A NEW NITRATE-SELECTIVE ELECTRODE BASED ON BIS-THIOUREA XANTHENE SPACER DERIVATIVE

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Abstract- A new nitrate selective electrode has been developed. This electrode uses a derivative of bis-thiourea as ionophore. Bis-thiourea derivatives obtained from the reaction between bis (aminomethyl) benzene with nitrophenylisothiocyanate. Nitrate selective electrode showed near Nerstian values -54.7± 3.5mV/dec with RSD value is 6.5% . Meanwhile, the linear range is 0.1 M - 10^{-5} M and the sensor has a detection limit is 4.1 x 10^{-6} M. In this study, Log K^{pot}a,b values are given for each interference ion is Cl^- -1.36 ± 0.12, HPO_4^{2-} -2.80 ± 0.24, Br^- -0.58 ± 0.10, CrO_4^{2-} -1.32 ± 0.21, SO_4^{2-} -2.42 ± 0.31. Artificial samples, fish pond and soil used as real samples. Nitrate sensors give a similar results with commercial sensor.

Keywords- Nitrate-selective electrode, Bis (aminomethyl) benzene, Nitrophenylisothiocyanate, Bis-thiourea.

I. INTRODUCTION

Nitrate is an essential nutrient for plants, but the excess nitrates in water may cause serious problems for the environment. Besides can cause algae bloom, nitrate can be converted into nitrites that are toxic [1]. Traditionally, the measurement of nitrate is using chromatography and spectroscopy methods. But this method has a complicated protocol and can not be done in situ [2]. Besides using chromatography and spectroscopy methods, other methods that are widely used today is to use ion-selective electrodes. This method has several advantages compared methods of chromatography and spectroscopy as well as there is no special treatment of the samples, easy to handle, inexpensive, faster and can be done in situ. So the method is suitable for field measurements [3]. Ion selective electrode works by using a thin layer membrane which selective to the presence of the target ion. The ability of this membrane layer to selectively against specific ions due to the presence of Ionophore or ion exchange salt [4-5]. Most of the nitrate ion selective electrode using ammonium quaternary salts as a ion exchanger to give selectivity [6]. However, some researchers have also reported the use of Ionophore nitrate based amide [7-8], metal complex Ionophore [9-10], cyclic bis-thiourea [11], porphyrins [12]. In this study, we proposed a new use nitrate Ionophore based on derivatives of bis-thiourea xylene. This Ionophore has four arms NH that interact with nitrate ions through hydrogen bonds. Nishizawa et al is one of the early researchers who have been using Ionophore from this set to use as Ionophore against several types of anions [13-15].

II. EXPERIMENTAL

A. Materials

High molecular weight poly(vinyl chloride) (PVC), 2-nitrophenyl octyl ether (NPOE), Tetradodecyl ammonium chloride (TDDACl) tetrahydrofuran (THF) and Pyrrole monomer were purchased from Sigma-Aldrich. Potassium nitrate (KCl) and potassium nitrate (KNO3) were purchased from Merck. □,□'-bis(NA-p-nitrophenylthioureylene)-m-xylene which was originally designed by Nishizawa and co-workers (16). Co-polymer methyl methacyrylate-butyl acrylate with ratio 2:8 (MB28) which designed by Lee and co-workers[17].

B. Electrodes

The carbon screen printed electrodes (SPE) with 4 mm diameter were cleaned ultrasonically with deionised water for 1 min. The electrochemical polymerisation was performed in a conventional three-electrode cell with a Pt as counter electrode and the Ag/AgCl double junction as reference electrode using Autolab PGSTAT MODEL 128N for 90 sec. The polypyrrole (Ppy) films were generated with current density of 2 mA cm-2 in aqueous solution of 0.5 M pyrrole containing 1M potassium chloride dopan. After forming electropolymerisation, cyclic voltammetry experiments were conducted between -1.0 V and +0.4 V with a potential sweep rate of 100 mV sec-1 in 0.1M potassium chloride (KCl) solution.

C. Membranes

Nitrate sensing membranes was prepared by mixing 29.7 % PVC, 3.3 % copolymer MB28, 67 % DOS, total mass of polymer and plasticizer is 100 mg. Add 6 wt % TDDACl relative to total mass of polymer and plasticzer and mix with 25 mole % □,□'-bis(NA-p-nitrophenylthioureylene)-m-xylene relative to TDDACl. All's component dissolve with 1 mL THF and shaking until homogen. Then, the homogenous cocktail was deposited on top of Ppy film and dried overnight at room temperature. This nitrate sensor was tested using single junction Ag/AgCl reference electrode from mimos. Meanwhile, selectivity studies carried out with different interference ion using the separate solution method (SSM) [18].

III. RESULTS AND DISCUSSION

Selection of a suitable ionophore in making ion-selective electrode is very important. Using of suitable ionophore and with the right amount will be able to increase the sensitivity and selectivity of the sensor. This paper used □□□'-bis(NA-p-nitrophenylthioureylene)-m-xylene ionophore as a recognition for the nitrate ion as shown in Fig.1. As seen in Fig.1., this ionophore has four hands NH groups. The interaction that occurs between the ionophore and nitrate ions are hydrogen bonds. A hydrogen bond occurs when two electronegative atoms, such as nitrogen and oxygen, interact with the same hydrogen [19].

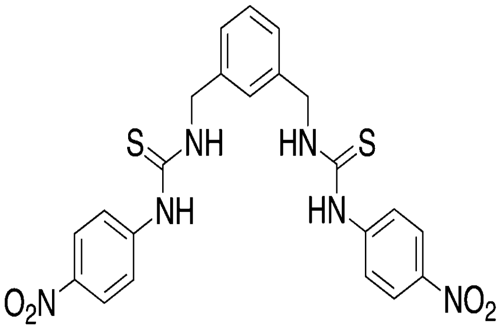

Fig. 1. **□□□'-bis(NA-p-nitrophenylthioureylene)-m-xylene ionophore**

A total of three nitrate ISE has been provided in this study. All of the sensors give value which near with nernstian values as showed in fig.2. and table 1. This shows that the ionophore used to recognition the presence of nitrate ions [15]. In addition, the addition of a few percent of the copolymer MB 28 still providing the flexibility of the membrane. Addition copolymers MB 28 is intended to improve the adhesion of the membrane on the surface of electrode. This is because PVC membranes have showed weak adhesion to the surface of the electrode. So will cause the membrane peel-off from the electrode surface and will cause the response of the sensor decreases [20].

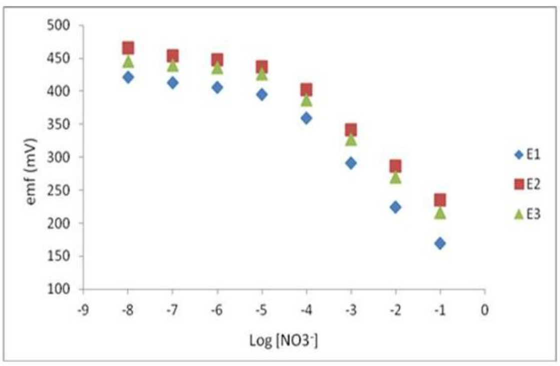

Fig.2. Response of Nitrate ISE based on □□□'-bis(NA-p-nitrophenylthioureylene)-m-xylene ionophore.

Data from Table 2 also shows that the nitrate sensor also has good selectivity towards several anions. It is a fact that ionophore used to working well with PVC/MB28 membrane. It also shows that the presence of a few percent of MB28 as supplementary material also does not reduce the sensitivity and selectivity of the nitrate ISE. This is because the copolymer MB28 has a Tg of between -20°C to -40°C, up to 28 MB can be used as the manufacturing material sensor [17].

TABLE 1. Performance of Nitrate ISE based on □□□'-bis(NA-p-nitrophenylthioureylene)-m-xylene ionophore

Sensor	Slope (mV/dec)	Linear Range (M)	LOD (x 10^{-6})(M)
E1	-58.7	0.1 - 10^{-5}	4.00
E2	-51.8	0.1 – 10^{-5}	3.16
E3	-53.7	0.1 - 10^{-5}	5.25

In the table 2 see Br^- ion providing the greatest interference effects, while the SO_4^{2-} ion and CrO_4^{2-} give the smallest interference effects. This is consistent with the Hofmeister series. The Hofmeister series or lyotropic series is a classification of ions in order of their ability to salt out or salt in proteins. But until now, the Hofmeister series are still under debate. The presence of ions of the series hofmister can change the structure of hydrogen bonds in water [21-22]. So this may affect the selectivity of the sensor [23-24].

TABLE 2. Selectivity coefficients (Log $K^{pot}_{a,b}$) of Nitrate ISE based on □□□'-bis(NA-p-nitrophenylthioureylene)-m-xylene ionophore

Interference Ion	Log $K^{pot}_{a,b}$
Cl^-	-1.36 ± 0.12
HPO_4^{2-}	-2.80 ± 0.24
Br^-	-0.58 ± 0.10
CrO_4^{2-}	-1.32 ± 0.21
SO_4^{2-}	-2.42 ± 0.31

In this study, nitrate ISE sensor provided on the test with real samples and artificial solution with a concentration of 100 ppm. Real samples used is a solution of fish ponds and soil samples. The results of the measurements were found to be compared with measurements using commercial nitrate ISE sensor. Data are shown by Table 3 shows the nitrate sensor used has a performance comparable to the commercial sensor.

TABLE 3. Performance of Nitrate ISE based on □□□'-bis(NA-p-nitrophenylthioureylene)-m-xylene ionophore in real samples measurement.

Sample	Nitrate ISE (ppm)	Commercial Nitrate Sensor (ppm)
Artificial solution 100 ppm	99.1 ± 2.8	103.8
Fish pond sample	25.8 ± 0.5	27.0
Soil sample	52.5 ± 3.1	51.1

Tests with real samples is very important to know the performance of the developed sensor. This is because in real samples usually contain many different types of interference ions with different concentrations. The selection of soil samples and fish ponds as a real samples is based on nitrate required information is very important for both samples. Nitrate is needed by plants as nutrients for growth.

Meanwhile, in the fish pond, the excess of nitrate ions can cause algal blooms, in addition, nitrate can be transformed into nitrite ions that are toxic to fish through the nitrogen cycle[1-2].

CONCLUSIONS

Sensor PVC/MB28 nitrate ISE with membranes and □□□'-bis(NA-p-nitrophenylthioureylene)-m-xylene ionophore has been successfully developed. The sensor shows a good performance include sensitivity, linear range, limit of detection and reproducibility. The sensor also showed good selectivity to the presence of interference ion. Nitrate sensor shows performance comparable to commercial nitrate sensors in testing with artificial samples of 100 ppm nitrate and real samples such as soil and fish pond samples.

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