Highly selective potentiometric determination of Fe(III) ions using Tris-(1,2-diiminocyclohexylmethyl-5-Cl-2-hydroxyl benzaldehyde) based membrane electrode

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ABSTRACT

A novel ion-selective poly(vinyl chloride) membrane sensor for Fe(III) ions based on Tris-(1,2-diiminocyclohexylmethyl-5-Cl-2-hydroxyl benzaldehyde) are reported in this paper. The electrode exhibits a good potentiometric response for Fe(III), response time ≤ 20 s, over a wide concentration range 1.0×10^{-5} to 1.0×10^{-1} M with a slope 19.4 ± 0.5 mV/decade. The potentiometric response is independent on the pH of solution in the range of 1.5-5.0. The proposed electrode can be used for at least two months without any considerable divergence in potentials.It exhibits very good selectivity relative to a wide variety of alkali, alkaline earth, transition and heavy metal ions. The electrode assembly was also used as indicator electrode in the potentiometric titration of Fe(III) with EDTA.

Keywords

PVC membrane, Fe(III), sensor, potentiometry, Tris-(1,2-diimino cyclohexylmethyl -5-Cl-2-hydroxyl benzaldehyde).

1.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].

Iron is the most abundant trace mineral in the body and is one of the most important elements in the biological systems, playing a significant role in the oxygen transport, storage and in the electron transport [5,6]. Enzymes involved in the making of amino acids, hormons and neurotransmitters require iron. In the foods ingested during a day, approximately 10-15 mg of iron is present and studies indicate that normal subjects absorb ten percent of iron in the food [7]. The absence of iron in the organism causes anemia, the eesult of decreased red blood cell content. However, if present in excess, iron accumulates in the heart, liver and other vital organs [8,9] and this surplus iron cannot be removed naturally by the body and it puts the organs at risk for serious damage [10].

Despite the urgent need for iron selective sensors for the potentiometric monitoring of Fe(III) ions, there have been only limited reports on Fe(III) ion selective electrods in the literature [11,16]. Some of them were prepared with ion exchangers [11,17] and a few of them with ionophores [18,19]. A few examples for the use of solid-state ISEs for Fe(III) were also reported [20-24]. Most of these ion-selective electrods were less selective and had long response time, low pH range and poor stability. The effect of various types of plasticizers on the selectivity of carrier based PVC electrods has been reported [25,26], but the systematic investigations about the role of the plasticizers in ion-selective electrodes are still desired.

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.

2. EXPERIMENTAL

2.1. Materials

Tris - (1,2-diiminocyclohexylmethyl-5-chloro-2-hydroxyl benzaldehyde), (Fig. 1) Tetrahydrofuran (THF), dibutyl phthalate (DBP), acetophenone (AP), oleic acid (OA), high relative molecular weight PVC, chloride and nitrate salts of all other cations and reagents used (all from Merck or Fluka) were of the highest purity available and used without any further purification.
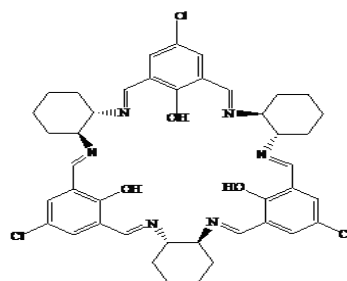

Fig. 1. Structure of used ionophore.

2.2. Instrumentation

Potentiometric and pH measurements were carrid 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 conjucation with the respective indicator electrode. A Haoke model FK2 circulation water bath was used control the temperature of the test solution.

2.3. Electrode preparation and potential measurement

A mixture of PVC, oleic acid, acetophenone and ionophore to give a total mass of 100 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) chloride with pH = 3. The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-2} M Fe(III) chloride solution with pH = 3. The potential measurements were carried out with the following assembly:

Ag/AgCl / 3 M KCl / internal solution (1.0×10^{-3} M FeCl3 , 1.0×10^{-3} M HCl) / PVC membrane / test solution / 3 M KCl / Ag-AgCl.

Table 1. Optimization of the membrane ingredients.

No.	Composition, %				Slope, mV/decade	Linear range, M
	Ionophore	PVC	Plasticizer	Additive		
1	-	32.0	63.0 (AP)	5.0 (OA)	2.7	-
2	1.5	29.0	63.5 (DBP)	6.0 (OA)	24.2	1.0×10^{-4} -1.0×10^{-1}
3	1.5	27.0	65.0 (AP)	6.5 (OA)	17.1	1.0×10^{-4}-1.0×10^{-1}
4	2.0	28.0	65.0 (AP)	4.5 (OA)	23.5	1.0×10^{-4} -1.0×10^{-1}
5	2.0	28.0	64.0 (AP)	6.0 (OA)	22.5	1.0×10^{-4}-1.0×10^{-1}
6	2 .9	28.6	62.8 (AP)	5.7 (OA)	19.4	1.0×10^{-5}-1.0×10^{-1}
7	4.7	28.0	62.0 (AP)	5.3 (OA)	18.5	1.0×10^{-4}-1.0×10^{-1}
8	5.0	30.0	60.0 (AP)	5.0 (OA)	28.9	1.0×10^{-5}-1.0×10^{-1}

3. RESULTS AND DISCUSSION

The Tris - (1,2-diiminocyclohexylmethyl-5-chloro-2-hydroxyl benzaldehyde) as a carrier was found to be highly responsive to Fe(III) with respect to several other metal ions. Therefore, we studied in detail the performance of the plasticized PVC membrane containing this ionophore for Fe(III) in aqueous solution. In order to test the performance of the membrane characteristics, various operation parameters including selectivity, response time, sensitivity, lifetime, linear range, the influence of pH and the membrane composition on the response of the electrode were investigated.

3.1. Effect of membrane composition on the electrode response

It is well Known that the sensitivity and selectivity of the ion-selective sensors not only depend on the nature of ionophore used, but also significantly on the membrane composition and the properties of plasticizers and additives used [27-30]. Thus, the influences of the membrane composition, the nature and amount of plasticizers and amount of oleic acid as an additive on the potential response of the Fe(III) sensor were investigated.
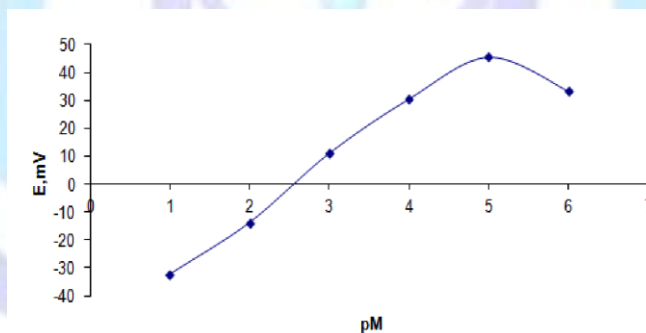

Fig. 2. Calibration plot of the Fe(III)-ISE based on ionophore.

Among the different composition studied, membrane 6 incorporating 28.6 % PVC, 62.8 % AP, 5.7 % OA and 2.9 % ionophore shows the best sensitivity. The calibration plot is shown in Fig. 2, which indicates a linear range from 1.0×10^{-5} to 1.0×10^{-1} M Fe(III) with a Nernstian slope of 19.4 ± 0.5 mV/decade of Fe(III) concentration. The characteristic parameters of the optimized membrane are summarized in Table 2.

Table 2. Specification of the Fe(III)-ISE based on ionophore.

Properties	Values/range
Optimized membrane composition	PVC (28.6 %), AP (62.8.6 %) OA (5.7 %), Ionophore (2.9 %)
Linear range, M	1.0×10^{-5} to 1.0×10^{-1}
Detection limit, M	8.9×10^{-6}
Slope, mV/decade	19.4 ± 0.5
Response time, s	≤ 20

3.2.Effect of pH

The influence of pH on the response of the PVC membrane electrode at 1.0×10^{-4} M concentration of Fe(III) is performed (Fig. 3). The potential remains constant from pH of about 1.5 to 5.0.The variation of the potential at pH < 1.5 could be related to protonation of the ligand in the membrane phase, which results in a loss of its ability to complex with Fe(III) ions. At pH > 5.5, the potential drope may be due to the hydrolysis of the Fe(III) ions and therefore, all of measurements were performed at pH = 3.0. The working pH range is slightly reduced at lower Fe(III) concentration, and therefore, all of the measurements were performed at pH = 3.0.
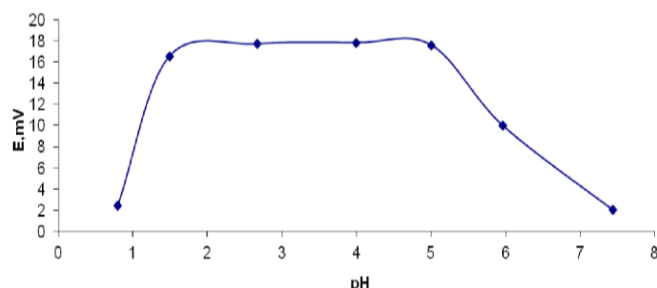
Fig. 3. The pH response of the Fe(III)-ISE based on ionophore.

3.3.The response time

The response time of the electrode was measured after successive immersion of the electrode in a series of chromium solution, in each of which the Fe(III) concentration was increased tenfold, from 1.0×10^{-5} to 1.0 M. At lower concentrations, however, the response time was longer and reached 20 s for a Fe(III) concentration of 1.0×10^{-4} M. The actual potential versus time traces is shown in Fig. 4 for Fe(III) concentration of 1.0×10^{-4} M.
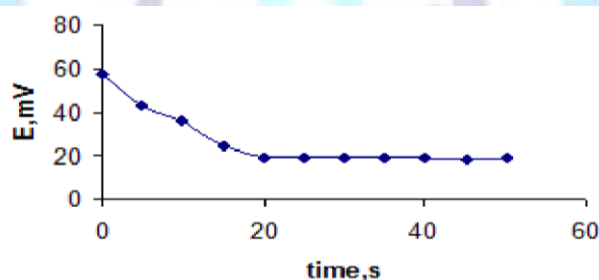
Fig. 4. The response time of Fe(III)-ISE based on ionophore for Fe(III) concentration of 1.0×10^{-4} M.

3.4.Reversibility of the electrode

To evaluate the reversibility of the electrode, a similar procedure in the opposite direction was adopted. The mmeasurements were performed in the sequence of high-to-low (from 1.0×10^{-2} to 1.0×10^{-3} M) sample concentration and the results are shown in Fig.5.This Figure shows that the potentiometric response of the electrode is reversible, although the times needed to reach equilibrium values were lomger than that of low-to-high sample concentration [31].
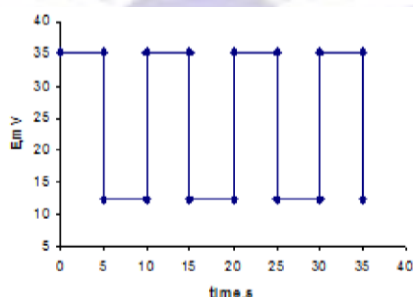
Fig. 5. Dynamic response characteristics of the Fe(III)-electrode for several high-to-low sample cycles.

3.5.Analytical application

The practical applicability of the electrode was tested by using it as an indicator electrode to determine the end point in the potentiometric titration of Fe(III) with EDTA solution. 20 ml of 1.0×10^{-4} M Fe(III) solution was titrated against 1.0×10^{-3} M EDTA solution.

The potential data are plotted against the volume of EDTA (Fig.6). Although the changes observed in potentials are not large, the end point is quite sharp and a perfect stoichiometry is observed.
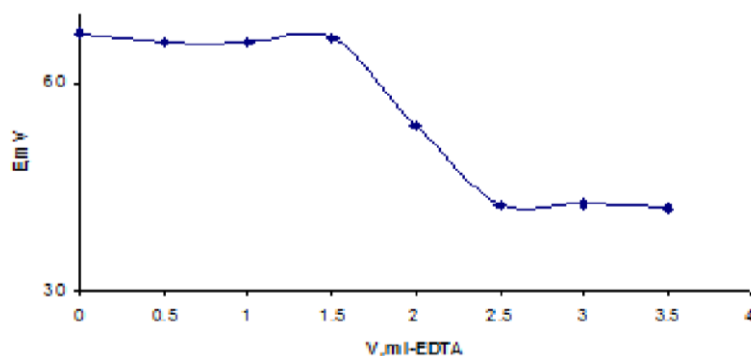

Fig. 6. Potentiometric titration curve for 20 ml 1.0 × 10^{-4} M Fe(III) with 1.0 × 10^{-3} M EDTA.

4.CONCLUSIONS

The membrane sensor incorporating ionophore 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 supervior to the existing electrodes with regard to the slope, pH range, response time and selectivity over a number of cation (Table 2). The present electrode permits the direct measurement of Fe(III) in real samples without prior separation steps, thus considerable simplifying the determination procedure with respect to the other analytical methods used.

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REFERENCES

[1]   1. T. S. Light, Industrial use and application of ion selective electrodes, J. Chem. Educ. 1997, 74, 171.

[2]   2. C. C. Young, Evolution of blood chemistry analyzers based on ion selective electrodes, J. Chem. Educ. 1997, 74, 177.

[3]   3. M. H. Fekri, H. Khanmohammadi, M. Darvishpour, Int. J. Electrochem. Sci., 2011, 6, 1679.

[4]   4. S. P. Parker, McGraw-Hill Concise Encyclopaedia of Science and Technology, McGraw-Hill, New York, 1984, p. 390.

[5]   5. R. A. Goyer, Toxic effects of metals, in : C. D. Klaassen (Eds.), Casarett & Doulls Toxicology: the basic science of poisons, 5th ed. New York City, NY, McGraw –Hill, 1996, pp.715.

[6]   6. W. F. Greentree and J. O. Hall, Iron toxicosis, in: J. D. Bonagura, (Eds.), Kirks current therapy XII small animal practice. Philadelphia, Pa, WB Saunders Co, 1995, pp. 240.

[7]   7. M. Wintrole, Clinical Hematology, Lea & Febiger, Philadelphia, 1961, pp.143.

[8]   8. J. Porter, Pathophysiology of iron overload, Hematol Oncol Clin North Am, 19, 2005, 7.

[9]   9. N. C. Andrews, N. Eng. J. Med., 341, 1999, 1986.

[10] 10. Z. I. Cabantchik, W. Breuer, G. Zanninelli, P. Cianciulli, Best Pract Res. Clin Haematol., 18, 2005, 277.

[11] 11. P. Buhlmann, E. Pretsch, E. Bakker, Chem. Rev., 98, 1998, 159.

[12] 12. W. H. Mahmoud, Anal. Chim. Acta., 436, 2001, 199.

[13] 13. M. Mashhadizadeh, I. S. Shoaei, N. Monada, Talanta, 64, 2004, 1048.

[14] 14. A. R. Fakhari, M. Alaghemand, M. Shamsipur, Anal. Lett., 34, 2001, 1097.

[15] 15. G. Ekmekci, D. Uzun, G. Somer, S. Kalayci, J. Memb. Sci., 288, 2007, 36.

[16] 16. V. K. Gupta, A. K. Agarwal, G. Maheshwari, Talanta, 71, 2007, 1964.

[17] 17. S. S. Hassan, S. A. M. Marzouk, Talanta, 41, 1994, 891.

[18] 18. Z. Chem, X. Yang, X. Lu, Electroanalysis, 10, 1998, 567.

[19] 19. M. B. Saleh, Analyst, 125, 2000, 179.

[20] 20. Y. Umezava, Handbook of ion-selective electrodes: Selectivity coefficients (Boca Raton: CRC Press), 1990.

[21] 21. V. L. Volkov, M. V. Kruchinina, J. Anal. Chem. , 48, 1993, 1108.

[22] 22. C. E. Koening, E. W. Granber, Electroanalysis, 7, 1995, 1090.

[23] 23. R. D. Marco, B. Pejcic, X. Dong, Wang, Lab. Rob. Autom., 11, 1999, 284.

[24] 24. R. D. Marco, D. J. Mackey, Mar. Chem., 68, 2000, 283.

[25] 25. D. Ammann, R. Bissing, E. Guggi Pretsch, W. Simon, I. J. Borowitz, L. Weiss, Helv. Chim. Acta., 58, 1975, 1535.

[26] 26. Y. Marcus, Biophys. Chem., 51, 1994, 111.

[27] 27. N.A.El-Ragheh, A.M.Kosasy, S.S.Abbas, S.Z.El-Khateeb, Anal. Chem. Acta, 418,2000,93.

[28] 28. M.hmsipur, M.Yousefi, M.R.Ganjali, Anal. Chem., 72,2000,2391.

[29] 29. S.R.Sheen, J.S.Shih, Analyst, 117,1992,1691.

[30] 30. S.S.Badavy, A.F.Shoukry, Y.M.Assa, Analyst, 111,1986, 1363.

[31] 31. T.Poursaberi, M.Hosseini, M.Taghizadeh, H.Pirelahi, M.Shamsipur, M.R.Ganjali, Microchem, J. 72,2002,77.

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