

### Application of a New Macrocyclic -PVC Electrode to Potentiometric Studies of Fe(III) Ion

R. Aminameli<sup>1</sup>, M. H. Fekri<sup>2,\*</sup>, H. Shafie<sup>3</sup>, M. Darvishpour<sup>4</sup> and H. Khanmohammadi<sup>5</sup>

<sup>1</sup>Department of Chemistry, Saveh Branch, Islamic Azad University, Saveh, Iran

<sup>2</sup>Department of Chemistry, Ayatollah Aaloza Boroujerdi University, Boroujerd, Iran

<sup>3</sup>Department of Chemistry, Arak Branch, Islamic Azad University, Arak, Iran

<sup>4</sup>Department of Chemistry, Razi University, Kermanshah, Iran

<sup>5</sup>Department of Chemistry, Arak University, Arak, Iran

Received June 2013; Accepted June 2013

#### ABSTRACT

A PVC membrane Fe(III) ion selective electrode has been constructed using a new macrocyclic as membrane carrier. The electrode exhibits a good potentiometric response for Fe(III) over a wide concentration range  $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-1}$  M with a slope  $19.4 \pm 0.5$  mV/decade and a working pH range of 6.5-9.0. It has a fast response time  $\leq 30$  s. The best performance was observed with the membrane having the 30.5% PVC, 3.0% ligand, 61.0% acetophenone and 5.5% oleic acid composition.

**Keywords:** Ion selective electrode; PVC membrane; Fe(III) determination; Macrocyclic ionophore

#### INTRODUCTION

Ion-selective electrodes (ISEs), especially those with neutral carrier-based solvent polymeric membranes, have been studied for more than three decades, and are now routinely employed for direct potentiometric measurements of various ionic species in environmental, industrial and clinical samples [1,2,3]. The increasing use of ion sensors in the fields of environmental, agricultural and medicinal analysis is stimulating analytical chemists to develop new sensors for the fast, accurate, reproducible and selective determination of various species. In the

past few decades, considerable efforts have led to the development of selective sensors for alkali and alkaline earth metals and for heavy metals. Among heavy metals, trivalent metals have received less attention in spite of their widespread occurrence

in rocks, alloys, food products, sea- and fresh-water, plants and animals [4].

A significant number of macrocyclic compounds including crown ethers, cryptands, aza-crowns and thiocrowns, which have been synthesized in various cavity sizes and shapes have already been

\*Corresponding author: m.h.fekri@abru.ac.ir

exploited for the fabrication of poly(vinyl chloride) membrane electrodes for transition and heavy metal ions [5-12].

Fabrication of a new ion specific ISE with high selectivity and sensitivity, wide linear concentration range, long lifetime, good reproducibility and low cost is always in need. A literature survey revealed that a large number of ISE based on PVC membrane were reported for many inorganic ions [13], but to the best of our knowledge, very little reports were appeared on PVC-based trivalent ions.

In this paper, we report the use of new ligand as a neutral carrier in the construction of a PVC membrane electrode selective to Fe(III) ion.

## EXPERIMENTAL

### Reagents

All of reagents and solvents involved in synthesis were of analytically grade and received without further purification. Tetrahydrofuran (THF), acetophenone (AP), oleic acid (OA), high relative molecular weight PVC were obtained from Aldrich and Merck. a new macrocyclic ionophore (Fig.1).

Chloride and nitrate salts of all other cations and detergent used (all from Merck or Fluka) were of the highest purity available and used without any further purification.

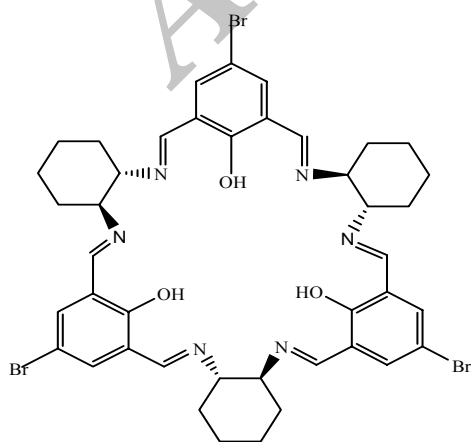


Fig. 1. Structure of  $H_3L$ .

### Apparatus

Potentiometric and pH measurements were carried out using a metrohm digital pH/mV meter ion analyzer in stirred solution. In all instances, an Ag-AgCl / KCl (sat.) electrode (Azar electrode company, Urmia, Iran) was used in conjunction with the respective indicator electrode. A Haoke model FK2 circulation water bath was used control the temperature of the test solution.

### Electrode preparation and potential measurement

A mixture of PVC, oleic acid, acetophenone and ionophore to give a total mass of 105 mg, was dissolved in about 2 mL of THF and the solution was mixed well. The resulting clear mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained.

A pyrex tube (5 mm o.d.) was dipped into the mixture for about 10 s so that a nontransparent membrane of about 0.2 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 2 h. The tube was then filled with internal solution  $1.0 \times 10^{-3}$  M Fe(III) with pH = 3. The electrode was finally conditioned for 24 h by soaking in a  $1.0 \times 10^{-2}$  M Fe(III) solution with pH = 3.

The potential measurements were carried out with the following assembly:

Ag/AgCl / 3 M KCl / internal solution ( $1.0 \times 10^{-3}$  M  $FeCl_3$ ,  $1.0 \times 10^{-3}$  M HCl) / PVC membrane / test solution / 3 M KCl / Ag-AgCl

## RESULTS AND DISCUSSION

### Effect of membrane composition on the electrode response

The potential responses of various ion-selective electrodes based on  $H_3L$  are in Fig. 2. Expect for the Fe(III) ion selective electrode, in all other cases the slope of the

corresponding potential-pM plots is much lower than the expected Nernstain slopes.

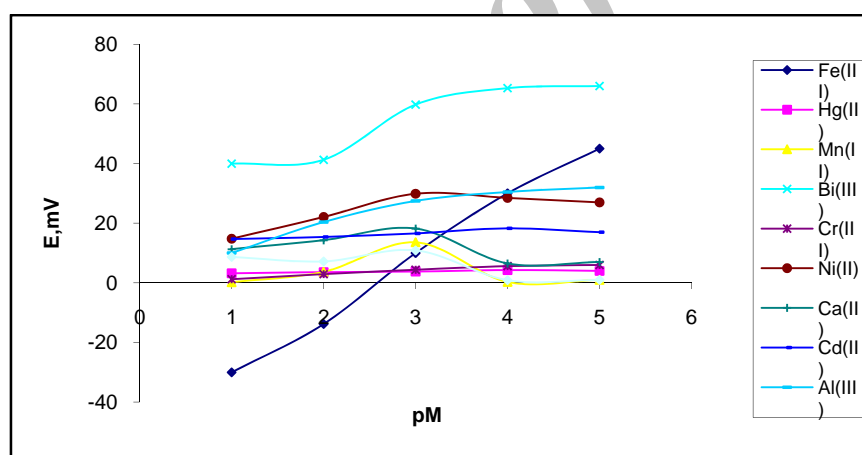
Besides the critical role of the nature of the ion carrier in preparing membrane-selective sensors, some other important features of the PVC membrane are known to significantly influence the sensitivity, linearity range and selectivity of ion-selective electrodes. These include the amount of ionophore, the nature of solvent mediator, the plasticizer/PVC ratio and especially the nature of additives used [14-20].

Thus, based on the results obtained on the optimaization of the membrane composition, the membrane with the optimized composition of PVC : ionophore : acetophenone : oleic acid ratio of

10:1:22:2 was selected for the preparation the polymeric membrane electrode. The characteristic parameters of the optimized membrane are summarized in Table 1.

### Reversibility of the electrode

To evaluate the reversibility of the electrode, a similar procedure in the opposite direction was adopted. The measurements were performed in the sequence of high-to-low (from  $1.0 \times 10^{-2}$  to  $1.0 \times 10^{-3}$  M) sample concentration and the results are shown in Fig. 3. Fig. 3. shows that the potentiometric response of the electrode is reversible, although the times needed to reach equilibrium values were longer than that of low-to-high sample concentration [21].



**Fig. 2.** Response at pH= 3 against some of cations for ion-selective electrodes containing H<sub>3</sub>L as ionophore.

**Table 1.** Specification of the Fe(III)-ISE based on H<sub>3</sub>L

Optimized membrane composition	PVC (28.6 %), AP (62.8 %) OA (5.7 %), Ionophore (2.9 %)
Linear range, M	$1.0 \times 10^{-5}$ to $1.0 \times 10^{-1}$
Detection limit, M	$8.9 \times 10^{-6}$
Slope, mV/decade	$19.4 \pm 0.5$
Response time, s	$\leq 30$

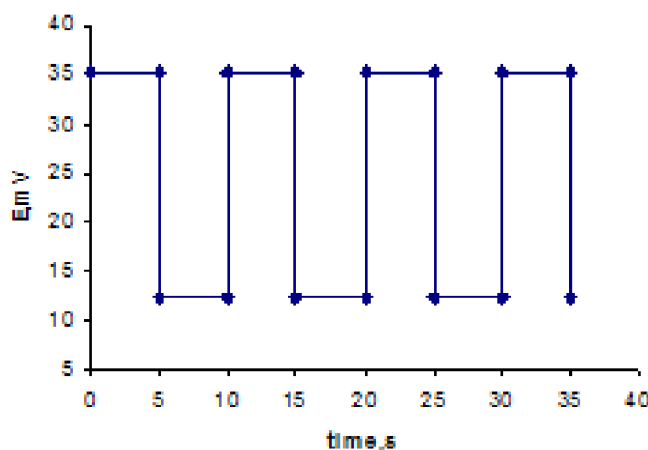


Fig. 3. Dynamic response characteristics of the Fe(III)-electrode for several high-to-low sample cycles.

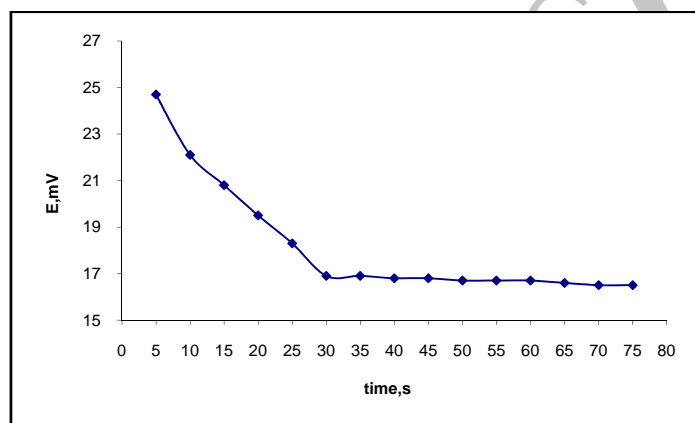


Fig. 4. The response time of Fe(III)-ISE based on H<sub>3</sub>L for Fe(III) concentration of  $1.0 \times 10^{-4}$  M.

### The response time

The response time of the electrode was measured after successive immersion of the electrode in a series of Fe solution, in each of which the Fe(III) concentration was increased tenfold, from  $1.0 \times 10^{-6}$  to 1.0 M. At lower concentrations, however, the response time was longer and reached 30 s for a Fe(III) concentration of  $1.0 \times 10^{-4}$  M. The actual potential versus time traces is shown in Fig. 4 for Fe(III) concentration of  $1.0 \times 10^{-4}$  M.

### CONCLUSION

The membrane sensor incorporating H<sub>3</sub>L as the electroactive phase can be used to determine Fe(III) in the wide concentration

range. The sensor exhibited good reproducibility over a useful lifetime about 2 months. This electrode is superior to the existing electrodes with regard to the slope, pH range, response time and selectivity over a number of cation.

### ACKNOWLEDGMENT

The authors express their appreciation to post-graduate office of Islamic Azad University of saveh branch for financial support of this work.

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