

A New Copper Ionophore N^1, N^3 -Bis [[3,5-Bis(Trifluoromethyl)Phenyl] Carbamothioyl] Isophthalamide for Potentiometric Sensor (Ionofor Kuprum Baru N^1, N^3 -Bis [[3,5-Bis(Trifluorometil)Fenil]-Karbamotioil] Isoftalamida sebagai Sensor Potensiometri)

KOOK SHIH YING, LEE YOOK HENG*, NURUL IZZATY HASSAN & SITI AISHAH HASBULLAH

ABSTRACT

*A copper ion sensor based on a new bis-thiourea compound N^1, N^3 -bis[[3,5-bis(trifluoromethyl)phenyl]carbamothioyl] isophthalamide (or TPC) as neutral carrier was investigated. The immobilization of the TPC into poly(*n*-butyl acrylate) (pBA) membrane via drop casting and the sensor was characterized by potentiometry. The sensor fabricated from TPC only showed a good Nernstian response towards copper ion with a sensitivity slope of 28.81 ± 0.53 mV/decade in the range of 1.0×10^{-6} - 1.0×10^{-4} M. The limit of detection of this sensor was found to be 6.11×10^{-7} M and with short sensor response time (60 - 80 s). This sensor also demonstrated reversibility and reproducibility with 3.69% and 1.84% (Relative Standard Deviation, RSD), respectively. Based on the separate solution method (SSM), the logarithm selectivity coefficients were better than -2.00 for monovalent, divalent and trivalent cations and this confirmed that the sensor exhibited good selectivity towards copper ion. The sensor could attain optimum function without the need in the inclusion of either lipophilic anions as a membrane additive nor plasticizer as a membrane softener. Thus, these are the main advantages. The addition of lipophilic anions into the pBA membrane could cause the sensitivity and selectivity of the copper ion sensor based on ionophore TPC to deteriorate.*

Keywords: Anionic lipophilic salt; neutral carrier; N^1, N^3 -bis[[3,5-bis(trifluoromethyl)phenyl]carbamothioyl] isophthalamide (TPC); potentiometric copper ion sensor

ABSTRAK

*Sensor ion kuprum yang berasaskan kepada sebatian bis-tiourea baru, N^1, N^3 -bis[[3,5-bis(trifluorometil)fenil] karbamotioil]isofthalamida (TPC) sebagai pembawa neutral telah dikaji. Pencirian sensor dijalankan melalui kaedah potensiometri dan TPC dipegunkan ke dalam membran poli(*n*-butil akrilat) (pBA) secara penyalutan. Sensor ion yang direka bentuk dengan menggunakan TPC sahaja menunjukkan rangsangan Nernstian, iaitu 28.81 ± 0.53 mV/dekad dengan julat kelinearan daripada 1.0×10^{-6} - 1.0×10^{-4} M. Had pengesanan adalah serendah 6.11×10^{-7} M dan masa rangsangan ialah 60 hingga 80 saat. Nilai sisihan piawai relatif bagi ujian kebolehbalikan dan kebolehasilan sensor ini masing-masing ialah 3.69% dan 1.84%. Berdasarkan kepada kaedah larutan berasingan (SSM), nilai pekali logaritma kepilihan bagi sensor ini adalah lebih baik daripada -2.00 bagi kation monovalen, divalen dan trivalen seterusnya memaparkan kepilihan yang baik terhadap ion kuprum. Kebaikan sensor ini adalah bahan penambahan membran seperti anion lipofilik dan pelembut membran seperti pemplastik tidak diperlukan untuk mencapai fungsi sensor yang optimum. Sebaliknya, penambahan anion lipofilik dalam membran pBA boleh menjejaskan kepekaan dan kepilihan sensor ion kuprum berasaskan ionofor TPC.*

Kata kunci: Garam anion lipofilik; kuprum ion sensor potensiometri; N^1, N^3 -bis[[3,5-bis(trifluorometil)fenil]karbamotioil] isofthalamida (TPC); pembawa neutral

INTRODUCTION

Since 1930s, potentiometric membrane sensors have been found to possess wide applications in various fields (Faridbod et al. 2008). They had been used frequently in the monitoring of environmental pollution, quality control in the industrial process, clinical analysis and biochemical analysis due to their advantages of simple construction, relatively fast response, wide linear range, reasonable selectivity and can be utilized for direct measurement of a wide variety of ions in complex samples (Ghaneimotlagh et al. 2014; Kopylovich et al. 2011; Perez-Marín

et al. 2000; Siswanta et al. 2016). This type of membrane sensor has been designed based on molecular recognition, consist an incorporated carrier or ionophore within the membrane that could strongly recognize the target ion in the presence of other interference ions (Kopylovich et al. 2011). In general, for an ionophore that has cationic recognition, it is much dependence on the nature of the chemical bond that is formed between the ionophore and the target cation. Thus, the ionophore should contain some donor atoms such as oxygen, nitrogen or sulfur and arrange in a suitable molecular structure that could bind

coordinatively to a metal ion (Ghanei-motlagh et al. 2014; Siswanta et al. 2016).

Compounds with the (>N-C(S)-N<) functionality are thioureas. There are mono-, di-, tri- or tetra-substituted thiourea derivatives depending upon the extent of substitution on the nitrogen atoms. The presence of a carbonyl group bonded to the thiourea core is known as 1-(acyl/aroil)-substitution. This substitution can occur on the second nitrogen atom, giving 1-(acyl/aroil)-3-(mono-substituted) or 1-(acyl/aroil)-3,3-(di-substituted) thioureas, with general formula $R^1C(O)N(\text{R}_1)HC(S)N(\text{R}_2)R^2R^3$, where R may be an alkyl, aryl, aralkyl or heterocyclic substituent. These compounds offer a huge bonding potential as ligand since both carbonyl (C=O) and thiocarbonyl (C=S) groups can coordinate with some metal ions such as Pd(II), Ag(I), Cd(II), Hg(II), Pb(II), Ni(II) or Cu(II) using both oxygen and sulfur atoms (Saeed et al. 2014). These unique properties of thioureas also fostered the application of thioureas as ionophore in the chemical sensor field (Jumal et al. 2012). Thioureas with different coordination sites in specific geometry and with different chemical structure flexibilities can influence significantly the selectivity towards different metals that lead to the selectivity of an ionophore towards a particular cation (Wilson et al. 2010).

In the past, most of the thioureas have been successfully applied as ionophores for heavy metals in ion selective electrode. Heavy metals such as cadmium, lead, copper and mercury are considered toxic due to their persistency and bioaccumulation behaviour in natural environment. Long terms exposure of these heavy metals can cause serious effects on human physiology and biological systems (Khan et al. 2017; Sajab et al. 2017). Therefore, heavy metals determination is important and a simple but efficient method such as potentiometric sensor is needed. Many thiourea compounds have been successfully used as ionophores for mercury ion-selective electrode. Hg(II) ion sensor based on 1,2-bis-(N'-benzoylthioureido)cyclohexane (Jumal et al. 2012), 4,4'-bis-(3-phenylthiourea)-diphenylmethane and 2-2-[10-[(E)-2-(aminocarbothioyl)hydrazono]-1,4-dihydroxy-9(10H)-anthracenyliden]-1-hydrazinecarbothioamide (Ghanei-motlagh et al. 2014), 1-diethyl-3-(4-methoxybenzoyl) thiourea (DMBT), 4-methoxy-N-(1-pyrrolidine carbonothioyl) benzamide (MPCB) and

4-methoxy-N-(piperidine-1-carbonothioyl) benzamide (MPyCB) (Khairi 2016) have been reported and showed good analytical performances. Besides, a Cd(II) ion sensor based on 1-furoyl-3-benzyl-3-phenylthiourea was also reported and showed a good Nernstian response towards cadmium ion (Lazo et al. 2006). In 2010, a Cu(II) ion sensor based on 1-furoyl-3,3-diethylthiourea and Pb(II) ion sensors based 1,3-bis(N'-benzoyl-thioureido)benzene (BTB) and 1,3-bis(N'-furoylthioureido)benzene (FTB) were reported (Motlagh et al. 2010; Pérez et al. 2010; Wilson et al. 2010). The Cu(II) and Pb(II) ion sensors showed good sensitivity, however, the Cu(II) ion sensor exhibited major interference from common ions such as zinc, sodium and potassium. Thus, a good potentiometric copper (II) ion sensor based on thiourea derivative has not yet been sufficiently explored and this has driven the interest to investigate new thioureas as ionophores in the preparation of copper ion sensors.

In this work, a new bis-thiourea, N¹,N³-bis[[3,5-bis(trifluoromethyl)phenyl]carbamothioyl]isophthalamide (TPC) (Figure 1(a)) was used to develop a copper ion sensor. This thiourea derivative is considered as a type of 1-(acyl/aroil)-3-(mono-substituted) thiourea with carbonyl (C=O) and thiocarbonyl group (C=S) as the donor sites. In general, the performance of a potentiometric ion selective electrode based on electrically charged and neutral ionophore are highly influenced by the presence of ionic sites in the membrane. The ionic sites are not only important for a good Nernstian response, but also beneficial in improving the selectivity (Amemiya et al. 2000). TPC is a neutral ionophore, thus the study of the ionic site effects is necessary. Therefore the effects of addition of different ratios of a lipophilic anion, i.e. NaTFPB (Figure 1(b)) and TPC in the membrane pBA for obtaining the best copper ion sensor was also evaluated in detail.

In addition, poly(n-butyl acrylate) (pBA) membrane was chosen as immobilization matrix instead of common membrane, poly(vinyl chloride) (PVC) in ion selective electrode. This is due to pBA membrane is photocurable, does not need any external plasticizer, fast and simple formation, excellent adhesion on solid surface with lower glass transition temperature value, T_g (Alva et al. 2005; Kook & Lee 2017; Lee & Hall 2001). Thus, it is well suitable for the application in solid state ion sensor. For

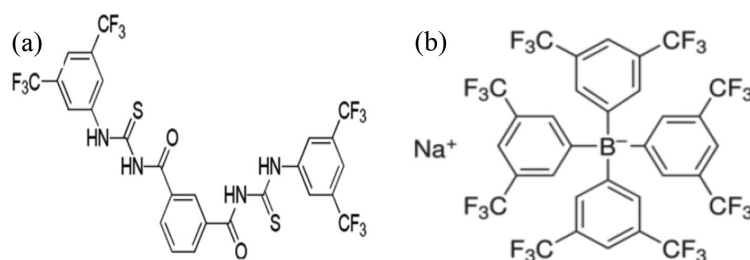


FIGURE 1. (a) N¹,N³-bis[[3,5-bis(trifluoromethyl)phenyl]carbamothioyl]isophthalamide (TPC)
(b) Anion lipophilic salt sodium tetrakis [3,5-bis(trifluoromethyl) phenyl] borate (NaTFPB)

the immobilization, the ionophore TPC was immobilized into the pBA membrane via drop coating to avoid any contamination or failure of membrane formation during the fabrication of the copper ion sensor.

MATERIALS & METHODS

MATERIALS

Chemicals used in this study included n-butyl acrylate (nBA), 2,2-dimethoxy-2-phenylacetophenone (DMPP), 1,6-hexanediol diacrylate (HDDA), 2-hydroxyethyl metacrylate (HEMA), sodium tetrakis [3,5-bis(trifluoromethyl) phenyl] borate (NaTFPB), Tris-HCl, copper (II) chloride dihydrate, sodium chloride, calcium chloride and potassium chloride (Sigma Aldrich), mercury chloride (Fisher), cadmium chloride, aluminium chloride, lead nitrate, lithium acetate dihydrate and tetrahydrofuran (THF) (Acros), zinc chloride and nickel chloride hexahydrate (Merck), iron(III) chloride (R&M Chemicals) and magnesium nitrate (Bendosan). All chemicals are analytical grade and used as obtained. Ionophore TPC was synthesized and purified from Chemical and Biosensor Research Group, UKM (Nurulain et al. 2016). Deionized water (specific resistance, $18.0\text{M}\Omega\cdot\text{cm}$) was used for solution preparation and cleaning glassware.

INSTRUMENTS

The potentiometric measurements were performed by using an Orion Versa Star Advanced Electrochemistry Meter. A double junction Ag/AgCl was used as the reference electrode with 0.1 M Tris HCl buffer at pH7.00 saturated with AgCl as internal reference solution and 0.1 M lithium acetate dihydrate as gel bridge electrolyte. The working electrode was an Ag/AgCl screen-printed electrode (Sprint Print Sdn. Bhd. Malaysia). An ultraviolet (UV) exposure unit (R.S.Ltd) were used during the photopolymerization of acrylate membrane. The UV exposure unit was installed with four light tubes transmitting UV light at the wavelength of 350 nm.

COPPER ION SENSOR FABRICATION

The sensor fabrication and photocuring technique were constructed according to the method reported previously (Jumal et al. 2012; Kook & Lee 2017) with minor modification. A monomer mixture (0.1 μL) consisted of 98.0 wt. % HEMA and 1.6 wt. % of photoinitiator, DMPP was dropped onto the tip of Ag/AgCl screen printed electrode. The mixture was photopolymerized in the UV-exposure unit for 180 s under constant flow of nitrogen gas. The polymer film (pHEMA) formed was then hydrated with 0.01 M of copper (II) chloride dihydrate solution for 15 min to form the 'inner solution' of the sensor. Another stock solution of nBA, was prepared by mixing 95.5 wt. % nBA with 0.1 wt. % of cross linker, HDDA. 100 μL of the stock solution was added to the eppendorf tube consisted of 1 mg of DMPP. An amount of 2 μL of the mixture was then dropped onto the pHEMA-SPE. The same photocure procedure was carried out for for 360 s. Finally, a required amounts of lipophilic salt, NaTFPB and ionophore, TPC was prepared as Table 1 and dissolved in 100 μL of THF. 2 μL of the stock solution (2 portions, 1 μL each) was dropped onto pBA-pHEMA-SPE, it was left overnight at room temperature to allow the evaporation of THF. This design of pBA-pHEMA-Ag/AgCl screen printed electrode (Figure 2) is similar to that reported by Alva (2008) and Kook & Lee (2017).

EVALUATION OF THE RESPONSE OF THE COPPER ION SENSOR

Copper ion sensor response was evaluated with an Orion Versa Star Advanced Electrochemistry Meter connected to reference electrode and copper ion sensor. Copper ion sensor was measured with the standard solution of copper (II) chloride dihydrate in the range of 10^{-8} to 10^{-1} M. The potential difference (emf) in mV unit for the two electrodes was recorded when a stable reading was reached. The graph emf versus logarithm of analyte concentration was plotted and the slope of the graph was determined.

EFFECT OF NATFPB ANION LIPOPHILIC SALT ON THE SENSITIVITY OF COPPER ION SENSOR

To evaluate the sensitivity behavior, the copper ion sensor with varying compositions of pBA membranes (Table 1)

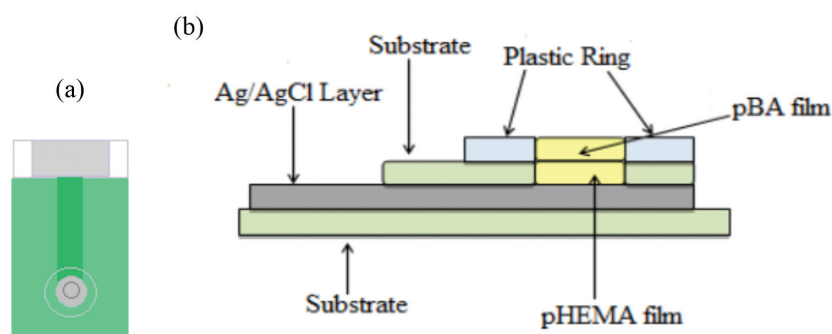


FIGURE 2. (a) Ag/AgCl screen-printed electrode and (b) the design of pBA-pHEMA-Ag/AgCl screen-printed electrode

TABLE 1. Different Compositions of pBA membrane

Sensor No.	TPC (Number of mole)	NaTFPB (Number of mole)	TPC:NaTFPB (Mole ratio)
1a	6.23×10^{-6}	0.89×10^{-6}	3.5:0.5
1b	-	0.89×10^{-6}	0.0:0.5
2a	6.23×10^{-6}	1.78×10^{-6}	3.5:1.0
2b	-	1.78×10^{-6}	0.0:1.0
3a	-	-	0.0:0.0
3b	6.23×10^{-6}	-	3.5:0.0

were measured three times in a reversible manner with the solution of copper (II) chloride dihydrate, calcium chloride, potassium chloride, lead nitrate and aluminium chloride in the range of 10^{-8} M to 10^{-1} M. For comparison purpose, sensor without the immobilized ionophore TPC for each membrane composition was also fabricated. For each membrane composition, the slope of the graph emf versus logarithm of each analyte concentration was determined.

REVERSIBILITY, REPRODUCIBILITY AND DETECTION LIMIT

For the reversibility, the sensor was measured with the same electrode from 10^{-8} to 10^{-1} M, followed by 10^{-1} to 10^{-8} M and finally 10^{-8} to 10^{-1} M whereas for reproducibility, the sensor was studied based on three different batches of electrodes. The limit of detection of the sensor was determined as recommended by IUPAC. It was calculated from the intersection of the two extrapolated segments of the calibration curve (Buck & Lindner 1994).

RESPONSE TIME

The response time of copper ion sensor was investigated in standard solutions copper (II) chloride dihydrate in the range from 10^{-8} till 10^{-1} M. The response time was the time taken when the copper ion sensor and the reference electrode were brought into contact with the solution of copper (II) chloride dihydrate until a stable reading was obtained for several minutes.

INTERFERENCE STUDIES

The selectivity behavior of the ion sensor was determined by separate solution method (SSM) with 0.1 M of interference ions NaCl, KCl, CaCl₂, NiCl₂, ZnCl₂, HgCl₂, CdCl₂, Mg(NO₃)₂, Pb(NO₃)₂, AlCl₃ and FeCl₃ (Umezawa et al. 2000). Triplicate measurements were done for each interference ion and the average value was taken to determine the logarithm selectivity coefficient of the sensor.

RESULTS AND DISCUSSION

EFFECT OF NATFPB ANION LIPOPHILIC SALT ON THE SENSITIVITY OF THE COPPER ION SENSOR

Sodium tetrakis [3,5-bis(trifluoromethyl) phenyl] borate, NaTFPB lipophilic salt (Figure 1(b)) was incorporated into pBA membrane phase to create an anionic site. Anionic site is important for a cation selective sensor to have better sensitivity and shorter response time. However, the selectivity of a sensor can decrease when too much of anionic sites present inside the membrane because this anionic salts will control over the cation exchange reaction and causes the ionophore losses its functionality (Yew & Lee 2014). Thus, the determination of the optimum composition of lipophilic salt NaTFPB and ionophore TPC inside the pBA membrane is vital due to their significant effects in sensitivity and selectivity (Lee & Hall 1996).

The sensitivity of a potentiometric ion sensor is based on a Nernstian response. Nernstian response is

TABLE 2. Performance of copper ion sensors with 3.5:0.5 (Sensor 1a) and 0.0:0.5 (Sensor 1b) mole ratio of TPC : NaTFPB

Sensor No.	TPC : NaTFPB (Mole Ratio)	Metal Ions	Linear Range (M)	Slope (mV/decade)	R ²
1a	3.5 : 0.5	Cu ²⁺	$10^{-6} - 10^{-1}$	52.17±3.63	0.998
		Pb ²⁺	$10^{-5} - 10^{-1}$	46.71±1.72	0.985
		Ca ²⁺	$10^{-6} - 10^{-2}$	36.15±2.54	0.989
		Al ³⁺	$10^{-6} - 10^{-3}$	30.21±4.58	0.978
		K ⁺	$10^{-5} - 10^{-1}$	50.96±3.23	0.995
1b	0.0 : 0.5	Cu ²⁺	$10^{-5} - 10^{-1}$	52.91±2.95	0.997
		Pb ²⁺	$10^{-5} - 10^{-1}$	43.86±2.02	0.981
		Ca ²⁺	$10^{-5} - 10^{-1}$	38.15±1.90	0.999
		Al ³⁺	$10^{-6} - 10^{-1}$	32.83±0.90	0.999
		K ⁺	$10^{-5} - 10^{-1}$	56.71±3.87	0.995

demonstrated when the graph of the measured potential (emf) versus logarithm of the cation concentration is linear with a slope of 59.16 mV/decade for single charge ion, 29.58 mV/decade for double charge ion and 19.72 mV/decade for triple charge ion at 298.15 K. The response of the ion-selective electrode is according to 'local' thermodynamic equilibrium over a given range of concentration. However, Nernstian response does not imply good selectivity because interfering ions may also give Nernstian response if the sensor is also respond to them (Buck & Lindner 1994). Therefore, besides the standard copper chloride solution, screening measurements were also done in some interfering cations in selected concentration range in order to determine the sensor sensitivity. According to Figure 3 and Table 2, Sensor 1a with membrane pBA composition (3.5: 0.5) gave bad performance in terms of sensitivity. It showed super-Nernstian response towards copper ion with slope of 52.17 ± 3.63 mV/decade in the range of 10^{-6} - 10^{-1} M. In terms of selectivity, a strong interference was observed to the other interference cations, lead, aluminium, potassium and calcium as the slopes of graph were more than 10 mV/decade. When compared with the sensor fabricated with NaTFPB only (Sensor 1b), the data presented in Table 2 clearly showed that the sensor also gave a similar response. It seems rational that Sensor 1b showed non-

selective response to the five cations because cations will also interact with the anion lipophilic salt, TFPB⁻ within the membrane pBA due to charge difference. That selectivity behavior will be improved when the ionophore TPC embedded inside the membrane pBA. However, this was not observed in Sensor 1a with immobilized ionophore TPC.

Anion lipophilic salt is well-known for its advantages to reduce membrane resistance and increase the polarity of the membrane, thus improves the sensitivity through the promotion of interfacial cation-exchange reactions at the membrane-solution interface (Kook & Lee 2017; Lee & Hall 1996). Super-Nernstian response in copper ion solutions indicated the phenomena of eager incorporation of copper ions to the membrane bulk has occurred (Kisiel et al. 2015; Woźnica et al. 2011). It might due to insufficient amount of NaTFPB within the pBA membrane, caused inefficient of cation-exchange reactions and thus, insensitive and non-selective responses were obtained. Therefore, it was instructive to investigate the performance of the sensor with higher amount NaTFPB inside the membrane pBA.

According to Figure 4 and Table 3, Sensor 2a with membrane pBA of higher amount of NaTFPB showed a Nernstian response of 28.18 ± 3.68 mV/decade towards copper ions in the range of 10^{-4} - 10^{-1} M. However, a

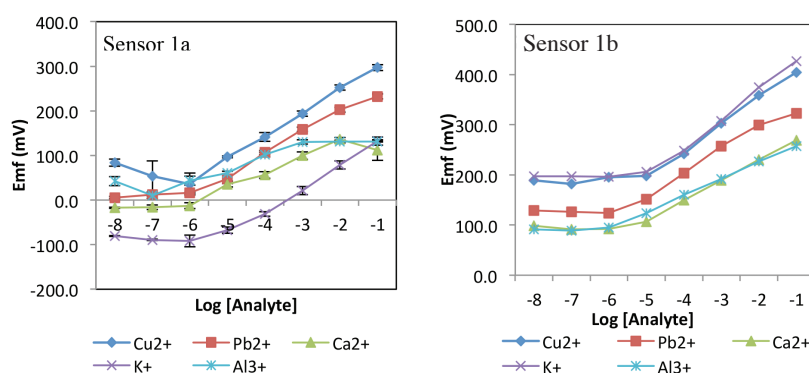


FIGURE 3. Potentiometric response of copper ion sensors with 3.5:0.5 (Sensor 1a) and 0.0:0.5 (Sensor 1b) mole ratio of TPC: NaTFPB

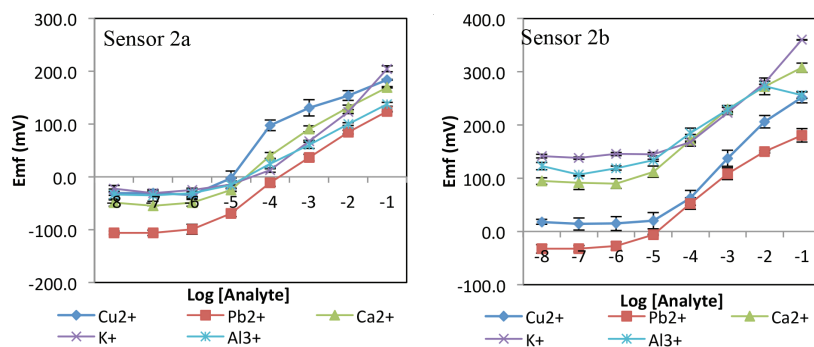


FIGURE 4. Potentiometric response copper ion sensors with 3.5:1.0 (Sensor 2a) and 0.0:1.0 (Sensor 2b) mole ratio of TPC: NaTFPB

TABLE 3. Performance of copper ion sensors with 3.5:1.0 (Sensor 2a) and 0.0:1.0 (Sensor 2b) mole ratio of TPC : NaTFPB

Sensor No.	TPC : NaTFPB (Mole Ratio)	Metal Ions	Linear Range	Slope(mV/decade)	R ²
2a	3.5 : 1.0	Cu ²⁺	10 ⁻⁴ - 10 ⁻¹	28.18±3.68	0.996
		Pb ²⁺	10 ⁻⁶ - 10 ⁻¹	46.40±1.53	0.995
		Ca ²⁺	10 ⁻⁶ - 10 ⁻¹	46.09±0.90	0.990
		Al ³⁺	10 ⁻⁶ - 10 ⁻¹	34.92±1.43	0.989
		K ⁺	10 ⁻⁵ - 10 ⁻¹	54.92±0.38	0.972
2b	0.0 : 1.0	Cu ²⁺	10 ⁻⁵ - 10 ⁻¹	60.00±2.93	0.992
		Pb ²⁺	10 ⁻⁵ - 10 ⁻¹	47.11±1.92	0.984
		Ca ²⁺	10 ⁻⁶ - 10 ⁻¹	46.56±2.25	0.988
		Al ³⁺	10 ⁻⁶ - 10 ⁻²	40.23±2.92	0.978
		K ⁺	10 ⁻⁵ - 10 ⁻¹	54.16±0.79	0.966

characteristic with significant super-Nernstian response with more than 70 mV/decade was still obtained in the range of 10⁻⁵ - 10⁻⁴ M. Super-Nernstian behavior is unfavorable due to such response is unstable and irreproducible (Kook & Lee 2017). Furthermore, increment of higher amount of NaTFPB also did not improve the selectivity towards copper ions as showed in data presented by Sensor 2a. The responses towards the other four interference ions were still very high (>10 mV/decade).

For Sensor 2b with the addition of higher amount NaTFPB only (compared to Sensor 1b), it was still responded to the five cations with the higher slopes of graph obtained and some of responses were similar with Sensor 2a especially for lead, calcium and potassium ions. Therefore, taking into account the above results, it seems rational to assume that all the five cations interact with the anion lipophilic salt rather than the ionophore TPC. The dominant effect of the cation exchange reaction by the anionic sites over the ionophore TPC had occurred. Thus, it was interested to study whether the copper ion sensor based ionophore TPC can operate without the addition of NaTFPB inside the membrane pBA.

Before the immobilization of ionophore TPC inside the membrane pBA, Sensor 3a with the pBA membrane free from the addition of NaTFPB and TPC the membrane pBA was tested for its response. As it can be seen in Table 4 and Figure 5, Sensor 3a gave responses towards all the five cations. This indicated that the blank pBA membrane might contained certain amount of anionic charge intrinsically (Kook & Lee 2017). Therefore, further addition of lipophilic anionic salt, NaTFPB caused the sensor to have no selectivity behavior as shown in the data presented here. For the Sensor 3b fabricated with the addition of 4.4 mg of TPC only (Table 4 & Figure 5), a good Nernstian response towards copper ions with the slope of 27.07 mV/decade in the range of 10⁻⁶ - 10⁻⁴ M was shown. Sensor 3b was also showing selectivity more favorable compared to the membrane sensor fabricated with the addition of NaTFPB. This was due to the slopes of graph for the four interference cations were small (<10 mV/decade) and with high standard deviation value (SD > 8.58). Such responses indicated that the Sensor 3b was unstable and non-selective to those interference cations. An excellent ionophore enable the sensor to respond exclusively to the desired ions while being almost irresponsive to the other ions (Huang

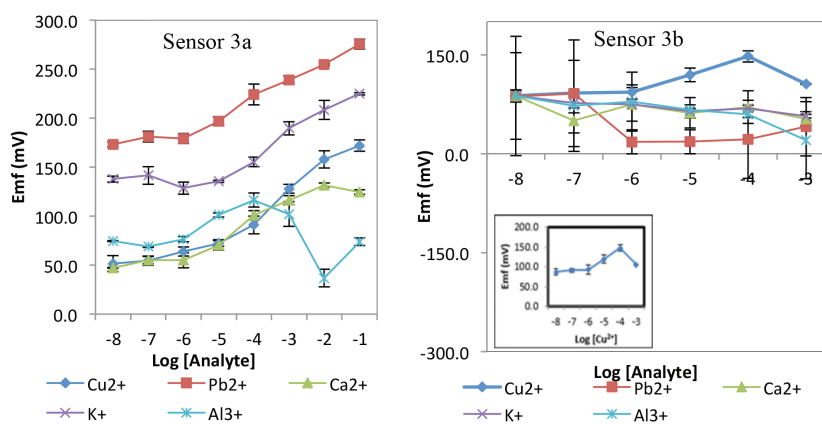


FIGURE 5. Potentiometric response of copper ion sensors with 3.5:0.0 (Sensor 3a) and 0.0:0.0 (Sensor 3b) mole ratio of TPC: NaTFPB

TABLE 4. Performance of copper ion sensors with 3.5:0.0 (Sensor 3a) and 0.0:0.0 (Sensor 3b) mole ratio of TPC: NaTFPB

Sensor No.	TPC : NaTFPB (Mole Ratio)	Metal Ions	Linear Range	Slope(mV/decade)	R ²
3a	0.0 : 0.0	Cu ²⁺	10 ⁻⁵ - 10 ⁻²	29.42±2.94	0.986
		Pb ²⁺	10 ⁻⁶ - 10 ⁻²	19.29±1.26	0.988
		Ca ²⁺	10 ⁻⁶ - 10 ⁻²	19.90±2.02	0.984
		Al ³⁺	10 ⁻⁶ - 10 ⁻⁴	19.88±3.10	0.982
		K ⁺	10 ⁻⁵ - 10 ⁻²	25.28±2.76	0.986
3b	3.5 : 0.0	Cu ²⁺	10 ⁻⁶ - 10 ⁻⁴	27.07±2.84	0.999
		Pb ²⁺	10 ⁻⁶ - 10 ⁻³	7.24±18.31	0.724
		Ca ²⁺	10 ⁻⁷ - 10 ⁻⁴	4.81±12.46	0.331
		Al ³⁺	10 ⁻⁷ - 10 ⁻²	-3.96±19.90	0.108
		K ⁺	10 ⁻⁵ - 10 ⁻²	-3.75±8.58	0.376

et al. 2012). Therefore, according to the results, it was confirmed that TPC was sensitive towards copper ion and this membrane composition was used for further studies.

REVERSIBILITY, REPRODUCIBILITY AND LIMIT OF DETECTION

According to Figure 6(a) and Table 5(a), the average slope of graphs and linear range were 28.43 mV/decade and 10⁻⁶ - 10⁻⁴ M. The relative standard deviation of the reversibility measurements was found to be 3.69%. This showed that this sensor had a good reversibility. To study the reproducibility of this electrode, a series of three electrodes were prepared and the performances of the three electrodes were showed in Figure 6(b) and Table 5(b). The linear response obtained was in the range of 10⁻⁶ - 10⁻⁴ M and the average slope of graphs was Nernstian, 28.81±0.53 mV/decade. The relative standard deviation for the average sensitivity value was 1.84%, which showed good reproducibility of the sensor in terms of sensitivity. A good reversibility and reproducibility of this sensor indicated that ionophore TPC was compatible with the pBA membrane and the amount of ionophore TPC was homogenous within the pBA membrane. Hence, the performance of this Sensor 3b was stable. The results of these two studies were also similar with the results obtained by Ghanei-motlagh et al. (2014).

The average limit of detection of three different batches of Sensor 3b was also calculated and showed in Table 5(b). The limit of detection was found to be 6.11 × 10⁻⁷ M.

RESPONSE TIME

The time taken by the sensor to attain a steady potential is taken as static response time. The response time was measured for a full range of concentration (10⁻¹ till 10⁻⁸ M). It was noticed that the response time was less than 80 s for 10⁻⁸ to 10⁻⁷ M and less than 60 s for 10⁻⁶ to 10⁻¹ M Cu²⁺ concentrations change. This response time was similar to that for mercury ion selective electrode with pBA membrane (Jumal et al. 2012).

INTERFERENCE STUDIES ON COPPER ION SENSOR

Another vital characteristic of an ISE is its selectivity to the primary ion over interfering ions. For potentiometric study, the selectivity coefficient is determined according to IUPAC recommendation, separate solution method (SSM). This method was used to determine the logarithm selectivity coefficient of the sensor with reference to Nicolsky-Eisenmann equation as below and Sensor 3b was used for this study. According to this theory, if log K_{A,B}^{pot} is larger than 1, that means the ISE is more responding to the

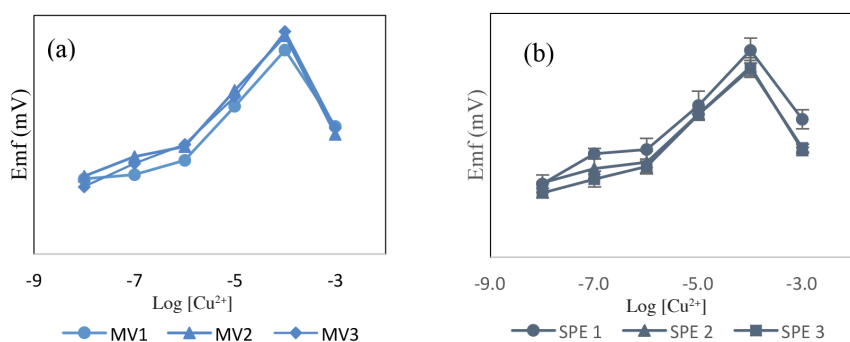


FIGURE 6. (a) Reversibility and (b) Reproducibility of sensor 3b

TABLE 5. (a) Reversibility and (b) Reproducibility of Sensor 3b

(a)			
Sensor 3b	Linear Range	Slope (mV/decade) \pm SD (RSD)	R ²
MV1	10 ⁻⁶ - 10 ⁻⁴	29.65	0.999
MV2	10 ⁻⁶ - 10 ⁻⁴	28.35	0.999
MV3	10 ⁻⁶ - 10 ⁻⁴	28.35	0.992
Average	10 ⁻⁶ - 10 ⁻⁴	28.43 \pm 1.05 (3.69)	0.999

(b)				
Sensor 3b	Linear range	Slope (mV/decade) \pm SD(RSD)	R ²	Limit of detection (M)
SPE 1	10 ⁻⁶ - 10 ⁻⁴	28.62 \pm 0.70	0.996	5.62 \times 10 ⁻⁷
SPE 2	10 ⁻⁶ - 10 ⁻⁴	27.07 \pm 2.84	0.995	6.24 \times 10 ⁻⁷
SPE 3	10 ⁻⁶ - 10 ⁻⁴	28.43 \pm 1.05	0.999	6.46 \times 10 ⁻⁷
Average	10 ⁻⁶ - 10 ⁻⁴	28.81 \pm 0.53 (1.84)	0.997	6.11 \times 10 ⁻⁷

interference ions than the primary ion. In the most cases, $\log K_{A,B}^{\text{pot}}$ is smaller than 1, which means the ISE is more responsive to the primary ions. Hence, the smaller the $\log K_{A,B}^{\text{pot}}$, the more selective the sensor towards the primary ion (Kook & Lee 2017; Umezawa et al. 2000).

$$\log K_{A,B}^{\text{pot}} = \frac{(E_B - E_A)Z_A F}{2.303RT} + \left(1 - \frac{Z_A}{Z_B}\right) \log a_a$$

From Table 6, the selectivity of the TPC-based electrode towards copper ion against some alkali, alkaline earth, transition metals and several heavy metals was high as indicated by the logarithm selectivity coefficient, which was less than -3 (e.g. for potassium, calcium, magnesium, nickel, cadmium, lead, zinc, mercury, aluminum and iron ions). Monovalent interference cation such as sodium gave higher logarithm selectivity coefficient. Such larger value is aroused from the $(1 - \frac{Z_a}{Z_b})$ in the Nicolsky-Eisenman

TABLE 6. Logarithm selectivity coefficient values, $\text{Log}(K_{\text{Cu}^{2+}, \text{M}^{n+}}^{\text{pot}})$ of Sensor 3b

Interference Ions	$\text{Log}(K_{\text{Cu}^{2+}, \text{M}^{n+}}^{\text{pot}}) \pm \text{SD}$
K ⁺	-3.22 \pm 0.30
Na ⁺	-2.69 \pm 0.53
Ca ²⁺	-3.94 \pm 0.69
Mg ²⁺	-4.09 \pm 0.47
Ni ²⁺	-4.08 \pm 0.13
Cd ²⁺	-4.28 \pm 0.10
Pb ²⁺	-4.08 \pm 0.01
Zn ²⁺	-3.46 \pm 0.10
Hg ²⁺	-3.28 \pm 0.23
Al ³⁺	-3.11 \pm 0.64
Fe ³⁺	-3.89 \pm 0.21

equation. Hence, the smaller the charge of the interference ion, Z_B , the larger the value of the logarithm selectivity coefficient (Kook & Lee 2017; Kopylovich et al. 2011).

TABLE 7. Comparison of analytical performance of Cu²⁺-selective electrode based on TPC in pBA membrane with the previously reported copper ion sensors

Ionophore & matrix	Plasticiser	Lipophilic anions	Linear Range (M)	Detection Limit (M)	Slope (mV/decade)	Response Time (s)	References
TPC based pBA membrane (drop casting membrane)	No	No	1.0 \times 10 ⁻⁶ – 1.0 \times 10 ⁻⁴	6.11 \times 10 ⁻⁷	28.81 \pm 0.53	60 - 80	This work
1-furoyl-3,3'-diethylthiourea based PVC membrane	Yes	Yes	1.0 \times 10 ⁻⁷ – 1.0 \times 10 ⁻²	3.84 \times 10 ⁻⁷	29.34 \pm 0.60	-	(Pérez et al. 2010)
1-phenyl-2-(2-hydroxyphenylhydrazo)butane-1,3-dione based PVC membrane	Yes	Yes	2.0 \times 10 ⁻⁶ – 5.0 \times 10 ⁻³	6.30 \times 10 ⁻⁷	28.80 \pm 0.11	10	(Kopylovich et al. 2011)
o-xyllylene bis(N,N-diisobutyldithiocarbamate) based poly(lauryl acrylate-hexyl acrylate) membrane	No	Yes	1.0 \times 10 ⁻⁶ – 1.0 \times 10 ⁻²	1.00 \times 10 ^{-6.5}	27.20 \pm 0.10	-	(Kisiel et al. 2015)

TABLE 8. Comparison of selectivity of Cu²⁺-electrode based on TPC in pBA membrane with the previously reported copper ion sensors

K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Ni ²⁺	Cd ²⁺	Pb ²⁺	Zn ²⁺	Hg ²⁺	Al ³⁺	Fe ³⁺	References
-3.22	-2.69	-3.94	-4.09	-4.08	-4.28	-4.08	-3.46	-3.28	-3.11	-3.89	This work
-1.20	-1.23	-	-	-	-	-	-0.90	-	-	-	(Pérez et al. 2010)
-3.92	-3.89	-3.89	-	-3.52	-3.89	-	-3.66	-	-3.92	-2.62	(Kopylovich et al. 2011)
-	-1.80	-	-6.10	-5.70	-	-	-	-	-	-	(Kisiel et al. 2015)

Therefore, from the results obtained, this sensor showed a very good selectivity towards copper ions.

COMPARISON WITH PREVIOUS STUDY

The performances of the potentiometric copper ion sensor in this work are compared with the previously reported copper ion sensor based thiourea compound and other potentiometric copper ionophores (Tables 7 & 8). When compared with copper ion sensor that based on thiourea as an ionophore, this new copper ion sensor showed better in selectivity performance and comparable sensitivity and detection limit. In terms of sensitivity and detection limit, this new copper ion sensor demonstrated slight improvement over those reported copper ion sensors so far.

CONCLUSION

This results of this work give an insight that the new compound TPC could be performed as an ionophore for the construction of a copper ion sensor based poly(n-butyl acrylate) membrane. An inherent anionic site response from the blank pBA membrane was observed from the studies and the introduction of NaTFPB into the pBA membrane failed to give good sensor performance. Therefore, the sensor fabricated without the addition of NaTFPB gave a better response towards sensitivity and selectivity. Furthermore, the sensitivity, detection limit and selectivity of this new copper ion sensor obtained was comparable or slightly better than other reported copper ion sensors.

ACKNOWLEDGEMENTS

We acknowledged the research funding from the Ministry of Higher Education (Malaysia) via grant PRGS/2/2015/SG01/UKM/02/1 and UKM for internal research grants DPP-2017-064 (Sensor Kimia dan Biosensor UKM) and UP-5179-2017. We are also grateful to MyBrainSc from Ministry of Higher Education (Malaysia) for providing scholarship to Kook Shih Ying to pursue her PhD at Universiti Kebangsaan Malaysia.

REFERENCES

- Alva, S. 2008. Pembinaan sensor ion dan biosensor potentiometri pepejal berasaskan elektrod bercetak skrin dan filem fotopolimer metakrilik-akrilik. Tesis Ph.D. Fakulti Sains & Teknologi, Universiti Kebangsaan Malaysia (Unpublished).
- Alva, S., Lee, Y.H. & Ahmad, M. 2005. A new lithium ion selective sensors based on self plasticising acrylic films and disposable screen printed electrode. *2005 Asian Conference on Sensors and the International Conference on New Techniques in Pharmaceutical and Biomedical Research - Proceedings 2005*: 48-51.
- Amemiya, S., Buhlmann, P., Pretsch, E., Rusterholz, B. & Umezawa, Y. 2000. Cationic or anionic sites? Selectivity optimization of ion-selective electrodes based on charged ionophores. *Analytical Chemistry* 72(7): 1618-1631.
- Buck, R.P. & Lindneri, E.R.N. 1994. Recommendations for nomenclature of ion-selective electrodes. *Pure and Applied Chemistry* 66(12): 2527-2536.
- Faridbod, F., Ganjali, M.R., Dinarvand, R. & Norouzi, P. 2008. Schiff's Bases and crown ethers as supramolecular sensing materials in the construction of potentiometric membrane sensors. *Sensors* 8: 1645-1703.
- Ghanei-motlagh, M., Fayazi, M. & Taher, M.A. 2014. On the potentiometric response of mercury (II) membrane sensors based on symmetrical thiourea derivatives - Experimental and theoretical approaches. *Sensors & Actuators: B. Chemical* 199: 133-141.
- Huang, M.R., Gu, G.L., Shi, F.Y. & Li, X.G. 2012. Development of potentiometric lead ion sensors based on ionophores bearing oxygen/sulfur-containing functional groups. *Fenxi Huaxue/Chinese Journal of Analytical Chemistry* 40(1): 50-58.
- Jumal, J., Yamin, B.M., Ahmad, M. & Lee, Y.H. 2012. Mercury ion-selective electrode with self-plasticizing poly (n-buthylacrylate) membrane based on 1, 2-bis- (N' - benzoylthioureido) cyclohexane as ionophore. *APCBEE Procedia* 3: 116-123.
- Khairi. 2016. New thiourea compounds as ionophores for potentiometric sensors Of H₂PO₄⁺ and Hg²⁺. Tesis Ph.D, Fakulti Sains & Teknologi, Universiti Kebangsaan Malaysia (Unpublished).
- Khan, M.A., Mehmood, S., Ullah, F., Khattak, A. & Alam Zeb, M. 2017. Health risks assessment diagnosis of toxic chemicals (heavy metals) via food crops consumption irrigated with wastewater. *Sains Malaysiana* 46(6): 917-924.
- Kisiel, A., Woznica, E., Wojciechowski, M., Bulska, E., Maksymiuk, K. & Michalska, A. 2015. Potentiometric

- layered membranes. *Sensors & Actuators: B. Chemical* 207: 995-1003.
- Kook, S.Y. & Lee, Y.H. 2017. A screen-printed copper ion sensor with photocurable poly(n-butyl acrylate) membrane based on ionophore o-xylylene bis(N,N-diisobutyl dithiocarbamate). *Malaysian Journal of Analytical Sciences* 21(1): 1-12.
- Kopylovich, M.N., Mahmudov, K.T. & Pombeiro, A.J.L. 2011. Poly(vinyl) chloride membrane copper-selective electrode based on 1-phenyl-2-(2-hydroxyphenylhydrazo) butane-1,3-dione. *Journal of Hazardous Materials* 186: 1154-1162.
- Lazo, A.R., Bustamante, M., Jimenez, J., Arada, M.A. & Yazdani-Pedram, M. 2006. Preparation and study of a 1-furoyl-3,3-diethylthiourea electrode. *J. Chil.* 3: 975-978.
- Lee, Y.H. & Hall, E.A.H. 2001. Assessing a photocured self-plasticised acrylic membrane recipe for Na⁺ and K⁺ ion selective electrodes. *Analytica Chimica Acta* 443(1): 25-40.
- Lee, Y.H. & Hall, E.A.H. 1996. Methacrylate-acrylate based polymers of low plasticiser content for potassium ion-selective membranes. *Analytica Chimica Acta* 324(1): 47-56.
- Motlagh, M.G., Taher, M.A. & Ali, A. 2010. Electrochimica Acta PVC membrane and coated graphite potentiometric sensors based on 1-phenyl-3-pyridin-2-yl-thiourea for selective determination of iron (III). *Electrochimica Acta* 55(22): 6724-6730.
- Nurulain, K., Sahilah, A.M., Fatin, I.N. & Hassan, N.I. 2016. Characterization and antimicrobial studies of five substituted bis-thioureas. *Malaysia Journal of Analytical Sciences* 20(1): 85-90.
- Perez-Marín, L., Castro, M., Otazo-Sánchez, E. & Cisneros, G.A. 2000. Density functional study of molecular recognition and reactivity of thiourea derivatives used in sensors for heavy metal polluting cations. *International Journal of Quantum Chemistry* 80(4-5): 609-622.
- Pérez, M.D.L.A.A., Yanes, S.L. & Cardona, M. 2010. Copper(II) selective electrodes based on 1-furoyl-3,3'-diethylthiourea as a neutral carrier. *Journal of the Chilean Chemical Society* 3: 371-373.
- Saeed, A., Flörke, U. & Erben, M.F. 2014. A review on the chemistry, coordination, structure and biological properties of 1-(acyl/aroil)-3-(substituted) thioureas. *Journal of Sulfur Chemistry* 35(3): 318-355.
- Sajab, M.S., Chia, C.H., Zakaria, S. & Sillanpää, M. 2017. Adsorption of heavy metal ions on surface of functionalized oil palm empty fruit bunch fibres: Single and binary systems. *Sains Malaysiana* 46(1): 157-165.
- Siswanta, D., Wulandari, Y.D. & Jumina, J. 2016. Synthesis of poly(benzyleugenol) and its application as an ionophore for a potassium ion-selective electrode. *Eurasian Journal of Analytical Chemistry* 11(3): 115-125.
- Umezawa, Y., Umezawa, K., Tohda, K. & Amemiya, S. 2000. Potentiometric selectivity coefficients of ion selective electrodes. *Pure and Applied Chemistry* 72(10): 1851-2082.
- Wilson, D., de los Ángeles Arada, M., Alegret, S. & del Valle, M. 2010. Lead(II) ion selective electrodes with PVC membranes based on two bis-thioureas as ionophores: 1,3-bis(N'-benzoylthioureido)benzene and 1,3-bis(N'-furoylthioureido)benzene. *Journal of Hazardous Materials* 181(1-3): 140-146.
- Woźnica, E., Mieczkowski, J. & Michalska, A. 2011. Electrochemical evidences and consequences of significant differences in ions diffusion rate in polyacrylate-based ion-selective membranes. *The Analyst* 136: 4787.
- Yew, P.L. & Lee, Y.H. 2014. A reflectometric ion sensor for potassium based on acrylic microspheres. *Sensors and Actuators, B: Chemical* 191: 719-726.

School of Chemical Sciences and Food Technology
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 UKM Bangi, Selangor Darul Ehsan
Malaysia

*Corresponding author; email: leeyookheng@yahoo.co.uk

Received: 28 February 2018

Accepted: 6 July 2018