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Mercury Ion-Selective Electrode With Self-plasticizing Poly(n-buthylacrylate) Membrane Based On 1,2-Bis-(*N*'-benzoylthioureido)cyclohexane As Ionophore

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Abstract

1,2-bis-(*N'*-benzoylthioureido)cyclohexane (BTCH), $C_{22}H_{24}N_4O_2S_2$, was successfully synthesized, characterized by infrared and NMR spectroscopic techniques and supported by X-ray structural studies. The compound was tested for the fabrication of a potentiometric sensor for Hg^{2+} metal ions. The sensor based on photocurable self-plasticizing poly(n-butylacrylate) membrane with immobilized BTCH as ionophore exhibits linear response in a Nernstian manner within the concentration range of 10^{-5} - 0.1 M mercury ions. The sensor displays low detection limit with response time between 50 - 100 seconds. The electrode reveals a good selectivity for mercury ion over several other tested cations.

Keywords: 1,2-bis-(*N'*-benzoylthioureido)cyclohexane, ionophore, potentiometric sensor, mercury ions

1. Introduction

The design and synthesis of new ionophores for the selective recognition of ions has attracted increasing interest due to its significant importance and potential application in environmental control, industrial processes and clinical analysis. Many organic and inorganic compounds have been tested as ionophores in producing ionic selective electrodes (ISEs), including crown ethers [1] and acyclic compounds such as

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diamines [2], dioxime [3], calixarine [4], thiazoles [5] and thiourea derivatives [6].

Thiourea derivatives are well known to be good ligands for metal ions as they contain S and N atoms which are donor sites available to coordinate with transition metals such as Ni(II), Zn(II), Cd(II), Pt(II), Pb(II) and Cu(II/I) [7-9]. This unique property as ligands has fostered the use of thiourea derivatives towards new applications in the field of chemical sensors.

In the past ten decades, only a few thiourea derivatives as neutral carriers in PVC electrode membranes for heavy metal ions have been studied. A Pb(II) ISE based on 1,3-bis(N'benzoylthioureido)benzene and 1,3-bis(N'furoylthioureido)benzene [10] and Cd(II) ISE based on 1-furoyl-3-benzyl-3-phenylthiourea [11] have been reported. Although several aroylthioureas also have been tested as new organic ionophores for heavy-metal ISE [12], investigations on mercury(II) sensors are still very limited. 1,3-diphenylthiourea as potential ionophores for mercury(II)-ISE was reported by Marin et al. [13].The lack of efficient mercury(II) electrodes certainly has driven the interest to investigate new thiourea ionophores in the preparation of mercury(II) sensors.

In the present work, we report a newly synthesized 1,2-bis-(*N'*-benzoylthioureido)cyclohexane, BTCH as a potential neutral carrier in the construction of mercury ion-selective membrane sensor. The performance results of the compound as ionophore based on photocurable self-plasticizing poly(n-butyl acrylate) membrane electrode for mercury(II) ions are presented.

2. Experimental

2.1. Reagents

The chemicals used in the bis-thiourea synthesis were ammonium thiocyanate (Sigma-Aldrich), benzoylchloride (Fluka) and cyclohexane diamine (Aldrich). The solvents used were acetone, ethanol and chloroform (J.T.Baker). Membrane materials such as 2-hydroxyethyl methacrylate (HEMA), n-butyl acrylate (n-BA), 2-hexane-dioldiacrylate (HDDA) and 2,2-dimethoxyl-2-phenylacetophenone (DMPP) were purchased by Sigma. Sodium tetrakis(4-chlorophenyl)borate (NaTFPB), chlorides or nitrates of mercury, zinc, lead, copper, iron, sodium and magnesium (all are analytical grade) were from Fluka. All standard solutions were prepared in deionised water.

2.2. Apparatus

The microelemental CHNS data were performed using a Thermo Finnigan Flash Model EA 1112 Series. Fourier Transform Infra Red (FT-IR) spectrum in a range of 4000 cm^{-1} to 400 cm^{-1} was recorded using KBr pellet on a Perkin Elmer Model Spectrum GX apparatus. Nuclear magnetic resonance (NMR) of ^{1}H and ^{13}C were obtained in d_6 $CDCl_3$ solutions on a JEOL EX400 instrument. Melting points were determined using Electrothermal 9300 Digital Melting Point Apparatus. X-ray data were collected at room temperature with a Bruker SMART APEX CCD spectrometer with Mo Kα radiation (λ=0.71073 Å). Difference in the potential of the cell or electromotive force (emf) was recorded using Orion pH meter and Voltmeter Model 420.

2.3. Synthesis of 1,2-bis-(N'-benzoylthioureido)cyclohexane, BTCH

A solution of 1,2-diamino cyclohexane (1.14 g, 0.01 mol) in acetone (40 ml) was added dropwise to an acetone solution (40 ml) containing an equimolar amount of benzoylchloride (3.5 g, 0.02 mol) and ammonium thiocyanate (1.52 g, 0.02 mol) in a 200 ml two-necked round bottomed flask. The solution was refluxed with stirring for 1 hr and then filtered into a beaker containing some ice cubes. The resulting white

precipitate was filtered off and washed with water and ethanol, then dried. Re-crystallization from ethanol yielded single crystals suitable for X-ray analysis.

2.4. Characterization of BTCH

The structure of BTCH was established through spectroscopic techniques (FTIR, ^{1}H and ^{13}C NMR) and microelemental CHNS analysis. The molecular weight and qualitative analysis data correspond with those expected. In the study of the thiourea derivatives using IR spectroscopy, usually a set of fundamentals involving the C-N and C=S bonds are identified and can be used as indicators of the electronic structure around these bonds. The characterization of the compound was supported by X-ray structural studies.

2.5. Sensor fabrication

The sensor fabrication and photocuring technique were constructed according to the method reported by Heng et al. [14,15]. The tip of Ag/AgCl screen printed electrode (diameter 2 mm, Scrint) was first deposited with the monomer of 98.0 wt% HEMA mixed with 1.6 wt% of photoinitiator, DMPP. The mixture (0.1 µL) was photocured under UV radiation in the UV-exposure unit (RS Ltd.) under constant flow of nitrogen gas for 180 s. The polymer film formed was then hydrated with 0.01 M of mercury(II) chloride solution for 15 min to form the "inner solution" of the sensor. The self-plasticising poly(n-butyl acrylate) film was then deposited on top of the hydrated poly (HEMA) inner layer by photocuring technique. The stock solution of n-BA, was prepared by mixing 95.5 wt% n-BA with 0.1 wt% of cross linker, HDDA. 100 µL of the stock solution was added to the mixture consisted of photoinitiator, DMPP and required amounts of lipophilic salt, NaTFPB and ionophore, BTCH according to Table 1. An amount of 2 µL of the mixture was then photocured in an ultra-violet exposure unit (RS Ltd.) under a nitrogen atmosphere for 180 s.

2.6. Sensor evaluation

The responses of the sensors were assessed in an electrochemical cell setup, which consisted of a double junction Ag/AgCl reference electrode. The internal reference solution was 0.1 M Tris-HCl (pH=7) whilst 1 M lithium acetate was used as a gel bridge electrolyte. Both the reference electrode and the mercury sensor were connected to an Orion meter. All standard solutions of mercury chloride in the range of 0.1 to 10^{-7} M were prepared in deionised water. The difference in the potential of the cell or electromotive force (emf) in mV was recorded when a stable value was reached after 2-3 min. Interference study was carried out by the separate solution method [16] with 0.1 M solution of zinc, lead, nickel, sodium and magnesium of chlorides or nitrates as interference ions. All the measurements were conducted at room temperature.

3. Results and Discussion

3.1. Synthesis and characterization of BTCH

Elemental analysis : Calc. (%) for $C_{22}H_{24}N_4O_2S_2$: C, 60.00; H, 5.45 ; N, 12.73; S, 14.54. Found : C, 59.44; H, 5.41 ; N, 12.47 ; S, 13.78 ; m.p. 196±1 ^{o}C. Yield 79.2%. FT-IR (cm^{-1}), ν : 3171 , 1672 , 1164 , 717. ^{1}H NMR ($CDCl_3$) δ : 11.12 (1H , s), 10.90 (1H, s), 8.92 (2H , d), 7.84-7.27 (10H , m). ^{13}C NMR ($CDCl_3$) δ : 180.04 (C=O), 166.54 (C=S), 127.72-133.66 (C aromatic).

The main IR bands have been identified and the above data shows their frequency values. The stretches of N-H group vibrates at 3171 cm^{-1}, C=S symmetric stretchings at 1164 cm^{-1} and carbonyl vibration, ν (C=O)

was detected at 1672 cm^{-1}. In the ^{1}H NMR spectrum of the compound, three important chemical shifts were observed: a doublet and two singlets were assigned to NH protons; thioamide amino proton δH(CSNH) at 8.92 ppm and amide amino proton δH(CONH) at 11.12 and 10.90 ppm, and a multiplet corresponding to aromatic protons, δH(Ar-H) at 7-84-7.27 ppm. The most deshielded signal (δ = 11.12 ppm) was assigned to δH(CONH) and this chemical shift is that high because these protons form intramolecular hydrogen bonds [17-18].

X-ray study [19] has shown that the two benzoylthioureido segments of the side-arm groups are not planar (Fig. 1(a)) but inclined with dihedral angle of 73.09 (9)°. There are two intrahydrogen bonds N2-H2A..O1 and N3-H3A...O2 forming two pseudo-six membered rings O1...H2A-N2-C8-N1-C7 and O2..H3A-N3-C15-N4-C16 respectively. In the crystal structure, the molecules are linked by intermolecular hydrogen bonds N1-H1A..O2 and N4-H4A..S2 as displayed in Fig. 1(b). The structural feature is useful for recognition study.

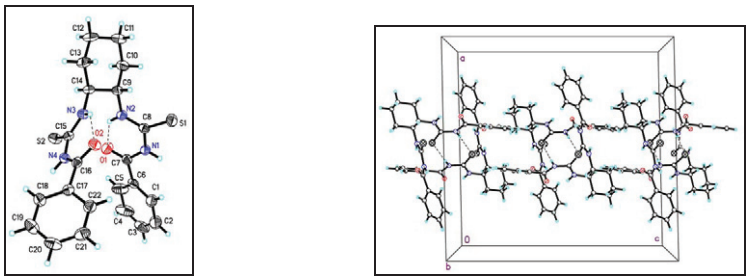

Fig. 1. (a) ORTEP diagram of BTCH with dashed lines indicating the intramolecular hydrogen bonds and displacement ellipsoids at 50% probability level; (b) Packing diagram of BTCH with dashed lines indicating the intermolecular hydrogen bonds

3.2. Potentiometric response

In the preliminary experiments, the BTCH ionophore was used as a potential carrier in construction of ion-selective sensors for different common metal ions, including alkali, alkaline earth, transition and heavy metal ions. The responses of these electrodes are shown in Fig.2. Among the different cations tested, it is seen that the membrane responds to Hg(II) ion was found to give the best response compared to other metal ions studied. We therefore studied in detail the properties of the membrane for the Hg(II) ion.

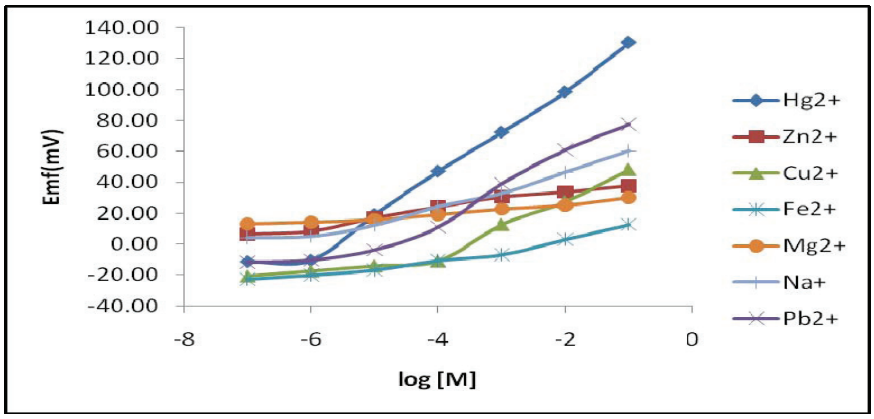

Fig. 2. Potential response of various cation-selective electrodes based on BTCH.

It is well understood that the performance characteristic for the ionophore-incorporated polymer membrane depend significantly on the electrode membrane composition, the presence of plasticizer and additives used [20]. Since the membrane used in the present work is self-plasticized poly(n-butyl acrylate), several membrane compositions were investigated by varying different amounts of ionophore and the lipophilic anionic additive, NaTFPB without the need of any plasticizer added. The results of the optimization of the membrane formulation with different amount of BTCH and NaTFPB are summarized in Table 1.

From the results, the membrane without lipophilic salt (E1) showed very narrow concentration range and the response slope was not reliable. The potentiometric response of the E2-E3 electrode membranes were greatly improved with minute amounts of lipophilic anionic additive, NaTFPB. Among the different compositions studied, the E3 electrode membrane with 95.5 wt.% n-BA, 0.1 wt.% HDDA, 1.0 wt.% DMPP, 0.8 wt.% NaTFPB and 24.0 wt.% BTCH relative to NaTFPB exhibited the best Nernstian response of 28.1 mV/decade over the widest concentration range. Hence, this particular membrane was studied as Hg(II) selective electrode and further investigations were carried out with this particular membrane.

Table 1. The composition of ISE membranes used for the potentiometric studies of BTCH ionophore

Electrode	n-BA (wt.%)	HDDA (wt.%)	DMPP (wt.%)	BTCH (wt.%)*	NaTFPB (wt.%)	Slope (mV/dec)	Linear range (M)
E1	95.5	0.1	1.0	24.0	0.0	19.8 ± 0.8	1.0×10^{-4} to 1.0×10^{-2}
E2	95.5	0.1	1.0	24.0	0.4	22.5 ± 1.2	1.0×10^{-4} to 1.0×10^{-2}
E3	95.5	0.1	1.0	24.0	0.8	28.1 ± 0.7	1.0×10^{-5} to 1.0×10^{-1}
E4	95.5	0.1	1.0	24.0	1.2	23.1 ± 1.6	1.0×10^{-5} to 1.0×10^{-2}
E5	95.5	0.1	1.0	20.0	0.8	20.3 ± 1.3	1.0×10^{-5} to 1.0×10^{-1}
E6	95.5	0.1	1.0	32.0	0.8	18.6 ± 2.1	1.0×10^{-5} to 1.0×10^{-2}

*Relative to NaTFPB

3.3. Performance of sensors

The most important characteristic of an ISE is its relative response for the principle ions over other interfering ions present in solution, which is expressed in terms of potentiometric selectivity coefficients, log K^{pot}. In order to investigate the selectivity of the proposed Hg(II)-selective electrode over other cations, the method of separate solution method (SSM) was employed with 0.1 M solution of various cations as interference ions [16]. The resulting potentiometric selectivity coefficients, log K^{pot} of Hg(II) ion selective electrodes are summarized in Table 2. It is clear that the proposed mercury sensor is highly selective with respect to other common cations, indicating they would not significantly disturb the functioning of the mercury(II) selective membrane.

Table 2. Selectivity coefficient values, log K^{pot} of Hg(II) ion selective electrodes in the presence of 0.1 M of various interference cations

Interfering ion	log K^{pot}
Na^{+}	-1.9
Mg^{2+}	-4.1
Pb^{2+}	-2.5
Zn^{2+}	-3.8
Ni^{2+}	-4.7

Reproducibility of the electrode was examined by using three similar constructed electrodes under the optimum conditions. Table 3 shows the changes in potential of the electrode cell, emf of the three mercury selective sensors with changes in concentration of mercury(II) chloride over the range of 0.1 to 10^{-7} M. All three sensors demonstrated very similar response indicating good reproducibility for the electrodes. The linear response obtained was in the range of 0.1 to 10^{-5} M and the sensitivity was almost Nernstian, close to 29 mV per decade change in mercury ion concentration. The limit of detection of the three membranes calculated, as recommended by IUPAC from the intersection of the two extrapolated segments of the calibration curve [16], are also displayed in the same table.

Table 3. The analytical performance of the mercury ion sensors

Electrode	Linear range (M)	Slope (mV/dec)	r^2	Detection limit (M)
S1	10^{-5} to 10^{-1}	28.1 ± 0.6	0.9989	2.5 x 10^{-6}
S2	10^{-5} to 10^{-1}	27.9 ± 0.8	0.9981	3.2 x 10^{-6}
S3	10^{-5} to 10^{-1}	28.0 ± 0.5	0.9985	3.7 x 10^{-6}

*Average of three measurements per sensor.

The time taken by the electrode assembly to attain steady potential is taken as static response time. The response time was measured for a full range of concentration and it was noted that the response time was less than 100 s for the change in concentration for 10^{-7} to 10^{-5} M Hg^{2+} and less than a minute for 10^{-3} to 10^{-1} M Hg^{2+} concentration change. The life time of the electrodes was determined by recording its potential and plotting its calibration curve for 10 weeks. The sensing behaviour of the membrane remained reasonably constant over a period of 9 weeks and swelled up due to which leaching ions from the membrane phase took place**.**

3.4. Comparison of the Hg2+ selective electrodes

The performance characteristics of the proposed sensor are compared with those of the previously reported Hg^{2+} PVC membrane sensors (Table 4). It is seen that the working concentration range and detection limit of the proposed sensor are comparable to those reported for ISEs.

Table 4. Comparison of the Hg^{2+} selective electrode with reported electrodes

Ionophore	Linear range (M)	Slope (mV/dec)	Detection limit (M)	Response time (s)	Reference
2-Amino-6-purinethiol	7.0 x 10^{-8} to 1.0 x 10^{-1}	30.0	4.4 x 10^{-8}	10	[21]
2-Mercaptobenzimidazole	10^{-6} to 10^{-1}	28.5	6.0 x 10^{-7}	20-100	[22]
Calixarene derivative	5 x 10^{-6} to 10^{-2}	28.7	4.5 x 10^{-7}	20	[23]
1,2-bis-(*N'*-benzoylthioureido)cyclohexane	10^{-5} to 10^{-1}	28.1	2.5 x 10^{-6}	50-100	This work

4. Conclusions

The newly synthesized BTCH can be used as an ionophore for the construction of a self-plasticising poly(n-butyl acrylate)-based membrane ISE for determination of Hg(II) ions. The electrode membrane composition, 95.5 wt. % n-BA, 0.1 wt.% HDDA, 1.0 wt. % DMPP, 0.8 wt.% NaTFPB and 24.0 wt.% BTCH

relative to NaTFPB showed the best potentiometric response characteristic and displayed a wide concentration range of 1.0 x10^{-5} to 1.0 x10^{-1} M with a Nernstian slope of 28.1 mV/dec. The potentiometric selectivity coeffient, K^{pot} values showed good selectivity over various metal cations studied. The application of the proposed membrane sensor in real water samples determination is in progress.

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