fe(III) in organic solution THF. The results are shown in Fig. 3. The isobestic points around 347 and 386 nm are good evidences for complex equilibria between iron(III) ion and the ligand L. As this figure discloses, the desired reaction can successfully occur in the organic solution that implies the tendency of the ligand to complex the metal ion in the organic phase. Due to this ability, we decided to incorporate this ionophore into a PVC membrane sensing element, as the heart of the potentiometric sensor, for monitoring the metal ion Fe$^{3+}$.

![Figure 3. The electronic spectra of titration of HNMB (1.0 ×10$^{-3}$ M) with standard solution of Fe$^{3+}$ in THF.](image)

Reviewing the literature, the fast ion exchange kinetics of the resulting HNMB–Fe(III) complex, at the membrane/solution interface, could be visualized as another effective parameter to couch such distinguished response of the membrane when exposed to Fe(III) ion.

3.1 The effect of membrane composition

We know that sensitivity and selectivity of ISEs depend on the membrane composition such as the nature and amount of ionophore, the plasticizer/PVC ratio, properties of the plasticizer and the additive applied [32]. Therefore, we investigated the influences of the above factors on the response of the sensor. The results are summarized in Table 1. The nature and amount of plasticizer influence the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the ligand state. Thus, it has important role on selectivity and response time of the electrode [32]. Among four different tested plasticizers, the electrode including NB demonstrated the best performance (Table 1) at 2:1 ratio of plasticizer/PVC.
Table 1. Optimization of the membrane ingredients.

<table>
<thead>
<tr>
<th>Electrode No.</th>
<th>Composition of the membrane (wt.%)</th>
<th>Slope (mV/decade)</th>
<th>Linear Dynamic Range (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PVC</td>
<td>Plasticizer</td>
<td>Ionophore</td>
</tr>
<tr>
<td>1</td>
<td>30</td>
<td>BEHS, 63</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>BEHP, 63</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>TEHP, 63</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>NB, 63</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>NB, 64</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>NB, 62</td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>30</td>
<td>NB, 64</td>
<td>3</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>NB, 65</td>
<td>2</td>
</tr>
<tr>
<td>9</td>
<td>30</td>
<td>NB, 62</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>NB, 62</td>
<td>0</td>
</tr>
</tbody>
</table>

The optimum amount of HNMB was chosen around 3% (No. 7, Table 1). The presence of a lipophilic anionic compound such as tetraphenylborat both reduces the ohmic resistance, improves selectivity and catalyzes the exchange kinetics at the sample-membrane interface [32, 33].

Figure 4. The potentiometric responses of the sensor with respect some common cations in the solution (a and b).

The findings presented in Table 1 showed that the membrane did not follow a Nernstian slope in the absence of NaTPB but a good Nernstian slope was observed in the presence of 3% NaTPB. The obtained results indicate that the electrode exhibits the best performance with a composition of 30% PVC, 64% NB, 3% NaTPB and 3% HNMB. A maximum slope of 19.9±0.4 mV/decade of Fe(III) concentration was observed for the optimized membrane (No. 7, Table 1). Finally, we constructed an
electrode with no ionophore to find the membrane components’ responses in the absence of the ionophore “called white electrode” (No. 10, Table 1). As seen, there is no considerable response for such an electrode, which confirms the vital sensing role of HNMB.

We found that the electrode shows the sharpest response toward Fe\(^{3+}\) ion rather than other cations listed in Fig. 4(a and b) after several different examination against some metal ions. The outstanding behavior illustrated in this figure could be attributed to the ability of the ionophore to attract the Fe(III) ion from the aqueous solution and complexing in the organic phase (membrane). In addition, the required time to establish the potential response (within ±1 mV) by the sensor was about 10 s.

3.2 Calibration curve and detection limit

The modified sensor showed a linear response to the activity of Fe\(^{3+}\) ion on the 1.0×10\(^{-2}\) to 5.0×10\(^{-9}\) M range (Fig. 5), under the optimized composition. The slope of the calibration curve was 19.9±0.4 mV/decade at 25 °C. We calculated the detection limit from the intersection of the two extrapolated segments of the calibration plot at the lowest point, where curves crossing. The evaluated detection limit was about 1.0×10\(^{-9}\) M of Fe\(^{3+}\) ion.

![Figure 5. The calibration curve plot of the linear dynamic range of the sensor function.](image)

3.3 Effect of pH

In order to find the influence of this important parameter on the performances of the modified sensor, the responses over the pH range 1.0 to 5.5 were investigated in a solution containing 1.0×10\(^{-3}\)
M of Fe$^{3+}$. pH values were adjusted with proper volumes of 0.01 M HNO$_3$ or NaOH. The results are given in Fig. 6, in which the electrode response is stable on pH of 2.4 to 4.0. The shift observed at higher pH values might be the result of the formation of some hydroxyl complexes of Fe$^{3+}$ in the solution.

![Figure 6. The plot of the response of the sensor versus various pH values.](image)

The increasing in response potentials at lower pH values may be due to the membrane sensor susceptibility to hydrogen ion in the solution. Thus, the suitable pH was selected in the range 2.4 to 4.0.

3.4 Statistics parameters

In order to test the merit of data given by the sensor, we used it to measure the potential of several solutions from 1.0×10$^{-8}$ to 1.0×10$^{-3}$ M, 10-fold series A to F, of Fe$^{3+}$ repeatedly. As can be seen in Fig. 7, the measured data is close to each other in all categories (RSD ±2.3%, within a data series) and the sensor reversibility is reasonable from one set of data to the other (RSD ±3.3%, between data series). These finding exhibited that the sensor responses are repeatable and reversible. The sensor was checked for frequent using during a 3 months period, 1 h per day. The deviation of 7% was observed after this period. Thus, the lifetime of the sensor could be evaluated as 3 months, which is a reasonable time-term for these devices.
Figure 7. The potential repose of the sensor toward several Fe(III) concentration sets A to F, 1.0×10^{-8} to 1.0×10^{-3} M.

3.5 Potentiometric selectivity

One of the most important characteristics of an ISE is selectivity, which explains the electrode performance in responsibility to primary ion respect to other interfering ions. The fixed interference method (FIM), based on Equation 1, is the most popular method for the above-mentioned purpose. The cell potential, including an ion selective electrode and a reference electrode, was determined for solutions with different concentrations of primary ions, named $a_A$, in the presence of a fixed concentration of the interfering ion (0.1 M), named $a_B$. At the intersection of the extrapolated curve of potential versus $-\log(a_A)$, the activity of the primary ion in the presence of a diverse ion was evaluated. The corresponding selectivity coefficient was calculated according Nikolsi-Eizenman equation [32, 34]:

$$k_{AB}^{pot} = \frac{\mu_A}{Z_A a_A},$$

(1)

$Z_A, Z_B$ are the electrical charges of the primary and interfering ions, respectively. The results are listed in Table 2. This table proves that there is no significant interference of the tested diverse ions.

Table 2. Selectivity coefficients of various interfering ions.

<table>
<thead>
<tr>
<th>M^{n+}</th>
<th>$k_{Fe,E}^{pot}$</th>
<th>M^{n+}</th>
<th>$k_{Fe,E}^{pot}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na^{+}</td>
<td>1.1×10^{-4}</td>
<td>Cu^{2+}</td>
<td>6.7×10^{-4}</td>
</tr>
<tr>
<td>K^{+}</td>
<td>2.0×10^{-4}</td>
<td>Zn^{2+}</td>
<td>2.8×10^{-4}</td>
</tr>
<tr>
<td>Mo^{6+}</td>
<td>5.1×10^{-3}</td>
<td>Cd^{2+}</td>
<td>5.0×10^{-4}</td>
</tr>
<tr>
<td>Ba^{2+}</td>
<td>4.5×10^{-4}</td>
<td>Pb^{2+}</td>
<td>9.2×10^{-4}</td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>4.9×10^{-4}</td>
<td>Al^{3+}</td>
<td>1.5×10^{-4}</td>
</tr>
<tr>
<td>Mg^{2+}</td>
<td>5.3×10^{-4}</td>
<td>Cr^{3+}</td>
<td>6.3×10^{-4}</td>
</tr>
<tr>
<td>Ni^{2+}</td>
<td>5.8×10^{-4}</td>
<td>Ce^{3+}</td>
<td>7.5×10^{-4}</td>
</tr>
</tbody>
</table>

3.6 Effect of non-aqueous solutions
The function of the modified electrode was also studied in partially non-aqueous media using ethanol–water mixtures. The important changes in the range of working concentration and the slope of the membranes were not observed in mixtures up to 15% (v/v) non-aqueous contents (see Table 3). However, an increase in the slope and a decrease in concentration range were observed above this content that may be due to the ionophore leaching into the measuring mixed solution.

**Table 3. Performance of Fe(III)-selective sensor in non-aqueous solutions**

<table>
<thead>
<tr>
<th>Non-aqueous content% (v/v)</th>
<th>Slope (mV/decade)</th>
<th>Linear range (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>19.9</td>
<td>1.0×10⁻² – 5.0×10⁻⁹</td>
</tr>
<tr>
<td>Ethanol</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>19.9</td>
<td>1.0×10⁻² – 5.0×10⁻⁹</td>
</tr>
<tr>
<td>10</td>
<td>20.1</td>
<td>1.0×10⁻² – 5.2×10⁻⁹</td>
</tr>
<tr>
<td>15</td>
<td>20.7</td>
<td>1.0×10⁻² – 5.3×10⁻⁹</td>
</tr>
<tr>
<td>20</td>
<td>21.6</td>
<td>1.0×10⁻² – 1.0×10⁻⁸</td>
</tr>
</tbody>
</table>

**3.6 Analytical applications**

**3.6.1 Using for titration of iron(III) with EDTA**

![Figure 8](image)

**Figure 8.** Using the sensor as a potentiometric indicator for titration of 50 ml Fe³⁺ solution (1.0×10⁻⁴ M) with standard EDTA (1.0×10⁻³ M).

The selective sensor showed a good performance under the laboratory conditions. Based on the obtained results, it was successfully applied as an indicator potentiometric sensor for titration of a 50.0
ml Fe(III) solution (1.0×10^{-4} M) with standard 1.0×10^{-3} M EDTA. The titration curve demonstrated that the sensor is able to successful detection of the amount of Fe(III) ion in the solutions (Fig. 8).

3.6.2 Fe(III) ion detection in different water samples

To test the analytical applicability, the sensor was applied for the determination of iron(III) in some water samples. First, 5.0 mL of H_{2}O_{2} solution (1.0 N) and 5.0 mL of HNO_{3} solution (1.0 N) were added to proper volume of each sample to oxidize any Fe(II) to Fe(III). Next, the pH of the solution was controlled at 3.0 with concentrated HNO_{3} and diluted with distilled water in a 100.0 mL volumetric flask. A calibration method was applied to measure Fe(III) concentration in the water samples. The samples iron(III) contents were also checked with AAS. There were good agreement between the results of the potentiometric method and atomic absorption spectrometry. Table 4 summarizes the results.

Table 4. Determination of the iron(III) ion concentrations in some different water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Potentiometry(^{a}) (ppm)</th>
<th>AAS(^{a}) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water</td>
<td>1.2±0.3</td>
<td>1.0±0.4</td>
</tr>
<tr>
<td>Mineral water</td>
<td>0.3±0.4</td>
<td>0.1±0.2</td>
</tr>
<tr>
<td>River water</td>
<td>3.8±0.4</td>
<td>3.6±0.3</td>
</tr>
<tr>
<td>Waste water</td>
<td>9.8±0.1</td>
<td>9.7±0.1</td>
</tr>
</tbody>
</table>

\(^{a}\) Number of repeated measurements= 4

3.7. Comparison with other reported electrodes

Table 5 shows the comparison between the performance characteristics of the designed electrode and other electrodes that are reported in literature for measuring iron(III). It can be clearly seen from this table that the detection limit of the electrode, linear range and Nernstian slope is truly satisfactory.

Table 5. Comparison of the proposed iron(III) sensor with other electrodes

<table>
<thead>
<tr>
<th>No.</th>
<th>Modifier</th>
<th>Slope (mV/decade)</th>
<th>LOD (M)</th>
<th>Linear range (M)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S-methyl N-(methylcarbamoyloxy) thioacetimidate</td>
<td>21.2 ± 0.2</td>
<td>-</td>
<td>1.0×10^{-1} - 9.1×10^{-6}</td>
<td>26</td>
</tr>
<tr>
<td>2</td>
<td>3-(2-diethylamino-ethylimino)-1,3-dihydro-indol-2-one</td>
<td>26 ± 1</td>
<td>5.5×10^{-7}</td>
<td>5.0×10^{-2} - 2.0×10^{-6}</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>2-[(thiophen-2-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4. CONCLUSION

Based on the results revealed in this work, we found that (E)-N’-(2-hydroxynaphthalen-3-yl)methylene) benzohydrazide acts as a superior selective carrier in a PVC membrane in the heart of a potentiometric sensor for determination of Fe(III) ion in samples. Giving a good Nernstian response over a wide concentration range of 1.0×10⁻² to 5.0×10⁻⁹ M, deep lower detection limit of 1.0×10⁻⁹ and very fast response time are outstanding capabilities of the sensor. Beside these, ease of use, simply preparation and reasonable measuring accuracy and precision pictured the sensor as a confident tool for successful determination of iron(III) in the environment.

References


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