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High-Sensitive and Selective Liquid Membrane Electrode for Direct Determination of Trace Amounts of Chromium

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Abstract

N-(2H-[1,2,4]thiadiazolo[2,3-a]pyridine-2-ylidene)benzamide was used as a selective sensing material in the PVC membrane to construction of a new chromium ion selective electrode. This liquid membrane electrode worked well with a Nernstian response of 19.7 ±0.4 mV decade^{-1} of Cr(III) in a wide dynamic concentration range of 8.0×10^{-6}-1.0×10^{-1} M. The electrode had relatively short response time (about 5 s), and it was found to produce stable responses for more than 60 days. The effects of some factors such as internal solution, pH, life time and selectivity were investigated. The electrode has a useful working pH range of 3.5–8. Selectivity coefficients determined with match potential method. The selectivity coefficients indicate high selectivity towards Cr(III) ions. The practical utility of the Cr(III) ion sensor has been demonstrated by using it as an indicator electrode in potentiometric titration of Cr(III) with EDTA and for direct determination of Cr(III) in tea and Cocoa powder samples.

Keywords: *Chromium, Potentiometric, PVC membrane electrode, N-(2H-[1,2,4]thiadiazolo[2,3-a]pyridine-2-ylidene)benzamide.*

Introduction

Potentiometer monitoring, based on the ion-selective membrane sensor as a simple method, offers several advantages such as speed and ease of preparation and procedure, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity and low cost. These characteristics have led to the growth of available electrodes over the last a few years [1-14]. Therefore, in the recent decades, many intensive studies have been introduced on the design and synthesis of highly selective ion-carrier as sensory molecules in the fabrication of ion-selective

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electrodes.

On the other hands, due to the vital importance of Cr(III) in many complex biological systems and industrial samples, the search for new selective and sensitive electrodes for its quick measurement is a challenging goal [15,20]. Chromium (III) is an essential nutrient for humans and Cr(III) compounds are playing a role in the metabolism of glucose and certain lipids, mainly cholesterol [21,22]. But the uptake of too much chromium (III) can cause health effects as well, for instance skin rashes. Several in vitro studies indicated that high concentrations of chromium (III) in the cell can lead to DNA damage [23]. Although sophisticated analytical techniques like atomic absorption spectroscopy (AAS) [24], X-ray fluorescence (XRF)[25]and inductively coupled plasma-atomic emission spectroscopy (ICP-AES)[26] are generally employed for the trace level determination of metals such as chromium, yet these techniques are disadvantageous in terms of cost of routine analysis and time consuming and tedious procedure of sample preparation.

Therefore, in this work, N-(2H-[1, 2, 4] thiadiazolo[2,3-a]pyridine-2-ylidene) benzamide (NTPYB) (figure 1) was used as a selective sensing material in the PVC membrane for the first time. The proposed sensor was successfully applied for potentiometer monitoring of the Cr(III) ions in Cocoa powder and tea samples without any separation or purification.

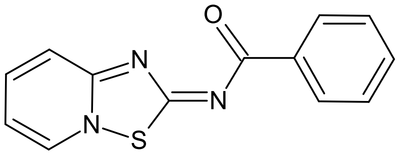

Figure 1. The structure of N-(2H-[1,2,4]thiadiazolo[2,3-a]pyridine-2-ylidene)benzamide (NTPYB).

Experimental

Apparatus

A Corning ion analyzer 250 pH/mV meters was used for the potential measurements at 25.0±0.1 °C. Two Ag/AgCl reference electrodes (Azar-Electrode, Iran) were used as the internal and external reference electrodes.

Reagents and Materials

Reagent grade dibutyl phthalate (DBP), nitrobenzene (NB), high relative molecular weight polyvinyl chloride (PVC), sodium tetraphenyl borate (NaTPB) and tetrahydrofurane (THF) were purchased from Merck and used as received. N-(2H-[1, 2, 4] thiadiazolo [2,3-a] pyridine-2-ylidene) benzamide was synthesized and purified as described elsewhere [27]. Nitrate salts of the cations used (from Merck and Aldrich) were all of the highest purity available, and used without any further purification except for vacuum drying over P2O5. Doubly distilled deionized water was used throughout.

Electrode Preparation

The general procedure to prepare the PVC membrane was as followed: Different amounts of the ionophore (N-(2H-[1, 2, 4]thiadiazolo [2,3-a] pyridine - 2 - ylidene)benzamide) along with appropriate amounts of additive were weighed. Then, known amounts of PVC and plasticizer were added to the mixture. The mixture was dissolved in 2 mL of tetrahydrofuran (THF), and the solution was mixed well. The resulting 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 (3-5 mm o.d.) was dipped into the mixture for about 10 s so that a transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 24 h. The tube was then filled with an internal filling solution (1.0×10^{-3} mol L^{-1} $Cr(NO_3)_3$). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} mol L^{-1} $Cr(NO_3)_3$ solution.

Emf Measurements

The following cell was assembled for the conduction of the emf (electromotive force) measurements; Ag–AgCl, KC1 (satd.) | internal solution, 1.0×10^{-3} mol L^{-1} $Cr(NO_3)_3$ | PVC membrane | sample solution | Ag–AgCl, KC1 (satd.). These measurements were preceded using calibration of the electrodes with several standard solutions. Activities were calculated according to the Debye- Huckel procedure.

Results and discussion

Membrane Composition Effect on the Potential Response of the Sensor

To find the best performance of the electrode, different compositions were made according to Table 1. The potential of different prepared membrane sensors was measured as function of chromium ion free concentration. The linear range and slope of the potential response plots have been evaluated and given in table 1.

The selectivity obtained for a sensor depends on the nature of the ionophore and membrane ingredients [28,29]. From table 1, it was obvious that in the absence of ionophore (NTPYB) (no. 1and 5), the response of the recommended electrode was quite low (slope of 4.5±0.2 and 6.5±0.3 mV per decade) which show significant effect of the ionophore. The sensitivity of the electrode response increases with increasing ionophore content until a value of 14% is reached. It shows the affinity of the NTPYB toward Cr(III) ion. The Cr (III) ion extraction into the liquid membrane is a result of the high concentration of the ligand in the membrane. Further addition of ionophore (no. 15and 16) will, however, result in diminished response of the sensor, most probably due to some inhomogenities and possible saturation of the membrane [30]. The second factor which helps the extraction of the Cr(III) ion is plasticizer. Plasticizer acts as a membrane solvent allowing homogeneous dissolution and diffusional mobility of the ion-pair inside the membrane [31]. The plasticizer should be water- immiscible liquid of low vapor-pressure, compatible with PVC and no functional groups which can undergo protonation reactions. The selectivity of such electrode can be significantly influenced by the choice of the membrane solvent. Nature of the plasticizer has a noticeable effect on analytical responses e.g. slope, linear domain and selectivity of PVC membrane electrodes [32-34]. Here, two plasticizers with different polarity (dielectric constant) were tested, dibutyl phthalate (DBP with DC of 6.4) and nitrobenzene (NB with DC of 35.7) as listed in table 1.

Table 1. The optimization of the membrane ingredients.

Membrane No.	Composition (%)				Slope (mV per decade)	Linearity Range (M)
	PVC (%wt.)	Plasticizer (%wt.)	Ionophore (%wt.)	NaTPB (%wt.)		
1	30	DBP, 70	----	----	4.5±0.2	1×10^{-1}-1×10^{-4}
2	30	DBP, 55	13	2	10.5±0.3	1×10^{-1}-1×10^{-4}
3	25	DBP, 60	13	2	9.4±0.2	1×10^{-1}-1×10^{-4}
4	30	DBP, 54	14	2	10.5±0.3	1×10^{-1}-1×10^{-4}
5	30	NB, 70	----	----	6.5±0.3	1×10^{-1}-1×10^{-4}
6	30	NB, 62	8	----	8.4 ± 0.3	1×10^{-1}-1×10^{-4}
7	28	NB, 58	14	----	12.9±0.4	1×10^{-1}-1×10^{-4}
8	28	NB, 60	14	2	19.7±0.4	1×10^{-1}-1×10^{-5}
9	25	NB, 60	13	2	17.2±0.3	1×10^{-1}-1×10^{-4}
10	30	NB, 55	13	2	16.4 ± 0.3	1×10^{-1}-1×10^{-4}
11	22	NB,62	14	2	17.1 ± 0.4	1×10^{-1}-1×10^{-4}
12	24	NB,60	14	2	18.9 ± 0.4	1×10^{-1}-1×10^{-4}
13	30	NB,54	14	2	17.5 ± 0.3	1×10^{-1}-1×10^{-4}
14	26	NB,57	14	3	18.6 ± 0.3	1×10^{-1}-1×10^{-4}
15	28	NB,55	16	2	18.2 ± 0.4	1×10^{-1}-1×10^{-4}
16	28	NB,54	16	2	16.3 ± 0.3	1×10^{-1}-1×10^{-4}

After the evaluation of two solvent mediators, it was observed that NB is the effective solvent mediator and provided an effective Nernstian response. This is due to the high dielectric constant of NB which facilitates the better extraction of Cr (III) with a relatively high charge density from water to an organic layer of the membrane.

The presence of lipophilic anions in a cation-selective membrane was also considered. The data given in table 1 revealed that NaTPB addition of 2% as an additive led to the slope increase of the potential sensor response from the sub-Nernstian value of 12.9±0.4 mV per decade (no. 7) to the Nernstian value of 19.7±0.4 mV per decade (no. 8). In fact, it has been demonstrated that the presence of such anions in a cation-selective membrane, which is based on a neutral carrier, decreases the ohmic resistance and improves the response behavior and selectivity. Furthermore, when the extraction capability is poor, it increases the membrane electrode sensitivity [35, 36].

Addition of ionic additive to the membrane composition has improved the slope. In fact, it helps to the ion-exchange of the Cr (III) ions from aqueous solution to organic layer of the membrane. As seen, membrane number 8 with a PVC: NTPYB:NaTPB:NB percent ratio of 28:14:2:56 resulted in the nernstian behavior of the membrane electrode over a wide concentration range.

pH Effect on the Electrode Response

The influence of the pH of the test solution on the potential response of Cr (III) ion sensor investigated at 1.0×10^{-4} M Cr(III) solution, in the pH range of 2.0 up to 10.0. The pH of the solution was adjusted by the addition of hydrochloric acid or sodium hydroxide. The resulting data was shown that the potentials remained constant from the pH range 3.5 to 8 for this sensor. Therefore, the pH range 3.5 to 8 was taken as the working pH range of the electrode. Beyond this range, relatively noteworthy fluctuations in potential were observed. Consequently, the behavior of the membrane electrode towards the Cr (III) ion concentration was found to be inaccurate beyond the pH range of 3.5 to 8.

Internal Solution

The concentration of the internal solution ($Cr(NO_3)_3$) of the electrode was changed from 1.0×10^{-2} M to 1.0×10^{-4} M and the potential response of the Cr(III) ion selective electrode was obtained (Fig. 2). It was found that the variation of concentration of the internal solution does not cause any significant differences in potential response, except for an expected change in the intercept of the resulting Nernstian plot. A 1.0×10^{-3} M concentration $Cr(NO_3)_3$ solution is quite appropriate for smooth functioning of the electrode system.

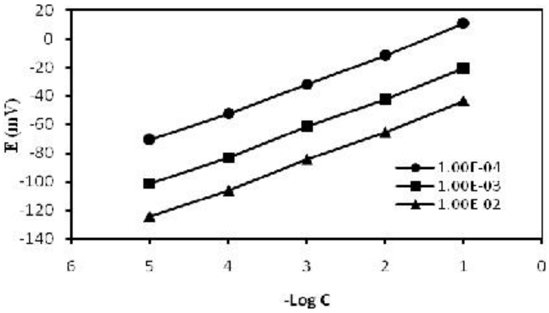

Figure 2. The effect of internal reference solution concentration on the electrode response.

Response Time

The response time of an electrode is evaluated by measuring the average time required to achieve a potential within ±0.1 mV of the final steady-state potential, upon successive immersion of a series of interested ions, each having a ten-fold difference in concentration. It is notable that the experimental conditions-like the stirring or flow rate, the ionic concentration and composition of the test solution, the concentration and composition of the solution to which the electrode was exposed before experiment measurements were performed, any previous usages or preconditioning of the electrode, and the testing temperature have an effort on the experimental response time of a sensor [3].

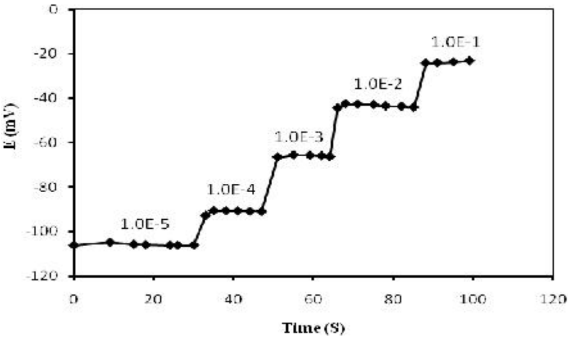

Figure 3. Dynamic response of chromium ion electrode for step changes in concentration of Cr(III)

In this work, dynamic response time was obtained by changing the Cr(III) concentration in solution, over a concentration range 1.0×10^{-5} to 1.0×10^{-1} M. The actual potential versus time traces is shown in Fig. 3. As can be seen, in whole concentration range the electrode reaches its equilibrium response in a very short time (~5s). This is most probably due to the fast exchange kinetics of complexation-decomplexation of Cr (III) ion with the ionophore at the test solution-membrane interface.

Calibration Curve and Statistical Data

The measuring range of a potentiometric sensor is the linear part of the calibration graph as shown in figure 4. Measurements could be performed in this range, but noted that more closely spaced calibration points are required for more precise determinations. For many electrodes the measuring range can extend from 1 molar to 10-6 molar concentrations [37-39].

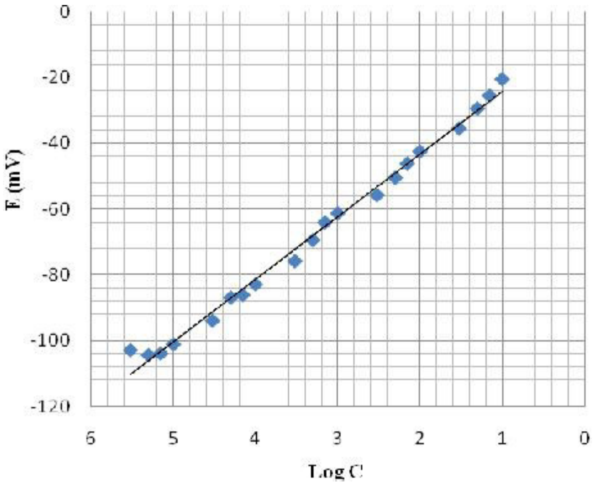

Figure 4. The calibration curve of the chromium ion-selective electrode.

Calibration graph slope for PVC membrane electrode is 19.7 mV per decade of the Cr (III) concentration and a standard deviation of ±0.4 mV after five replicate measurements. A linear response towards the Cr (III) concentration was from 8.0×10^{-6}-1.0×10^{-1} M. Detection limit was calculated from the intersection of two extrapolated segments of the calibration graph. In this work, detection limit of proposed sensor was 7.0×10^{-6} M which was calculated by extrapolating the two segments of the calibration curves.

Selectivity

The potentiometric selectivity coefficients of the Cr(III) sensor were evaluated by the matched potential method (MPM) [40]. The resulting val ues of the selectivity coefficients are given in Table 2. The selectivity coefficients clearly indicate that the electrode is more selective to Cr (III) than to a number of other metal ions. A value of KMPM =1.0 indicates equal response to primary and interfering ions. Further, the smaller the value of the selectivity coefficient, the higher is the selectivity of the sensor. It is seen from the table that the selectivity coefficient values are much smaller than 1.0 indicating that they exhibit sufficient selectivity towards Cr (III) over all the interfering ions studied. The selectivity coefficients seem to indicate negligible interferences in the performance of the electrode assembly.

Table 2. The selectivity coefficients of various interfering cations for the membrane

Ion	K_{MPM}
Hg^{2+}	7.8×10^{-3}
Mn^{2+}	1.7×10^{-2}
Co^{2+}	5.0×10^{-2}
Pb^{2+}	6.9×10^{-2}
Cu^{2+}	2.2×10^{-2}
Zn^{2+}	1.5×10^{-2}
Cd^{2+}	6.6×10^{-3}
Ag^{+}	2.2×10^{-2}

Lifetime

Lifetime of the membrane electrode was studied by periodically recalibrating and using the electrode to measure its potentiometric response to chromium ion in the standard solutions in a period of time. After the conditioning step the electrodes were repeatedly calibrated three times a day during a period of two months (the electrode worked one hour per day). Before 60 days no significant change in the performance of the electrode was observed. This shows that the lifetime of the proposed electrode was about two month. After 60 days, the slope of the chromium selective electrode decreases from 19.7 to 18.5 mV per decade. It is well established that the loss of plasticizer, carrier, or ionic site from the polymeric film due to leaching into the sample is a primary reason for the limited lifetimes of the sensors [41,42].

Analytical Application

Ion-selective electrodes tend to be; low in cost, simple to use, easily automated for rapid sampling, with low interferences from the matrix and can be applied to small volumes. These characteristics make them an ideal choice for environmental measurements.

The practical utility of the proposed membrane sensor was tested by its use as an indicator electrode for the titration of 25.0 mL of 1.0×10^{-4} M of Cr(III) solution with 0.01M standard solution of ethylene diamine tetraacetic acid (EDTA) solution. The resulting titration curve is shown in figure 5. As can be seen, the amount of Cr (III) ions in solution can be accurately determined with the electrode.

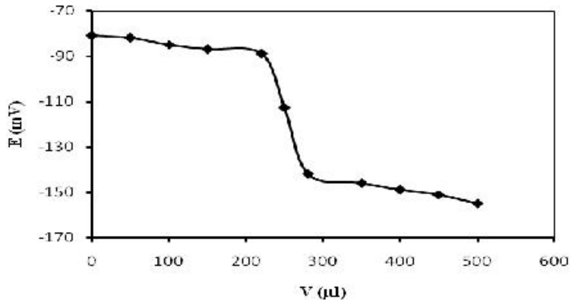

Figure 5. Potentiometric titration curve of 1.0×10^{-4} M Cr(III) solution (25 ml) with 1.0×10^{-2} M EDTA using the proposed sensor as an indicator electrode.

To assess the applicability of proposed electrode in real samples an attempt was made to determine Cr (III) ions in tea and cocoa powder samples. A 1.0 g black tea and cocoa powder was taken in a beaker and dissolved in concentrated HNO_3 (10 mL) and $HClO_4$ (4 mL) with heating. The solution was cooled, neutralized with NaOH solution, diluted and filtered. The filtrate was made to 100 ml with water in a calibrated flask.

Table 3. Determination of Cr(III) ions in various samples.

Sample	Measured with FAAS (mg L^{-1})	Measured with proposed sensor (mg L^{-1})
Black tea	1.18 (±1.7)[a]	1.20 (±1.73)
Cocoa powder	1.37 (±2.3)	1.39 (±1.72)

[a] % RSD based on three replicate analysis

An aliquot of the sample solution was taken and Cr (III) ions was determined by the calibration procedure by proposed electrode and flame atomic absorption spectroscopy (FAAS). The results are given in Table 3. As seen the results obtained by the proposed method and FAAS are in satisfactory agreement.

Comparison of the proposed Cr^{3+} sensor and some of the best previously reports

The Nernstian slope, detection limit, linearity range, response time and selectivity of proposed Cr(III) electrode with some of the best previously reports are compared in Table 4.

Table 4. Comparison of the proposed Cr(III) ion electrode and the some previously reports.

Ionophore	Slope	Linear range(M)	Detection limit(M)	Response time (S)	Interferences ions	Ref.
Glyoxal bis (2-hydroxyanil)	19.8	3.0×10^{-6}-1.0×10^{-2}	6.3×10^{-7}	20	Cu^{2+},Cr^{2+},Zn^{2+}, Co^{2+}	5
N- (1- thien-2-ylethylene) benzen-1,2-diamine	19.9	1.0×10^{-6}-1.0×10^{-1}	7.0×10^{-7}	12	Fe^{3+}	10
4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one	19.7	1.0×10^{-6}-1.0×10^{-1}	5.8×10^{-7}	10	La^{3+},Ce^{3+},Al^{3+}	11
2-acetylpyridine and nanoporous silica gel	19.8	1.0×10^{-8}-1.0×10^{-3}	8.0×10^{-9}	55	Ce^{3+},Pb^{2+},Ni^{2+}	13
5-amino-1-phenyl-1H-pyrazole-4-carboxamide	19.6	1.0×10^{-6}-1.0×10^{-1}	5.3×10^{-7}	10	Fe^{3+}, Al^{3+}, La^{3+}	19
1-[(2- hydroxy ethyl) amino]-4-methyl-9H-thioxanthen-9-one	20.5	3.2×10^{-7}-1.0×10^{-1}	1.6×10^{-7}	8	Zn^{2+} Ni^{2+}	20
4-(5-bromothiophen-2-carboxylidene amino)-3-methyl-5-mercapto-s-triazole	19.8	2.0×10^{-7}-1.0×10^{-1}	9×10^{-8}	10-15	---	43
1-(2-(1H-imidazole-1-yl)-1-(4-methoxyphenyl)ethylidene)-2-phenyl hydrazine	19.6	8.4×10^{-8}-1.0×10^{-2}	6.8×10^{-8}	10	---	44
This work	19.7	8.0×10^{-6}-1.0×10^{-1}	7.0×10^{-6}	5	---	---

As is obvious, the results clearly indicate that in linearity range and detection limit, proposed sensor is not superior but is closed to the most previously reports. But the proposed sensor is superior to the previously reported ones in response time and selectivity coefficients. It has the shortest response time (5 s) between them and its selectivity toward the Cr (III) ions is not influenced by the presence of the common transition and heavy metal ions. However, there are some interference ions in many of previously reports [5, 10, 11, 13, 19, 20].

Conclusion

The results obtained from the above mentioned study revealed that N-(2H-[1,2,4] thiadiazolo[2,3-a]pyridine-2-ylidene) benzamide can be used as a selective sensing element in construction of a liquid membrane sensor for measurement of chromium ions in the presence of considerable concentrations of common interfering ions. Applicable pH range, fast response time, low detection limit, and potentiometric selectivity coefficients of the proposed sensor make it a very good device used for the determinations of Cr (III) ions. The proposed electrode was be applied successfully for the direct determination of Cr (III) ions in tea and cocoa powder samples.

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