Chromium (III) ion selective electrode based on di(benzylamino)glyoxime

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ABSTRACT

A new poly(vinylchloride) membrane sensor for Cr^{3+} ions based on di (benzylamino)glyoxime as an ionophore was prepared. The electrode has a linear dynamic range 1×10^{-6}-1×10^{-1} mol l^{-1},with a Nernstian slope of 20.3 ± 0.5 mV per decade and a detection limit of 2×10^{-7}. It has a fast response time of <15 s and can be used for at least 3 months without any considerable divergence in potential. The proposed electrode revealed good sensitivity for Cr(III) over a wide variety of metal ions and could be used in a pH range of 2-5.5. The proposed sensor was used for the determination of Cr^{3+} ions in real samples such as tea leaves, coffee and cacao powder by direct potentiometry.

Keywords: Ion-selective electrode; Chromium(III); Di(benzylamino)glyoxime; Poly(vinyl chloride) membrane

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INTRODUCTION

The increasing use of ion sensors in the fields of environmental, agricultural and medicinal analysis is forcing analytical chemists to develop new sensors for the fast, accurate, reproducible and selective determination of various species. Among heavy metals, trivalent metals have received less attention in spite of their widespread occurrence in food products, sea and fresh water, plants and animals [1].

A literature survey revealed that a large number of ISEs based on PVC membrane were reported for many inorganic ions [2], but very little was published on PVC-based trivalent ions. The first report on Cr(III) was in 1980 [3] in which a PVC based chromium-wire electrode was made by incorporating (Aliquat $336S^+$-$Cr(SCN)_4^-$)ion-pair studied, and the electrode gave a full response in the $Cr(SCN)_4^-$ concentration range of 10^{-5}-10^{-2} mol l^{-1} and has the Nernstian slop of 58 mV per pCr.

In 1987 a Cr(III) selective electrode with PVC membrane based on 8-quinline-dithiocarboxilate was described [4]. In 1989 another ion selective electrode based on chromium dithizonate was built that was a precipitate based selective electrode [5]. Singh et al. used a Cr(III)-selective electrode based on the macrocyclic compound for determination of chromium ion in some food materials [6]. A PVC-based Cr(III)-selective electrode, was prepared, based on 4-methylaminoazobenzene with a linear concentration range of $1.7×10^{-6}$-$1.0×10^{-2}$ mol l^{-1} and a limit of detection of $8.0×10^{-7}$ mol l^{-1} [7]. A Nernstian slope of 19.5 mV per decade and pH range of 3.0-5.5 were reported for this electrode. The selectivity coefficient of some metal ions such as Ag(I) and Mn(II) are small enough to be considered (about 10^{-1}) for foregoing electrode. Recently been prepared a PVC-based Cr(III)-selective electrode based on glyoxal bis(2-hydroxyanil) has which has a linear range of $3.0×10^{-6}$-$1.0×10^{-2}$ mol l^{-1} , with a Nernstian slope of 19.8±0.5 mV [8]. However these sensors [3-8] suffer from the disadvantages of significant interferences by some cations, deviation from Nernstian behavior, small linear range and narrow pH range.

In this paper, we describe the construction and evaluation of a piasticized PVC membrane chromium(III) - selective electrode based on di (benzylamino) glyoxime (DBAG) as neutral carrier (Fig. 1).
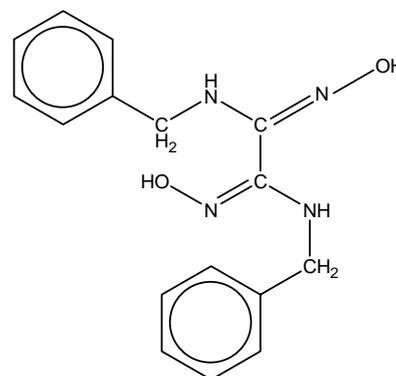
Fig. 1. Structural representation of the DBAG used as ionophore in the chromium(III)-selective electrode.

Experimental

1. Reagents and materials

Reagent grade of dibuthyl phthalate (DBP), acetophenone (AP), dioctyl phthalate (DOP), tetrahydrofuran (THF), potassium tetrakis(p-chlorophenyl)borate (KTpClPB), oleic acid(OA), high relative molecular weight PVC and nitrate or chloride salts of all cations obtained (from Merck or Fluka) were used as received. The ionophore DBAG was synthesized. Double distilled deionized water used throughout.

2. EMF measurements

Potentials were measured with a Corning ion analyzer pH/mV meter against a double junction saturated calomel electrode (SCE) at constant temperature (25±0.1°C). The chamber of the SCE was filled with a potassium chloride solution. A silver/silver chloride electrode containing 3 M solution of KCl was used as the internal reference electrode. The electrode cell assembly of the following type was used:

Ag-AgCl│ KCl (3 M) │ internal solution, $1×10^{-3}$ M $Cr(NO_3)_3$│ PVC membrane│ test solution│ Hg-Hg_2Cl_2,KCl(saturated).
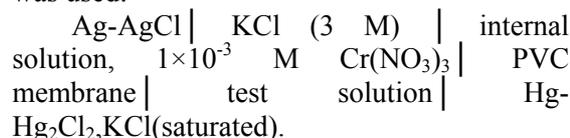
3. Electrode preparation

The general procedure to prepare the PVC membrane was similar to our previous work [9]. First, we mixed thoroughly 5 mg of ionophore DBAG, 30 mg of powdered PVC, and 65 mg of plastisizer AP in a 2 cm diameter glass dish. The mixture was then dissolved in 5 ml of THF. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube was dipped into the mixture for ~10 s so that a membrane was formed. The tube was then pulled out of the mixture and kept at room temperature for 24 h. The tube was filled with internal filling solution (1.0×10^{-3} mol l^{-1} Cr(NO$_3$)$_3$). The electrode was finally conditioned for 24 h in a 1.0×10^{-3} mol l^{-1} solution of Cr(NO$_3$)$_3$. A silver/silver chloride electrode was used as an internal reference electrode.

Results and discussion

1. Effect of membrane composition

The DBAG 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 solutions.

In order to test the performance of the membrane, various operation parameters including selectivity, response time, sensitivity, life time, linear range, the influence of pH and the membrane composition on the response of the electrode were investigated.

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 [9,11-13].

Thus, the influences of the membrane composition, the nature and amount of plasticizers on the potential response of the Cr^{3+} sensor were investigated. The results are summarized in Table 1.

It is seen that, among the different compositions studied, membrane 5 incorporating 30% PVC, 65% AP, 5% ionophore DBAG shows the best sensitivity with Nernstian slope of 20.3 mV per decade over a wide concentration range of 1×10^{-6}-1×10^{-1} M. The data in Table 1 also show that the presence of additive in the membrane slightly decreases the linear range of the electrode.

2. Calibration curve and statistical data

The Potential responses of various ion-selective membranes based on DBAG are shown in Fig. 2. As it is seen, among different cations tested, the largest sensitivity was obtained for Cr^{3+} ion. The e.m.f. vs. $-\log a_{Cr3+}$ of the PVC membrane based on DBAG, prepared under optimal composition, indicated a rectilinear range from 1×10^{-6}-1×10^{-1} M. The slope of the calibrations curve was 20.3 ± 0.5 mV per decade of Cr^{3+} concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 7.7×10^{-7} M.

Table 1.

Optimization of the membrane ingredients

Number	Composition(%)				Slope	Response range
					(±0.5 mV per decade)	(mol l^{-1})
	PVC	Plasticizer	Ionophore	Additive		
1	30	65(AP)	0.0	5(OA)	0.72	1×10^{-6}-1×10^{-1}
2	30	60(AP)	5.0	5(OA)	21.2	1×10^{-4}-1×10^{-1}
3	30	57(AP)	8.0	5(OA)	24.6	1×10^{-4}-1×10^{-1}
4	30	62(AP)	3.0	5(OA)	23.1	1×10^{-4}-1×10^{-1}
5	30	65(AP)	5.0	-	20.3	1×10^{-6}-1×10^{-1}
6	30	65(AP)	5.0	5(KTpClPB)	22.7	1×10^{-6}-1×10^{-1}
7	30	65(DBP)	5.0	-	17.5	1×10^{-5}-1×10^{-1}
8	30	65(DOP)	5.0	-	18.3	1×10^{-5}-1×10^{-1}

The standard deviation of sixteen replicate measurements is ±0.5 mV. The prepared electrode could be used for more than 3 months without any measurable change in potentials.
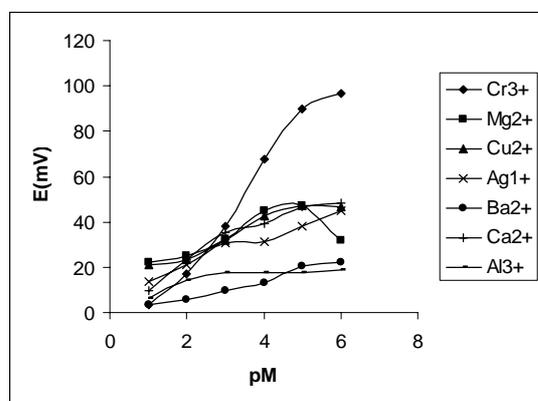
Fig. 2. Potential response of various metal ion-selective electrodes based on DBAG.
Composition of membrane: membrane ingredients, 30%PVC, 65%AP, 5% DBAG; internal solution, 1.0×10^{-3} mol l^{-1} Cr(NO$_3$)$_3$.

3. Influence of pH
The pH dependence of the potentials of the proposed electrode for different concentrations of chromium(III) ion were tested over the pH range 1-7 and the results are depicted in Fig. 3. The pH was adjusted with nitric acid or sodium hydroxide solution. As it can be seen, the potential response remains almost constant over the pH range 2-5.5, which can be taken as the working pH range of the electrode. At pH higher than 5.5, the potential of electrode decreases due to the formation of chromium hydroxides in solution. The variation of

potentials in pH<2 could be related to protonation of the ligand DBAG in the membrane phase, which results in a loss of its ability to complex with Cr(III) ions, and probably response of the electrode to H$^+$ ions in high acidic media.
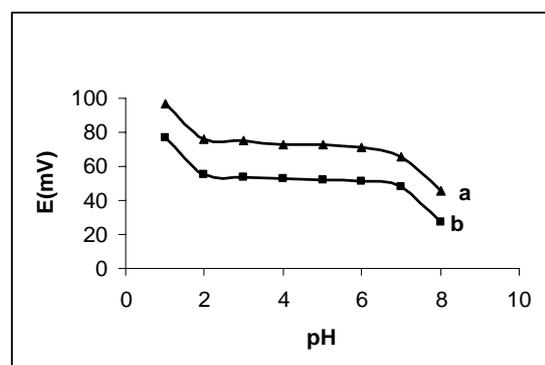
Fig. 3. Influence of pH of test solution on the potential response of Cr(III) electrode at different Cr^{3+} concentrations: (a)1.0×10^{-2} M and (b)1.0×10^{-3} M.

3.4. Selectivity of the electrode
The influence of interfering ions on the response behavior of ion-selective membrane electrodes is usually described in terms of selectivity coefficients, $K_{A,B}^{Pot}$. The methods based on the Nicolsky-Eisenman equation for the determination of potentiometric selectivity coefficients (e.g. the fixed interference method and the mixed solution method) are among the most commonly methods used thus far [13-17].

Table 2 .

Selectivity coefficients ($K_{A,B}^{SSM}$) of various interfering cations obtained using SSM.

[Cr^{3+}]=1×10^{-3} M, [M^{n+}]=1×10^{-3} M, pH=3

Cation	$K_{A,B}^{SSM}$	Cation	$K_{A,B}^{SSM}$
Na$^+$	1.2×10^{-3}	Zn^{2+}	1.6×10^{-3}
Mg^{2+}	2.4×10^{-3}	Ni^{2+}	7.1×10^{-1}
Al^{3+}	1.8×10^{-3}	Li$^+$	1.8×10^{-3}
Ca^{2+}	3.2×10^{-3}	Ag$^+$	2.7×10^{-3}
Cu^{2+}	4.9×10^{-3}	Co^{2+}	5.2×10^{-3}
K$^+$	1.7×10^{-3}	Ba^{2+}	3.3×10^{-3}
Pb^{2+}	4.6×10^{-1}	Cd^{2+}	6.7×10^{-3}

However, it has been shown that these methods suffer some limitations in terms of values for ions of unequal charges, non-Nernstian behavior of interfering ions, and activity dependence, of values. Thus, in this work, the recommended separate solution method (SSM) was used for selectivity measurements [18-24].

According to the SSM, the potential of a cell comprising an ion-selective electrode and a reference electrode is measured with two separate solutions, one containing the ion A at the activity a_A (but no B), the other one containing the ion B at the same activity $a_A=a_B$ (but no A). If the measured values are E_A and E_B, respectively, the value of $k_{A,B}^{Pot}$ is calculated from the equation:

$$\log \kappa_{A,B}^{Pot} = \frac{(E_B - E_A)}{RT \ln 10} + (1 - \frac{z_A}{z_B}) \lg a_A$$

which is equivalent to

$$\kappa_{A,B}^{Pot} = a_A^{(1-\frac{z_A}{z_B})} e^{(E_B - E_A)z_A F / (RT)}$$

good detection limit. The electrode is characterized by a fast response, reproducibility, a reasonable long-term stability and low cost. The electrode also has a life time of more than three months. The proposed sensor has successfully been used as an indicator electrode to determine Cr(III) ion in some real samples.

5. Application

The electrode has been used successfully for determination of Cr^{3+} in various real samples.
The experimental conditions employed and the resulting values are given in Table 2. A perusal of selectivity coefficient data presented in Table 2 indicates that the electrode is sufficiently selective over a large number of cations except Pb^{2+} and Ni^{2+}.

The results (Table 3) indicate a very good agreement between the two values (obtained by AAS and the proposed sensor).

Table 3 .

Results of determination of chromium in different real samples.

Sample	Average chromium concentration (ppm)	
	Proposed sensor	AAS
Tea leaves	1.1±0.1	1.2±0.1
Coffee	1.1±0.2	1.3±0.1
Cacao powder	0.9±0.2	1.0±0.2

4. Conclusion

The results obtained in the present work demonstrate that the DBAG as a ionophore can be used in the development of a PVC-based ion-selective electrode. The electrode response to the Cr^{3+} ions in a Nernstian fashion, and presents good selectivity and a

Acknowledgments

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