

Chromium(III) ion selective electrode based on 2H-1,4-benzothioazine-2,3(4H)dione dioxime as a neutral carrier

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ABSTRACT

A poly(vinyl chloride) membrane based on a new α -dioxime derivative as membrane carrier was prepared and investigated as a Cr(III) selective electrode. The electrode exhibits a good potentiometric response for Cr(III) over a wide concentration range 1.0×10^{-6} to 1.0×10^{-1} M with a slope 19.5 ± 0.5 mV/decade and low detection limit of 8.9×10^{-7} M. It has a fast response time ≤ 15 s. The best performance was observed with the membrane having the PVC-ligand-acetophenone-oleic acid composition 6:1:13:1. The proposed electrode works well in a wide pH range 1.5-5.5. The proposed sensor was successfully used for the determination of Cr(III) ions in samples and real samples and as indicator electrode in potentiometric titration of Cr(III) ion. The application of this electrode for Cr(III) determination in real samples is described. The results obtained with this procedure are in close agreement with those obtained using AA spectrophotometry.

Keywords: Ion selective electrode, PVC membrane, Cr(III) determination, α -dioxime

INTRODUCTION

Ion selective electrodes (ISE_s) are membrane electrodes that respond selectively to ions in the presence of others. These include probes that measure specific ions and gasses in solution. The most commonly used ISE is the pH probe. For this type of electrodes, the formation constant of the ion-ionophore complex within the membrane phase is very important parameter that dictates the practical selectivity of the sensor [1].

The ion selective electrode (ISE) approach to trace analysis is advantageous because of the speed and ease of ISE procedures in which little is required. Further, ISEs possess wide dynamic ranges, and are relatively low in cost. Ion selective electrodes based on neutral carrier ligands are well established for alkali and alkaline-earth metal cations [2-5].

A significant number of macrocyclic compounds including crown ethers, cryptands, aza-crowns and

thiacrowns, which have been synthesized in various cavity sizes and shapes have already been exploited for the fabrication of poly(vinyl chloride) membrane electrodes for transition and heavy metal ions [6-13].

Fabrication of a new ion specific ISEs 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 [14]. but very little was publishes on PVC-based trivalent ions.

The first report on Cr(III) was in 1980 [15]. In 1987 a Cr(III) selective electrode with PVC membrane based on 8-quinoline-dithiocaboxilate was described [16]. In 1989 another ion selective electrode based on chromium dithizonate was built that was a precipitate based selective

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electrode [17]. A PVC-based Cr(III)-selective electrode, which was recently been prepared, is based on 4-methylaminoazobenzene [18]. Gholivand et al. used a Cr(III)-selective electrode based on glyoxal bis(2-hydroxyanil) [19].

In this paper, we report the use of 2H-1,4-benzothiazine-2,3(4H)dione dioxime (BTD) as a neutral carrier in the construction of a new PVC membrane electrode selective to Cr(III) ion.

EXPERIMENTAL

Reagents

2H-1,4-benzothiazine-2,3(4H)dione dioxime (BTD) as ligand (Fig. 1) was prepared according to previously reported method [20]. 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.

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. Membrane compositions are listed in Table 1. 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 1.0×10^{-3} M Cr(III) chloride with pH = 3. The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-2} M Cr(III) chloride solution with pH = 3.

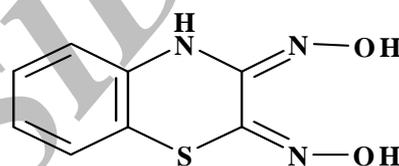


Fig. 1. Structure of 2H-1,4-benzothiazine-2,3(4H)dione dioxime (BTD) used as ionophore.

The potential measurements were carried out with the following assembly:

Ag/AgCl / 3 M KCl / internal solution (1.0×10^{-3} M CrCl₃, 1.0×10^{-3} M HCl) / PVC membrane / test solution / 3 M KCl / Ag-AgCl

A Metrohm digital research pH meter was used for measuring potential at 25.0 ± 1.0 °C. Activities were calculated according to the Debye-Huckel procedure [21].

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) | 3.1 | - |
| 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^{-5} - 1.0×10^{-1} |
| 4 | 2.0 | 28.0 | 65.5 (AP) | 4.5 (OA) | 22.5 | 1.0×10^{-5} - 1.0×10^{-1} |
| 5 | 2.0 | 28.0 | 64.0 (AP) | 6.0 (OA) | 23.5 | 1.0×10^{-5} - 1.0×10^{-1} |
| 6 | 3.0 | 30.5 | 61.0 (AP) | 5.5 (OA) | 21.0 | 1.0×10^{-4} - 1.0×10^{-1} |
| 7 | 4.7 | 28.0 | 62.0 (AP) | 5.3 (OA) | 19.5 | 1.0×10^{-6}-1.0×10^{-1} |
| 8 | 5.0 | 30.0 | 60.0 (AP) | 5.0 (OA) | 19.9 | 1.0×10^{-4} - 1.0×10^{-1} |
| 9 | 9.5 | 32.0 | 52.5 (AP) | 6.0 (OA) | 31.7 | 1.0×10^{-4} - 1.0×10^{-1} |

Preparation of 2H-1,4-benzothioazine-2,3(4H) dionedioxime

To a stirring solution of 2-aminothiophenole (2.5 g, 20 mmol) in 20.0 mL of absolute ethanol, a solution of dichloroglyoxime (1.56 g, 10 mmol) in 17.0 mL of ethanol-water mixture (80 % v/v) and 1.5 g of sodium bicarbonate was added at room temperature. The solution was stirred for 1.0 h and then 15.0 mL of distilled water was added. The mixture was stirred for 5.0 h at room temperature, until precipitate was formed. The crude product was collected by filtration and was washed with hot ethanol-water mixture (50 % v/v) to afford 1.91 g of white pure precipitate with a crystal m.p. of 234.0-234.5 °C. The identity and purity of 2H-1,4-benzothioazine-2,3(4H)dione dioxime were confirmed by FTIR, ¹H NMR, ¹³C NMR, MS, CHN elemental analyzer, and XRD structure analyzer. IR (KBr): ν (cm⁻¹) = 3400 (NH), 2800-3400 (OH), 1600, 1640 (C=N), 1250 (C-N), 920, 980 (N-O); ¹H NMR (500 MHz, DMSO-d₆-25): δ (ppm) = 12.3 (2H, OH), 10.8 (2H, OH), 9.4 (bs, 2H, NH), 6.8-7.4 (8H, CH_{Ar}); ¹³C NMR (500 MHz, DMSO-d₆-25): δ (ppm) = 137.5, 137.2, 133.7, 127.0, 125.9, 120.9, 116.6, 112.8; The mass spectrum, m/z (relative intensity): 209 (m⁺, 100), 179 (100), 161 (100), 149 (46.4), 136 (100).

RESULTS AND DISCUSSION

The 2H-1,4-benzothioazine-2,3(4H)dione dioxime as a carrier was found to be highly responsive to Cr(III) with respect to several other metal ions. Therefore, we studied in detail the performance of the plasticized PVC membrane containing this ionophore for Cr(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.

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

[22-25]. 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 Cr(III) sensor were investigated

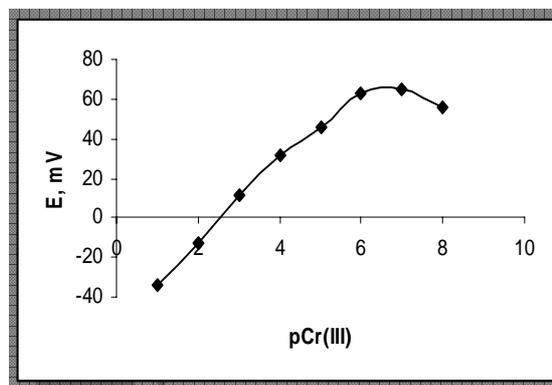


Fig. 2. Calibration plot of the Cr(III)-ISE based on BTM.

Among the different composition studied, membrane 7 incorporating 28 % PVC, 62 % AP, 5.3 % OA and 4.7 % ionophore shows the best sensitivity. The calibration plot is shown in Fig. 2, which indicates a linear range from 1.0×10^{-6} to 1.0×10^{-1} M Cr(III) with a Nernstian slope of 19.5 ± 0.5 mV/decade of Cr(III) concentration. The characteristic parameters of the optimized membrane are summarized in Table 2.

Table 2. Specification of the Cr(III)-ISE based on BTM

| Properties | Values/range |
|--------------------------------|--|
| Optimized membrane Composition | PVC (28 %), AP (62 %), OA (5.3 %), Ionophore (4.7 %) |
| pH range | 1.5-5.5 |
| Linear range, M | 1.0×10^{-6} to 1.0×10^{-1} |
| Detection limit, M | 8.9×10^{-7} |
| Slope, mV/decade | 19.5 ± 0.5 |
| Life time, months | ~ 2 |
| Response time, s | ≤ 15 |

Effect of pH

The influence of pH on the response of the PVC membrane electrode at 1.0×10^{-4} M concentration of Cr(III) is performed (Fig. 3). The potential remains constant from pH of about 1.5 to 5.5. 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 Cr(III) ions. At pH > 5.5, the potential drop may be due to the hydrolysis of the Cr(III) ions and therefore, all of measurements were performed at pH = 3.0. The working pH range is slightly reduced at lower Cr(III) concentration, and therefore, all of the measurements were performed at pH = 3.0.

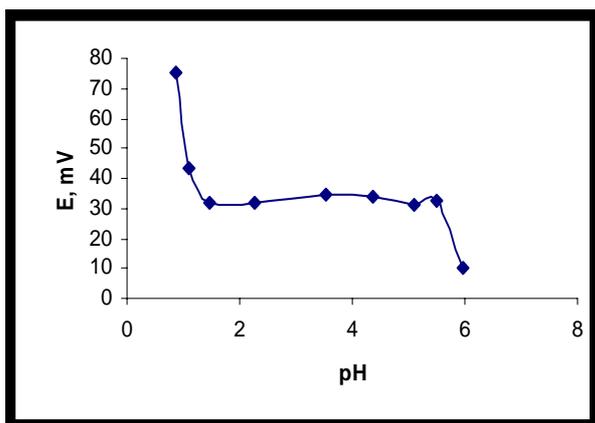


Fig. 3. The pH response of the Cr(III)-ISE based on BTD.

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 Cr(III) concentration was increased tenfold, from 1.0×10^{-6} to 1.0 M. At lower concentrations, however, the response time was longer and reached 15 s for a Cr(III) concentration of 1.0×10^{-4} M. The actual potential versus time traces is shown in Fig. 4 for Cr(III) concentration of 1.0×10^{-4} M.

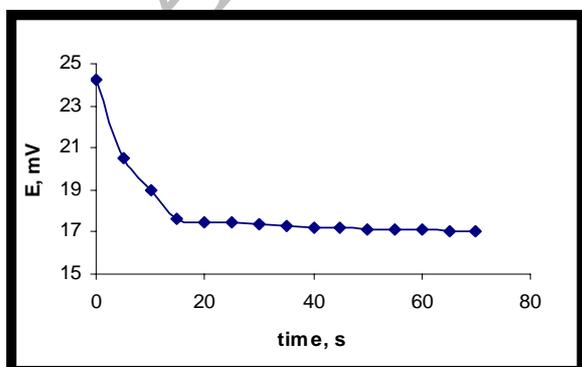


Fig. 4. The response time of Cr(III)-ISE based on BTD for Cr(III) concentration of 1.0×10^{-4} M.

Selectivity of the electrode

The selectivity is clearly one of the most important characteristics of any ion-selective sensor. The selectivity coefficient should preferably be evaluated by measuring the response of an ion selective electrode in solution of the primary ion, Cr(III) and an interfering ion, M^{n+} . The selectivity coefficients of the proposed electrode obtained by the separate solution method (SSM) [26].

The selectivity coefficient pattern clearly indicates that the electrode is highly selective to Cr(III) over alkali, alkaline earth and several common transition and heavy metal ions. From the potentiometric selectivity data in Table 3. It is obvious that BTD interacts relatively strongly with Cr(III) ion and can be used successfully as a sensing agent in Cr(III) selective electrode.

Table 3. Selectivity coefficients of the electrode obtained by the separate solution method (SSM)

| Interferent | K^{Pot} | Interferent | K^{Pot} |
|-------------------------------|----------------------|------------------|----------------------|
| Pb ²⁺ | 5.6×10^{-3} | Ca ²⁺ | 2.3×10^{-2} |
| UO ₂ ²⁺ | 3.8×10^{-3} | Ba ²⁺ | 1.4×10^{-3} |
| NH ₄ ⁺ | 2.8×10^{-4} | K ⁺ | 2.3×10^{-4} |
| Al ³⁺ | 6.3×10^{-1} | Ni ²⁺ | 1.4×10^{-2} |
| Ag ⁺ | 1.8×10^{-4} | Hg ²⁺ | 2.9×10^{-3} |
| Sn ²⁺ | 3.9×10^{-2} | | |

APPLICATION

The new Cr(III)-selective electrode was satisfactorily applied to the determination of Cr(III) in tea leaves, cacao powder and coffee. The analyses were performed by direct potentiometry using the standard addition technique. In the absence of samples containing Cr(III), known amounts of Cr(III) were added. The results obtained are summarized in Table 4. Good recoveries in all matrices were obtained.

Table 4. Practical applications of proposed sensor

| Sample | Average chromium concentration ($\mu\text{g/g}$) | |
|--------------|--|---------------|
| | Proposed sensor | AAS |
| Coffee | 2.6 ± 0.1 | 3.1 ± 0.1 |
| Cacao powder | 1.9 ± 0.1 | 2.3 ± 0.1 |
| Tea leaves | 1.4 ± 0.1 | 1.8 ± 0.1 |

CONCLUSIONS

The membrane sensor incorporating BTD as the electroactive phase can be used to determine Cr(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 (Table 2). The present electrode permits the direct measurement of Cr(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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