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Cobalt(II) selective membrane electrode based on palladium(II) dichloro acetylthiophene fenchone azine

I.M. Isa [a,*], S. Mustafar [a], M. Ahmad [a], N. Hashim [a], S.A. Ghani [b]

[a] *Chemistry Department, Faculty of Science and Mathematics, Sultan Idris Education University, 35900 Tg. Malim, Perak, Malaysia*
[b] *Mathematics Department, Faculty of Science and Mathematics, Sultan Idris Education University, 35900 Tg. Malim, Perak, Malaysia*

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ABSTRACT

A new cobalt(II) ion selective electrode based on palladium(II) dichloro acetylthiophene fenchone azine(**I**) has been developed. The best membrane composition is found to be 10:60:10:21.1 (**I**)/PVC/NaTPB/DOP (w/w). The electrode exhibits a Nerstian response in the range of 1.0×10^{-1}–1.0×10^{-6} M with a detection limit and slope of 8.0×10^{-7} M and 29.6 ± 0.2 mV per decade respectively. The response time is within the range of 20–25 s and can be used for a period of up to 4 months. The electrode developed reveals good selectivity for cobalt(II) and could be used in pH range of 3–7. The electrode has been successfully used in the determination of cobalt(II) in water samples.

1. Introduction

Determination of cobalt assumes importance because of its widespread occurrence in air, water, animals and plants [1]. Cobalt is both a toxic and essential element. In the form of Vitamin B12, cobalt is an essential component of the human diet and established treatment for anaemia [2] while long term exposure of cobalt may increase occurrence of lung cancer [3]. In the field of metallacarborane chemistry, cobalt(III) ion has been inserted into carborane anions in solution to prepare cobaltabisdicarbollide [4]. Cobaltabisdicarbollide has been used as a model compound in the development of radiotransition-metal carriers for the antibody-mediated y-imaging and P-therapy of tumour [5], development of ion-selective PVC membrane electrode for tuberculosis drug analysis [6] and also in preparing membrane for enantiomer recognition with no chiral additives [7]. A number of methods such as spectrophotometric [8–14], atomic absorption spectrometry [15–21] and voltammetric [22–25] have been reported for the determination of cobalt. Most of the methods are time consuming, involving sample manipulation, relatively expensive and require large infrastructure back up. Ion-sensors provide analytical procedures that overcome the above drawbacks since they are fast, convenient and require no sample pretreatment and also suitable for online analysis [26]. However, literature survey reveals that very little work has been done on the development of ion-selective electrodes for cobalt(II) ions [27–41] and several number of sensor materials such Schiff base [27,28], chelates [35], macrocycles [29–41], mercapto compounds [35] and variety of other ligands [36,37] have been used for the past years. Most of these ion-selective electrodes have been suffering from near or non-Nernstian response, short working concentration range and significant interferences from various ions. In this study, new palladium(II) dichloro acetylthiophene fenchone azine (Fig. 1) was used as an excellent ionophore in a plasticised PVC matrix. The chemical and structural features of the complex can be recognized by incorporating different soft donor in the chelating ring. This promotes the stabilization of both low and high oxidation state of the metal and forces the metal ion to adopt typical coordination geometry. The presence of hard N-donor atoms and excellent π-acceptors has a marked influence on the coordinating geometry of different metal ions [42]. Thus, the ionophore has been used as a suitable neutral carrier in constructing membrane selective electrode for metal cations.

2. Experimental

2.1. Chemicals and reagents

Reagent grade of high-molecular weight poly (vinyl chloride) (PVC), dioctylphthalate (DOP), tetraethyl methylenediphosphonate (TMDP), fenchone hidrazone monohydrate, sodium chloride,

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* Corresponding author. Tel.: +60 5 4506431; fax: +60 5 4583616.
E-mail address: illyas@upsi.edu.my (I.M. Isa).

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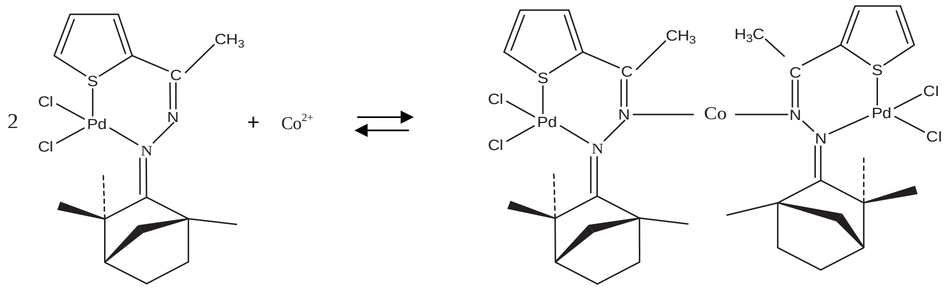

Fig. 1. Possible mechanism for potentiometric response.

sodium acetate, 2-asetiltiophene and sodium tetraphenyl borate (NaTPB) were obtained from Fluka (Switzerland). Tetrahydrofuran (THF), glacial acetic acid, ethanol, benzonitrile and dichloromethane were obtained from Merck (Germany). All solutions were prepared using distilled deionised water from Barnstead EasyPure LF, (USA). The pH adjustments were made with dilute hydrochloric acid and sodium hydroxide solution that were received from Fluka (Switzerland). A stock solution of cobalt(II) was freshly prepared by dissolving appropriate amount of analytical grade cobalt(II) chloride-6-hidrate in distilled deionised water. Cobalt(II) chloride-6-hidrate and all analytical grade chloride salts of all cations were obtained from Merck (Germany).

2.2. Instrumentation

Potential measurements were carried out using pH/ion meter Orion 720A (Mass., USA). A Ag|AgCl electrode of BASi, MF-2052 (USA) with a fiber junction was used as a reference electrode. The pH values were determined by using glass electrode Orion 915600 (Mass., USA). The Fourier transform infrared (FTIR) spectrometer model Thermo Nicolet 6700 using ATR diamond was used to characterize the membrane and a Perkin Elmer, Analyst 400 atomic absorption spectrophotometer with air acetylene flame was used at 240.13 nm to analyze cobalt(II) in real samples.

2.3. Synthesis of ionophore

Palladium(II) dichloro acetylthiophene fenchone azine (**I**) was synthesized in the laboratory of the Department of Chemistry, Universiti Pendidikan Sultan Idris using procedures developed by Ahmad et al. [43]. The following procedure was used to couple $PdCl_2$ $(NCPh)_2$ through a –C=N– group. The $PdCl_2$ $(NCPh)_2$ (0.20 g, 0.5 mmol) was mixed with ligand acetylthiophene fenchone azine (0.15 g, 0.5 mmol) and liquefied in chloroform. The mixture was left for the next 24 h and the solvent was distilled out thoroughly. The infrared spectrum showed a band at 1645 cm^{-1} which characterized of νC=N.

2.4. Electrode preparation

Membrane solutions were prepared by dissolving varying amounts of ionophore, powdered PVC and NaTPB that acted as anion excluder in THF. Plasticisers were added to produce membranes of different composition. The mixture was vigorously stirred and air bubbles were removed. When the solution became homogeneous, it was transferred into a glass ring (3.5 cm i.d.) resting on a smooth glass plate. The glass ring was covered with a filter paper and left overnight to allow slow evaporation of the solvent at room temperature. The transparent membranes were detached from the surface of glass plate, cut to suitable size and glued to one end of a Pyrex® glass tube with Araldite®. The glass tube was then filled with an internal filling solution (1.0×10^{-1} M $CoCl_2$). The prepared membrane was equilibrated for 72 h in 1.0 M cobalt(II) chloride solution [38]. A number of such membranes were designated and those which generate stable potentials and exhibited satisfactory responses with regard to working concentration range and slope were selected for further investigation.

2.5. Potential measurements

The potentials were measured by varying the concentration of cobalt(II) chloride in the solution over the range 1.0×10^{-7}–1.0×10^{-1} M. The potential measurements were carried out at 25.0 ± 0.1 °C by using the Ag|AgCl electrode as the reference electrode with the following assembly:

Pt|Co(0.1 M)|PVC membrane|sampel||KCl (3.0 M)|AgCl|Ag

3. Results and discussion

3.1. Performance characteristics, working concentration range and slope

Fenchone has been used widely as chiral auxiliaries to prepare chiral ligand. The existence of nitrogen atoms in the structure of ionophore make the cobalt(II) ion possible to form interaction with the ionophore through a lone pair of electron to one of the nitrogen atom. The possible mechanism that is responsible for the potentiometric response is shown in Fig. 1. Several membranes of different compositions were prepared and investigated. The potential responses of various ISEs based on palladium(II) dichloro acetylthiophene fenchone azine (**I**) were obtained. To investigate the suitability of (I) as an ion carrier in PVC membranes, the preliminary experiments of various ion-selective electrode (ISEs) based on (I) (with the same composition) for a variety of metal ions were obtained separately and is shown in Fig. 2. As it can be seen, among the different cations tested, the membrane responds to cobalt(II) best in terms of wide working concentration range and slope. This is probably due to both selective behaviour of the ionophore with cobalt(II) ions, in comparison to other metal ions, and rapid change kinetics of the resulting palladium(II) dichloro acetylthiophene fenchone azine–cobalt(II) ion complex [44].

The working concentration range, slope of the calibration plot, sensitivity and selectivity obtained for a given ionophore depend significantly on the membrane composition and the nature of plasticisers. The effects of the membrane composition, nature and amount of plasticiser, quantity of additives on the potential response of the cobalt(II) ion-selective electrodes were investigated and summarized in Table 1. Different plasticisers such as DOP and TMDP and sodium tetraphenyl borate (NaTPB) as anion excluder were added in order to improve the performance of the sensors. The improvement in the performance was attempted by the addition of plasticiser to the membranes. The addition of plasticisers not only improves the workability of the membranes but also

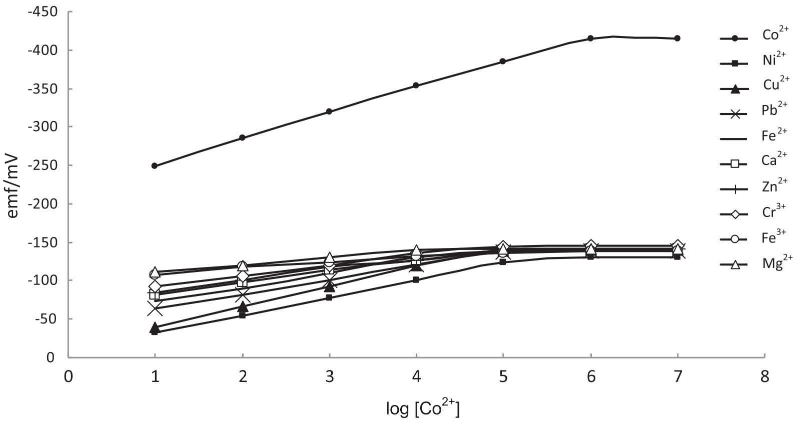

Fig. 2. Potential response of ion-selective electrode based on (I) for various metal ions.

Table 1
Optimized membrane composition and their potential response.

Sensor number	Ionophore (mg)	PVC (mg)	Plasticiser (mg)	Additives; NaTPB (mg)	Working range (M)	Slope ± 0.2 (mV/decade)	Response time (s)
1	6	72	Without	Without	1.0×10^{-1}–1.0×10^{-5}	25.2	30–40
2	6	72	14.1 (TMDP)	5	1.0×10^{-1}–1.0×10^{-4}	37.0	20–25
3	6	72	42.4 (DOP)	5	1.0×10^{-1}–1.0×10^{-5}	29.0	20–25
4	10	60	21.1 (DOP)	10	1.0×10^{-1}–1.0×10^{-6}	29.6	20–25
5	10	80	14.1 (DOP)	10	1.0×10^{-1}–1.0×10^{-4}	30.2	20–25

contributes significantly towards the improvement in the working concentration range, stability and shelf life of the sensor [45]. Membrane no.4 exhibited a wide working concentration range of 1.0×10^{-1}–1.0×10^{-6} M and Nernstian slope of 29.6 mV/decade while membrane no. 1 without plasticiser and NaTPB showed linearity in the concentration range of 1.0×10^{-1}–1.0×10^{-5} M and Nernstian slope of 25.2 mV/decade (Fig. 3). The limit of detection for membrane no. 1 and membrane no. 2 were calculated, as recommended by IUPAC from the intersection of two extrapolated segments of the calibration curve, to be 8.9×10^{-6} M and 3.2×10^{-5} M, respectively. The membrane no. 3 and no. 5 with DOP as plasticiser also performed well with a working concentration range of between 1.0×10^{-1}–1.0×10^{-5} M (with detection limit of 7.9×10^{-6} M) and 1.0×10^{-1}–1.0×10^{-4} M (with detection limit of 7.1×10^{-5} M) respectively. Meanwhile, the Nernstian slopes were found to be 29.0 mV/decade and 30.2 mV/decade respectively. Membrane no. 4 was chosen for further electroanalytical investigation. The sensing behaviour of the membranes did not change, when potentials were recorded from lower to higher concentrations or vice versa. The deviation for the slope value was found to be ±0.2 mV, which showed good reproducibility.

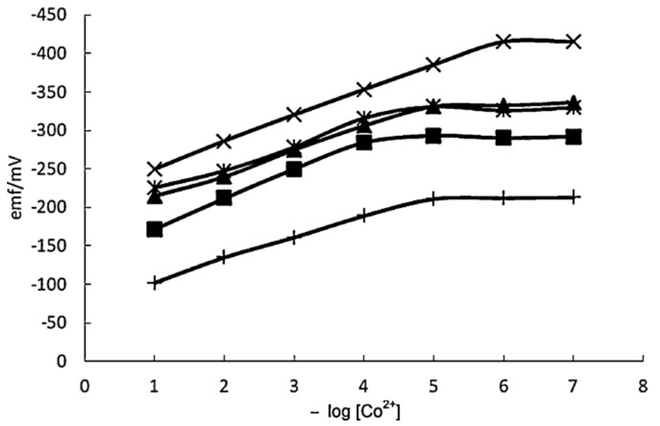

Fig. 3. Potential response of cobalt(II) ion selective electrode based on palladium(II) dichloro acetylthiophene fenchone azine (membrane no.: 1 [+], 2 [*], 3 [▲], 4 [×], 5 [■]).

3.2. *Response time and lifetime*

The response time was measured by recording the potential response of the electrode as a function of time. The electrode was usually first dipped in the lowest concentration, 1.0×10^{-5} M Co (II) and immediately shifted to another solution (1.0×10^{-4} M). The potential response of the Co (II) solution was read as zero second that was, just after the immediate dipping of the electrode in the second solution and subsequently recorded at the intervals of 5 s. The time during which the potential response attained a constant value represented the response time of the electrode. The membrane without plasticiser and NaTPB (No. 1) showed a response time of 30–40 s which was reduced to 20–25 s when the NaTPB and plasticisers were added (Table 1). The main factor for the limited lifetime is the loss of one or more of its components, while contacting with aqueous solution. Palladium(II) dichloro acetylthiophene fenchone azine(**I**) that is used as ionophore has sufficient lipophilicity to prevent leaching of the membrane matrix into the aqueous solution surrounding the membrane electrode compared to ligand itself. Sufficient lipophilicity of ionophore and plasticiser will ensure stable potentials and long lifetimes [45,46]. The membranes electrode could be used for at least 4 months without any significant changes in the potentials. During usage, they were stored in 0.1 M cobalt(II) solution and re-equilibrated with 1.0 M cobalt(II) solution whenever any drift in the potentials was observed. The result indicated that a longer life and stable electrode could be obtained.

3.3. *pH effect on the electrode response*

To study closely the effect of pH on membrane no. 4, the potentials were measured over the pH range of 3.0–10.0 at cobalt(II) ions concentration of 1.0×10^{-3} M as shown in Fig. 4. The pH of the solutions was adjusted by adding either HCl or NaOH. It was clear that the useful range were between 3.0 and 7.0 because the potential remained constant in this range. The sharp change in potential at

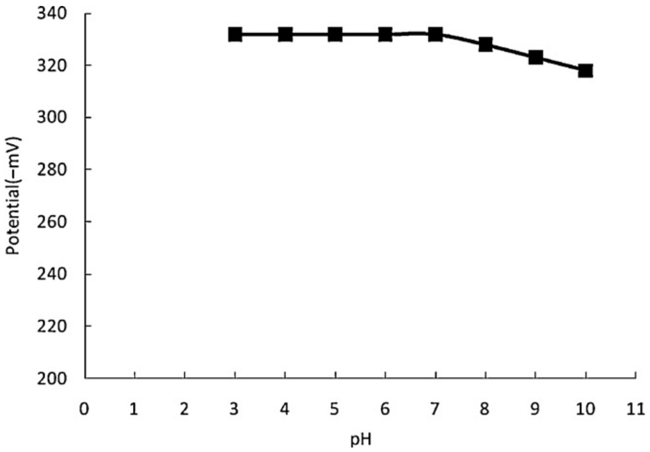

Fig. 4. Effect of pH on potential: $[Co^{2+}] = 1.0 \times 10^{-3}$ M for membrane no. 4.

higher pH values may be due to the formation of some hydroxyl complexes of cobalt(II) ions, while at lower pH values hydronium ions start to contribute to the charge transport process by the membrane thereby causing interference [28].

3.4. Potentiometric selectivity

The potentiometric selectivity coefficient, $K^{pot}_{M,N}$ is perhaps the most important characteristics of an ion selective electrode. The proposed electrode is reliable if values of $K^{pot}_{M,N}$ are less than one [47]. The selectivity of potentiometric electrodes proposed was determined by fixed interference method (FIM) [48]. In FIM, the potentials were measured in a series of varying cobalt(II) ion (1.0×10^{-1}–1.0×10^{-7} M) and fixed interfering ions concentration (1.0×10^{-2} M). In all experiments, the potential response was done at an optimum pH, i.e. pH 4.5. The selectivity of the membrane towards cobalt(II) in the presence of interfering ion was obtained by plotting electromotive force (emf) values versus the logarithm of the cobalt(II) ion concentration. The intersection of the extrapolated linear portions of this plot indicated the value of concentration of cobalt(II) ions and was then used to calculate selectivity coefficient by Nicolsky–Eisenman equation. The resulting values of the selectivity coefficients are summarized in Table 2. It is shown that the selectivity coefficient for different interfering cations are sufficiently smaller than 1.0, indicating that the present sensor is significantly selective to cobalt(II) ions over other ions. In Table 3, the response characteristics of the proposed membrane sensor are compared with those of cobalt(II) ion-selective electrode reported before. It is obvious that the proposed cobalt(II) ion-selective electrode is comparable with other works done before.

Table 2
Selectivity coefficient values for cobalt(II) selective membrane electrode (membrane no. 4) for several interference cations.

Interfering ion	Selectivity coefficient
Fe^{2+}	1.2×10^{-2}
Zn^{2+}	1.0×10^{-2}
Ca^{2+}	7.9×10^{-2}
Fe^{3+}	2.5×10^{-2}
K^{+}	7.9×10^{-2}
Mg^{2+}	7.9×10^{-2}
NH_4^{+}	6.3×10^{-2}
Cu^{2+}	1.9×10^{-2}
Ni^{2+}	6.6×10^{-2}
Cr^{3+}	3.9×10^{-3}
Pb^{2+}	3.9×10^{-3}

Table 3
Comparison of the proposed Co^{2+} selective electrode with the reported electrodes.

Reference number	Ionophore	Concentration range (M)	Detection limit (M)	Slope (mV/decade of activity)	pH range	Response time (s)	Life time
[27]	5-((4-Nitrophenyl)azo)-N-(2′,4′-dimethoxylphenyl)salicylaldimine	9.0×10^{-7}–1.0×10^{-2}	8.0×10^{-7}	29 ± 1	3.5–6.0	5–10	1
[29]	9-t-Butyl-3,9,15,21-tetraaza-4,5,13,14-dibenzo-6,12-dioxabicyclo[15.3.1]henicosa-1(21),17,19-triene-2,16-dione	2.0×10^{-6}–1.0×10^{-2}	6.0×10^{-7}	29.0	3.0–8.0	10–15	2
[30]	2,3,4-Pyridine-1,3,5,8,11,14-hexaazacyclohexadeca-2-ene	6.3×10^{-6}–1.0×10^{-1}	8.5×10^{-7}	30.0	2.5–6.5	15	4
[32]	1-(2-Oxocyclohexyl)-1,2-cyclohexanediol	1.0×10^{-1}–1.0×10^{-6}	9.0×10^{-7}	29.8	3.5–8.0	25	2
This work	Palladium(II) dichloro acetylthiophene fenchone azine	1.0×10^{-1}–1.0×10^{-6}	8.0×10^{-7}	29.6 ± 0.2	3.0–7.0	20–25	4

Table 4
Comparison of results of the membrane electrode no. 4 and atomic absorption spectrophotometer (AAS) method for determination of Co(II) in water samples.

Method	Sample no.	
	1	2
Membrane electrode (ppm)	2.45 ± 0.03	5.72 ± 0.03
AAS (ppm)	2.33 ± 0.03	5.68 ± 0.03

3.5. Analytical application

The proposed cobalt(II)-ion selective electrode was found to work well under laboratory conditions. The electrode was also successfully applied directly into the different lakes in Perak in determining the presence of cobalt in the lakes' water and the results obtained from the proposed method were in good agreement ($R^2 = 0.9984$) with those obtained by atomic absorption spectrophotometer (Table 4).

4. Conclusions

Throughout the inquisition of various membranes compositions, it was shown that membrane with chiral palladium(II) dichloro acetylthiophene fenchone azine complex (**I**) gave the best performance in terms of reproducibility and other sensor characteristics such as good selectivity, broad working range, wide pH range and reasonable shelf life. Its performance was compared with reported electrodes (Table 3). Hence, the complex (**I**) can be used as new ionophore in the development of PVC-based cobalt ion-selective electrode.

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