

**RESEARCH REPORT**

**SYNTHESIS OF BIS-THIOUREA DERIVATIVES AND STUDIES ON ITS  
APPLICATION AS CHEMICAL SENSOR**

**CODE : PPP/FST-05-10109**

Perpustakaan USIM



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SEPTEMBER 2009**

## ABSTRACT

Three new bis-thiourea derivatives namely 1,2-bis(4-chlorobenzoylthiourea)-propane (S1), 1,4-bis(4-chlorobenzoylthiourea)-butane (S2) and 1,2-bis(4-chlorobenzoylthiourea)-ethane (S3) were successfully synthesized by the reaction of the mixture of 4-chlorobenzoylchloride and ammonium thiocyanate with selected diamine compounds namely 1,2-diaminopropane, 1,4-diaminobutane and 1,2-diaminoethane. FTIR spectra of all the compounds show the presence of  $\nu$  (N-H),  $\nu$  (C=O),  $\nu$  (C=S),  $\nu$  (C-N) stretching frequencies at  $3173\text{-}3297\text{ cm}^{-1}$ ,  $1630\text{-}1672\text{ cm}^{-1}$ ,  $843\text{-}846\text{ cm}^{-1}$  and  $1092\text{-}1094\text{ cm}^{-1}$  respectively. Proton NMR spectra show the presence of three important chemical shifts in all the compounds : amino proton  $\delta\text{H}$  (N1)  $11.33\text{-}11.38\text{ ppm}$ ,  $\delta\text{H}$  (N2)  $10.77\text{-}10.86\text{ ppm}$  and  $\delta\text{H}$  (aromatic proton) at  $7.49\text{-}7.90\text{ ppm}$ . While  $^{13}\text{C}$  NMR spectra show that the thiono, C=S and ketone, C=O chemical shifts at  $180.06\text{-}181.18\text{ ppm}$  and  $165.0\text{-}167.29\text{ ppm}$  respectively. Solid-state ammonium ion sensors based on photocured poly(n-butyl acrylate) membrane with immobilized newly synthesized compounds were successfully used for the determination of ammonium ion. The sensor membrane does not require any plasticizer and the S1- and S2- based membrane electrodes gave near Nernstian responses ( $57.3\text{ mV}$  per decade and  $50.6\text{ mV}$  per decade respectively) throughout the ammonium ion concentration range of  $10^{-1}$  to  $10^{-4}\text{ M}$  with detection limits approaching  $10^{-5}\text{ M}$  ammonium ion. However, the S3-based electrode has a typical Nernstian response with a slope of  $35.6\text{ mV}$  per decade in the concentration range of  $10^{-2}$  to  $10^{-4}\text{ M}$ .

## ABSTRAK

Sebanyak tiga sebatian baru terbitan bis-tiourea telah berjaya disintesis iaitu 1,2-bis(4-klorobenzoiltiourea)-propana (S1), 1,4-bis(4-klorobenzoiltiourea)-butana (S2) and 1,2-bis(4-klorobenzoiltiourea)-ethana (S3) melalui tindak balas di antara 4-klorobenzoil klorida, ammonium tiosianat dan kumpulan diamina yang dipilih iaitu 1,2- diaminoetana, 1,2-diaminopropana and 1,4-diaminobutana. Spektrum FTIR bagi semua sebatian tersebut menunjukkan kehadiran frekuensi regangan  $\nu$  (N-H),  $\nu$  (C=O),  $\nu$  (C=S),  $\nu$  (C-N) masing-masing pada  $3173-3297\text{ cm}^{-1}$ ,  $1630-1672\text{ cm}^{-1}$ ,  $843-846\text{ cm}^{-1}$  and  $1092-1094\text{ cm}^{-1}$ . Spektrum NMR pula menunjukkan tiga isyarat utama anjakan kimia bagi semua sebatian tersebut iaitu proton amino,  $\delta\text{H}$  (N1) di sekitar  $11.33-11.38\text{ ppm}$ ,  $\delta\text{H}$  (N2)  $10.77-10.86\text{ ppm}$  dan  $\delta\text{H}$  (proton aromatik) pada  $7.49-7.90\text{ ppm}$ . Manakala anjakan kimia bagi tiono, C=S and keton, C=O spektrum  $^{13}\text{C}$  NMR adalah masing-masing di sekitar  $180.06-181.18\text{ ppm}$  dan  $165.0-167.29\text{ ppm}$ . Sensor ion amonium keadaan pepejal yang berasaskan membran poli(n-butyl akrilat) dengan sebatian baru terpegun telah berjaya digunakan untuk mengenal pasti ion ammonium. Sebarang pemplastik tidak diperlukan untuk pembinaan membran sensor tersebut dan didapati sebatian S1 menunjukkan respon Nernstian sebanyak  $57.3\text{ mV}$  per dekad dan S2  $50.6\text{ mV}$  per dekad dalam julat kepekatan ion ammonium  $10^{-1}$  to  $10^{-4}\text{ M}$  dengan had pengesanan  $10^{-5}\text{ M}$ . Walau bagaimanapun, sebatian S3 memberikan respon Nernstian dengan kecerunan  $35.6\text{ mV}$  per dekad dalam julat kepekatan  $10^{-2}$  to  $10^{-4}\text{ M}$ .

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