Journal of Physical & Theoretical Chemistry
Islamic Azad University of Iran 3 (3)
(2006)
Science and Research Campus
ISSN: 1735-2126

Application of a dioxime-PVC electrode to potentiometric studies of Cr(III) ion

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ABSTRACT

A PVC membrane Cr(III) ion selective electrode has been constructed using 2H-1,4-benzothioazine-2,3(4H)dione dioxime (BTD) as membrane carrier. The influence of membrane composition on the electrode response was studied. The electrode exhibits a Nernstian response over a Cr(III) concentration range of 1.0×10^{-6} to 1.0×10^{-1} M ($r = 0.99$) with a slope of 19.5 ± 0.5 mV per decade of concentration, and a detection limit of 8.9×10^{-7} M. The selectivity coefficient values as determined by separate solution method (SSM) indicate excellent selectivity for Cr(III) ion over a large number of other ions. Applications of the proposed electrode to the determination of Cr(III) in real samples and as an indicator for potentiometric titration of Cr(III) ion with EDTA, are reported.

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

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INTRODUCTION

The dioxime ligands are known to coordinate metal ions as neutral dioximes [1,2]. The chemistry of the bis-dioxime complexes of transition metal ions has attracting continues attention because of their importance with reference to dioxygen carriers [3], catalysis in chemical transformations [4-6], intramolecular hydrogen bonding and metal-metal intraction [7-9]. In the past years, a large variety of mainly cation-selective carriers have been synthesized by various research groups and published articles on ionophore based ion selective electrodes are increasingly developed [11-14].

Very little work has been done on the development of ion selective electrodes for Cr(III) ions. The first report on Cr(III) appeared in 1980 [15]. In 1989, an ion selective electrode based on chromium dithizonate was built, that was a precipitate based selective electrode [16].

In addition to these, chromium selective electrodes based on nickel tris (1,10-bathophenanthroline) hydrogen chromate [17], 2,4,9,11-tetraphenyl-1,5,8,12-tetraazacyclotetradeca-1,4,8,11-tetraene dihydrogen perchlorate [18], glyoxal bis(2-hydroxyanil) [19], 3,10-c-meso-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetrad-ecane diperchlorate [20], 4-dimethylaminoazobenzene [21] and tetraaza macrocyclic based [22] ionophores have also been constructed.

Some of the recent electrodes have been compared to the proposed electrode assembly which shows that the electrode presented in this paper has a Nernstian response with a wide working concentration range and fast response time than the earlier reported electrodes (Table 1). The results presented in this article show that the sensor, developed for Cr(III) ions based on a newly synthesized BTD, due to its highly selective comlexation with Cr(III) ions and its negligible solubility, has a wide working concentration range, fast response time and gives reproducible results.

Table 1. Comparative studies of previously reported Cr(III) ion selective electrodes

No.	Ionophore	Working conc. range, M	Slope mV/dec.	Response time, s	Ref.
1	Nickel tris(1,10-batho-phenanthroline) Hydrogen chromate	$8.0\times10^{-6}-2.0\times10^{-2}$	55.5	-	[16]
2	Macrocycle based	$1.8\times10^{-6}-1.0\times10^{-1}$	20.0	15	[17]
3	4-Dimethyl-aminoazobenzene	$1.7\times10^{-6}-1.0\times10^{-2}$	19.5	10	[18]
4	Glyoxal bis(2-hydroxyanil)	$4.0\times10^{-6}-1.0\times10^{-1}$	19.8	20	[20]
5	Tetraaza macrocyclic based	$1.6\times10^{-6}-1.0\times10^{-1}$	19.5	18	[22]
6	2H-1,4- benzothioazine-2,3(4H) dione dioxime	$1.0\times10^{-6}-1.0\times10^{-1}$	19.5	15	this work

EXPERIMENTAL

1. Reagents

2H-1,4-benzothioazine-2,3(4H)dione dioxime (BTD) as ligand (Fig. 1) was prepare according to previously reported method [23]. Tetrahydrofuran (THF), dibutyl phthalate (DBP), acetophenone (AP), oleic acid (OA), ethylene diamine tetra acetic acid (EDTA), high relative molecular weight PVC, 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.

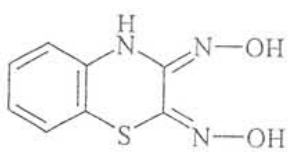

Figure 1. structure of 2H-1,4-benzothiozine-2,3(4H)dione dioxime (BTD) used as ionophore.

2.Apparatus

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, Urumia, Iran) was used in conjunction with the respective indicator electrode. A Haoke model FK_2 circulation water bath was used to control the temperature of the test solution .

3. Electromotive force measurements

All electromotiveforce (emf) measurements were carried out with the following assembly: Ag-AgCl / 3 M KCl / internal solution (1.0×10^{-3} M $CrCl_3$ + 1.0×10^{-3} M HCl) / PVC membrane / test solution / 3 M KCl / Ag-AgCl

RESULTS AND DISCUSSION

1. Effect of membrane composition on the electrode response

The potential responses of various ion-selective electrodes based on BTD are shown in Fig. 2. Except for the Cr(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 [24-33].

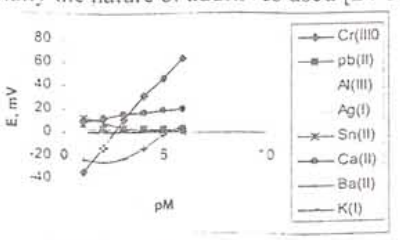

Figure 2. Response at pH 3 against some of cations for ion-selective electrodes containing BTD as ionophore.

Thus, based on the results obtained on the optimization of the membrane composition, the membrane with the optimized composition of PVC:ionophpre:acetophenone:oleic acid ratio of 6:1:13:1 was selected for the preparation the polymetric membrane electrode. The characteristic parameters of the optimized membrane are summarized in Table 2.

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

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

2. Effect of internal solution

The internal solution may affect the electrode response when the membrane internal diffusion potential is appreciable [30]. Thus, the influence of the concentration of the internal solution of the PVC electrode was studied as follows. Three similar membranes were prepared under optimal membrane composition, and each electrode was filled with an internal solution of different Cr(III) concentration of 1.0×10^{-1}, 1.0×10^{-2}, and 1.0×10^{-3} M. The electrodes were then conditioned for 24 h by soaking in a 1.0×10^{-2} M Cr(III) solution. Finally, the emf versus pCr(III) plot for each electrode was constructed in a pCr(III) range of 1.0-6.0. It was found that the variation of the concentration of the internal solution does not cause any significant difference in the corresponding potential [Fig.3].

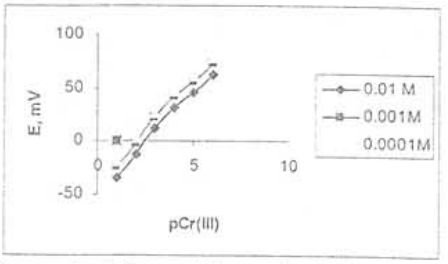

Figure 3. Effect of internal solution on the response of electrode.

3. 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 1.0×10^{-2} to 1.0×10^{-3} M) sample concentration and the results are shown in Fig. 4. Fig. 4. 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 [30].

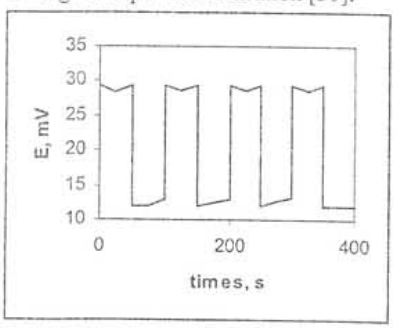

Figure 4. Dynamic response characteristics of the Cr(III)-electrode for several high-to-low sample cycles.

4. Selectivity of the electrode

The potentiometric selectivity coefficients, which reflect the relative response of the membrane sensor towards the primary ion over other ions present in solution, are perhaps the most important characteristics of an ion-selective electrode.

The selectivity of the electrode in presence of various cations was evaluated by the separate solution method (SSM) [34] at 1.0×10^{-3} M concentration of Cr(III).

A perusal of selectivity coefficient data presented in Table 3 indicates that the electrode is sufficiently selective over a large number of cations except Al^{3+}. Table 5 compares the selectivity coefficients of the Cr(III) sensor with those of the best Cr(III) electrodes reported in literature [35], [36], [37], and [38].

Table 3. Comparision of the selectivity coefficients of different Cr(III) electrodes

Ions	Ref. 35 FIM	Ref. 36 MPM	Ref. 37 MPM	Ref. 38 MPM	this work SSM
Pb^{2+}	-1.96	-2.22	-3.20	-3.00	-2.25
UO_2^{2+}	-	-	-	-	-2.42
NH_4^+	-0.62	-	-	-	-3.55
Al^{3+}	-3.20	-2.96	-2.44	-	-0.20
Ca^{2+}	-	-2.44	-3.37	-	-1.64
Ba^{2+}	-2.10	-	-3.43	-	-2.85
K^+	-1.99	-2.62	-3.55	-3.20	-3.64
Ni^{2+}	-2.05	-2.92	-3.07	-	-1.85
Hg^{2+}	-1.75	-	-3.21	-2.80	-2.54

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 Cr(III) with EDTA solution. 20 ml of 1.0×10^{-4} M Cr(III) solution was titrated against 1.0×10^{-3} M EDTA solution.

The potential data are plotted against the volume of EDTA (Fig. 5). Although the changes observed in potentials are not large, the end point is quite sharp and a perfect stoichiometry is observed.

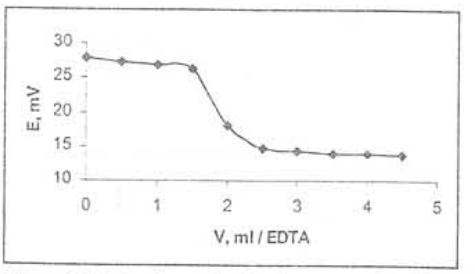

Figure 5. Potentiometric titration curve for 20 ml 1.0×10^{-4} M Cr(III) with 10^{-3} M EDTA.

CONCLUSION

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 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 Cr(III) in real samples without prior separation steps, thus considerably simplifying the determination procedure with respect to the other analytical methods used.

ACKNOWLEDGEMENTS

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

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