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An electrochemical Cr(III)-Selective Sensor-Based on a Newly Synthesized Ligand and Optimization of Electrode With a Nano Particle

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A novel ion-selective poly(vinyl chloride) membrane sensor for Cr(III) ions based on a crown ether as a new ionophore has been prepared and studied.The electrode exhibits a good potentiometric response for Cr(III), response time ≤ 15 s, over a wide concentration range 1.0×10^{-5} to 1.0×10^{-1} M with a slope 20.4 ± 0.5 mV/decade and low detection limit of 8.9×10^{-6} M. The best performance was observed with the membrane having the PVC-ligand-acetophenone-oleic acid-TiO_2 nano particle composition 5:1:7:1:1.

Keywords: Ion selective electrode, PVC membrane, Cr(III) determination, nano particle

1. 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, ISE possess wide dynamic ranges 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 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 [14], but to the best of our knowledge, very little reports were appeared 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 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 new ligand as a neutral carrier in the construction of a PVC membrane electrode selective to Cr(III) ion.

2. EXPERIMENTAL

2.1. Materials

All of reagents and solvents involved in synthesis were of analytically grade a received without further purification. dibutyl phthalate (DBP), Tetrahydrofuran (THF), acetophenone (AP), oleic acid (OA), TiO_2 high relative molecular weight PVC were obtained from Aldrich and Merck. 2,6-Diformyl-4-methylphenol was prepared according to the literature method [20]. trans-(R, R)-Cyclohexanediamine was separated from the cis, trans mixture according to the literature procedure [21].

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.

2.2.Instrumentation

The structure of all synthesized compounds was confirmed by ^1H NMR spectra, recorded on a Bruker AV 300 MHz spectrometer. FT-IR spectra were recorded as pressed KBr discs, using Unicom Galaxy Series FT-IR 5000 spectrophotometer in the region of 400-4000 cm^{-1}. Melting points were determined on Electrothermal 9200 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, 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. Synthesis of macrocycle, H3L

To a solution of 2,6-diformyl-4-methylphenol (1.64 g, 10 mmol) in 100 ml of methanol was added trans-(1R,2R)- cyclohexanediamine (1.14 g, 10 mmol) in 100 ml of methanol. The reaction mixture was stirred vigorously at room temperature. The Schiff base macrocycle H_3L (Figure1) separated as a yellow solid and the mixture was refluxed for 3 h and filtered. Yield 1.8 g (75%). IR (KBr, cm-1): 1639 (C═N), 1253 (C-O), ^{1}H NMR (CDCl3, ppm): δH 8.66 (3 H, s, HC═N), 8.30 (3 H, s, HC═N), 7.57 (3 H, s, ArH), 6.89 (3 H, s, Ar H), 3.30 (6 H, m, N–CH), 2.07 (9 H, s, CH3) and 1.88–1.46 (24 H, m, CH2CH2). Calc. for C45H54N6O3: C, 74.35; H, 7.49; N, 11.57; Found: C, 74.12; H, 7.67; N, 11.72%. UV.Vis. λmax (nm) (ε (M-1cm-1)): 272, 371(11800) in CHCl3.

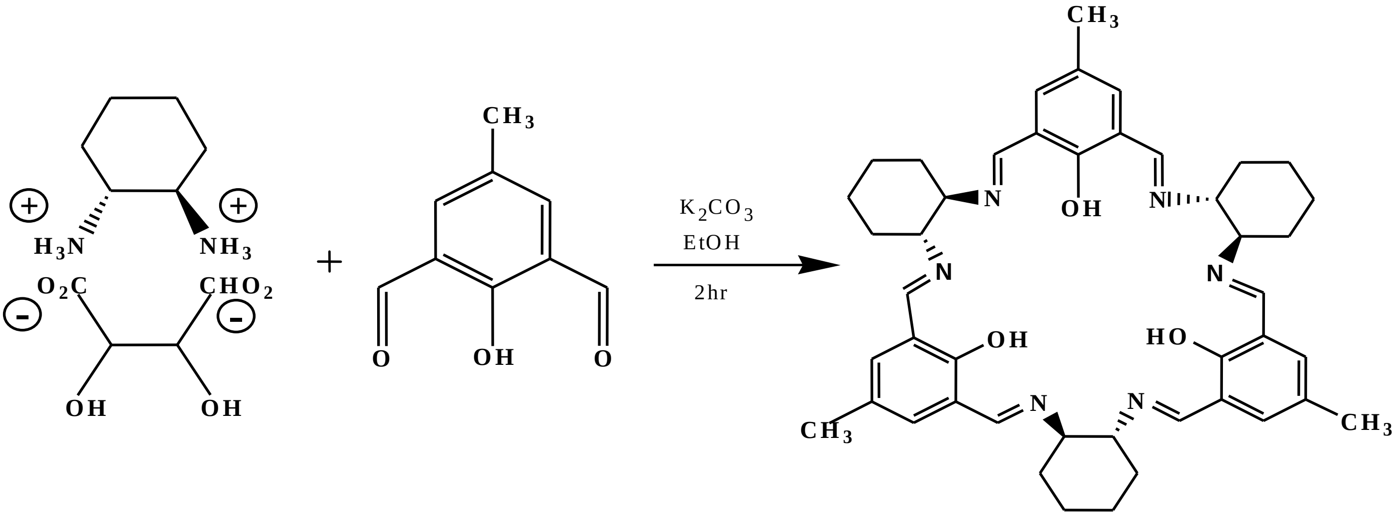

Figure 1. Structure of H_3L

3. RESULTS AND DISCUSSION

3.1. 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 composition 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.

Table 1. Optimization of the membrane ingredients

NO	Composition, %					Slope	Linear range, M
	Ionophor	PVC	Plasticizer	Additive	TiO_2		
1	-	32.0	63.0(AP)	5.0(OA)	-	3.1	-
2	1.5	29.0	63.5(DBP)	6.0(OA)	8.3	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^{-3}-1.0 × 10^{-1}
4	2.0	28.0	65.5 (AP)	4.5 (OA)	-	22.5	1.0 × 10^{-3} -1.0 × 10^{-1}
5	2.0	28.0	64.0 (AP)	6.0 (OA)	-	23.5	1.0 × 10^{-4} -1.0 × 10^{-1}
6	3.0	30.5	61.0 (AP)	5.5 (OA)	-	21.6	1.0 × 10^{-4} -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	48.7	5.9	59.0 (AP)	5.1 (OA)	-	19.3	1.0 × 10^{-4} -1.0 × 10^{-1}
9	6.8	40.0	47.4 (AP)	5.8 (OA)	6.1	19.2	1.0 × 10^{-5} -1.0 × 10^{-1}
10	9.5	32.0	52.5 (AP)	6.0 (OA)	-	31.7	1.0 × 10^{-3} -1.0 × 10^{-1}

The potential 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

A Metrohm digital research pH meter was used for measuring potential at 25.0± 1.0^{0}C. Activities were calculated according to the Debye-Huckel procedure [22].

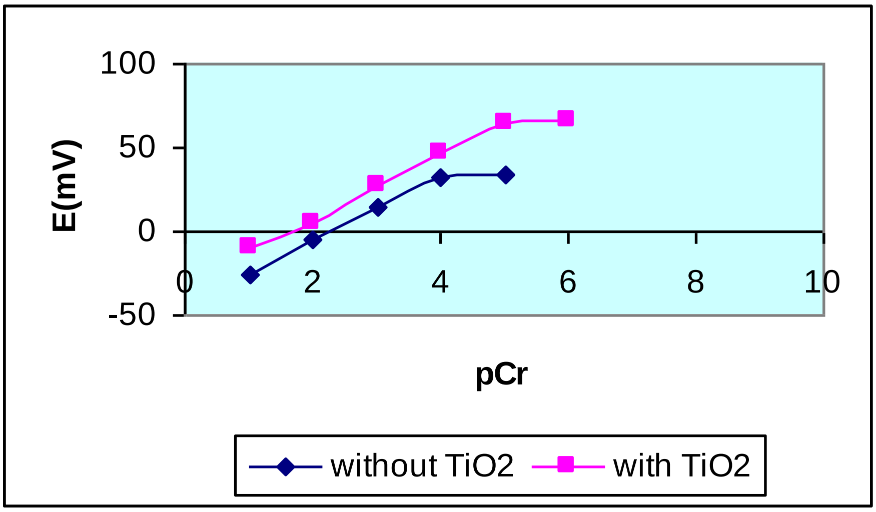

Figure 2. Calibration plot of the Cr(III)-ISE based on ligand.

3.2.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, but also significantly on the membrane composition and the properties of plasticizers and additives used [23-26]. 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.

Among the different composition studied, membrane 9 incorporating 37.7 % PVC, 44.6 % AP, 5.6 % OA , 6.4 % ionophor and 5.7 % TiO_2 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 Cr(III) with a Nernstian slope of 19.2 ± 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 H_3L.

Properties	Values/range
Optimized membrane composition	PVC (37.7 %), AP (44.6 %) OA (5.6 %), Ionophore (6.4 %),TiO_2(5.7)
Linear range, M	1.0×10^{-5} to 1.0×10^{-1}
Detection limit, M	8.9×10^{-6}
Slope, mV/decade	20.4 ± 0.5
Response time, s	≤ 15

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 Cr(III) concentration was increased tenfold, from 1.0×10^{-4} to 1.0 M.

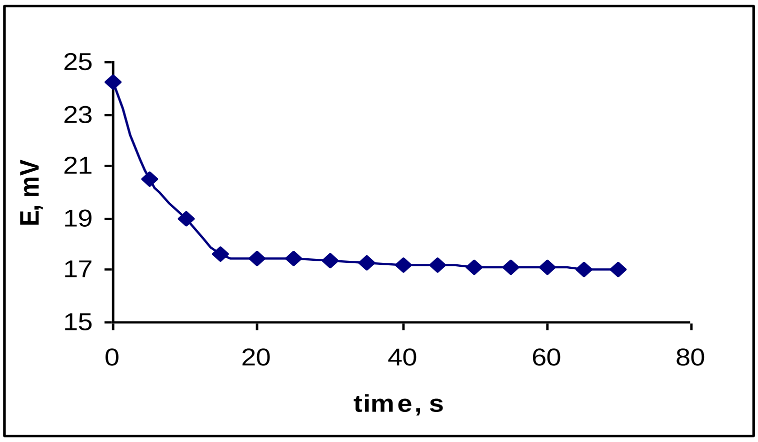

Fig. 3. The response time of Cr(III)-ISE based on ligand for Cr(III) concentration of 1.0×10^{-4} M.

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. 3 for Cr(III) concentration of 1.0 × 10^{-4} M.

3.4. Effect of internal solution

The internal solution may affect the electrode response when the membrane internal diffusion potential is appreciable [27]. 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 varying 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 1.0-5.0. It was found that the variation of the concentration of the internal solution does not case any significant difference in the corresponding potential response [Fig.4].

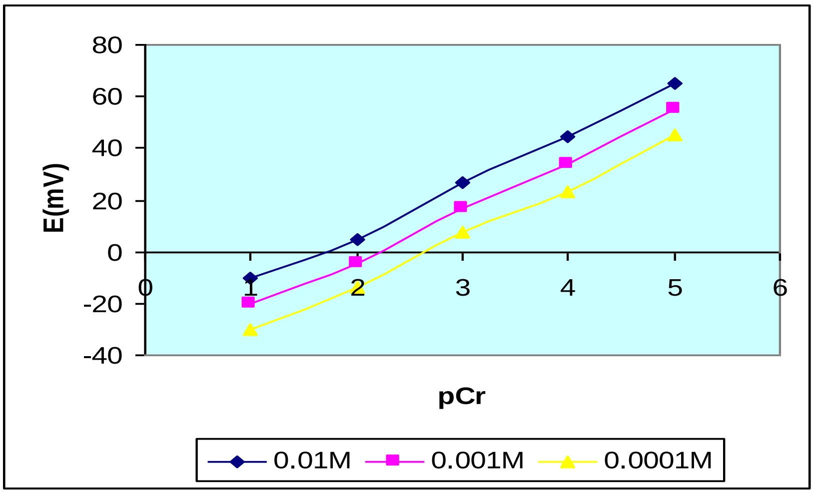

Figure 3. Effect of internal solution on the response of electrode.

4.CONCLUSIONS

The membrane sensor incorporating H_3L as the electroactive phase can be used to determine Cr(III) in the wide concentration range. The sensor exhibited good reproducibility over a useful life time about 2 months.This electrode is supervior to the existing electrodes with regard to the slope, response time and selectivity over a number of cation[28,29].

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