Development of Ammonium-Selective Electrode Based on PVC/MB28 Membrane

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Abstract. In this study, the ISE-NH₄⁺ sensor based on hybrid membrane of the poly (vinyl chloride)/methyl methacrylate-butyl acrylate 2:8 co-polymer (PVC/MB28) has been successfully developed, where the ratio between PVC: MB28 is 9:1. Meanwhile, the plasticized material used is dioctyl sebacate (DOS) of 66.34 wt. %, the amount of lipophilic salt of the potassium tetrakis (4-chlorophenyl) borate (KTPCIPB) used is 0.99 wt. %, and nonactine as much as 2.97 wt.%. The addition of the MB28 co-polymer has successfully improved the performance and mechanical strength of ISE-NH₄⁺ especially at measurements at 40°C. The ISE-NH₄⁺ sensor based on PVC/MB28 has a Nernstian number of 55.4 and 58.7 mV/dec for measurement at 25°C and 40°C with the linear range between 0.1 - 10⁻⁵ M. While the ISE-NH₄⁺ sensors based on PVC used as benchmarking have Nernstian numbers of 54.2 and 35.3 mV/dec for measurements at 25 °C and 40 °C, where the linear range is 0.1 - 10⁻⁵ M and 0.1 - 10⁻³ M. The addition of MB28 also does not cause the selectivity of the ISE-NH₄⁺ sensor to decrease, where the result of the selectivity between PVC/MB28 is comparable to PVC.

Keywords: PVC, MB28, ISE-NH₄⁺, PVC/MB28 membrane, ammonium ion

1. Introduction

The ammonium ion (NH₄⁺) together with the ammonia (NH₃) is one of the important parameters in the determination of water quality. The NH₄⁺ has a lower toxicity level than NH₃. This is due to NH₃ will be easier to absorb into the system of body tissue of aquatic life such as fish versus NH₄⁺, thus causing the fish to be poisoned. However, once the NH₄⁺ at any time can turn into toxic ammonia in case of changes in the temperature and pH of the environment. This makes the presence of the NH₄⁺ in the environment necessary to be monitored. Exposure of the ammonia for 96 hours at a concentration of 1.5 - 3.3 ppm will cause 50% of fish in the pond to die [1]. Thus an instrument is needed to detect the presence of NH₄+ quickly and inexpensively. One technique that can be used is potentiometric technique using an ion-selective electrode (ISE).

The potentiometric technique is an electrochemical measurement technique based on measuring the potential difference that occurs between the ion-selective electrodes (ISE) with the reference electrode in a zero current state. The resulting potential difference will be proportional to the logarithmic concentration of the ion sample by following the Nernst equation [2].

\[ E = E^o + \frac{2.303RT}{nFz} \log[a_A] \] (1)

Where \( E^o \) is the standard potential energy, \( R \) is the ideal gas constant (8.314 J/Kmol), \( T \) is the temperature in K, \( n \) is the number of moles of the ion, \( F \) is the Faraday number (96,485 C/mole), \( z \) is the ion charge, and \( a_A \) is ionic activity (M).

An ISE usually has a thin film which is generally a polymeric membrane and selectively in the presence of certain ions such as NH₄⁺. The commonly used polymer in the fabrication of the NH₄⁺
selective electrode is polyvinyl chloride (PVC) [3]. However, this polymer has a fundamental weakness that has poor adhesive properties on the electrode surface, so it will be easily detached from the surface of the electrode [4]. This causes the ISE response to decrease. In addition to the PVC membrane, other polymers that have been used in the development of ISE NH₄⁺ are poly (butyl acrylate) (pBA) membranes [5]. This membrane has better adhesion than PVC, but this membrane also has weaknesses such as tear easily because it is too soft.

There needs to be a solution to overcome the problems shown from the PVC and pBA membranes. One potential alternative is to use a hybrid membrane of PVC/MB 28. This membrane has been successfully used as a material for the fabrication of nitrate sensors [4]. This membrane has advantages such as having a good adhesive properties on the surface, flexible, not too soft and rigid. The aim of the study is to develop alternative polymers that have good mechanical strength so as to improve ISE-NH₄⁺ sensor performance.

2. Experimental
2.1. Material
The materials used in this research are High molecular weight poly (vinyl chloride), dioctyl sebacate, (DOS), potassium tetrakis (4-chlorophenyl) borate (KTpClPB), nonactine from Sigma Aldrich. Tetrahydrofuran solution (THF), pyrrole monomer, and salts such as NH₄Cl, KCl, NaCl, LiCl, CaCl₂, H₂O and MgCl₂.6H₂O from Merck. Co-polymer methyl methacrylate-butyl acrylate with ratio 2:8 (MB28) which synthesized by Heng and co-workers [6]. Carbon screen printed electrode (SPE) from Screen Print BhD-Malaysia.

2.2. Instrumentations
In this study, some of the equipment used among them is the potentiostat PGSTAT MODEL 128N from Metrohm, an ion meter with type Orion 4-Star Plus pH/ISE Benchtop Multiparameter Meter from Thermo Scientific, the single junction of the Ag/AgCl reference electrode from Mimos Bhd, water baths and also the microscope optic OGP SmartScope Flash 300 from Optical Gaging Products Inc.

2.3. Methods
A total of 27 mg of PVC membrane was mixed with 3 mg of MB28 co-polymer, 67 mg DOS, 3 mg nonactine and 1 mg KTpClPB. The whole mixture was dissolved with 600 μL THF and shaken until all the mixes dissolved perfectly and formed a clear viscous solution. A further 20 μL of the mixture is placed on the polypyrrole (PPy) surface of the carbon from SPE surface and allowed to dry at room temperature for overnight. Prior to the membrane coating on the PPy surface, the PPy layer on the surface of the SPE was prepared following the work by the previous researcher [4]. After drying, the ISE-NH₄⁺ response is performed at 25°C and 40°C in various concentrations of the NH₄⁺ solution. In this test, the an ISE-NH₄⁺ is paired with an Ag/AgCl reference electrode and then connected to an ion meter device. After testing the response, the ISE-NH₄⁺ is placed on an optical microscope to see the physical changes of the membrane that occur after the measurement. Furthermore, the good of the ISE-NH₄⁺ is used for selectivity testing with several interference ions such as K⁺, Na⁺, Li⁺, Mg²⁺ and Ca²⁺ using separate solution methods (SSM) [7] where all of the test samples have a concentration of 0.1 M. The results obtained were compared with the ISE-NH₄⁺ sensor prepared by using membrane composition without MB28.

3. Result and Discussion
Membranes are an important component in the preparation of the ISE sensors. The performance of an ISE depends heavily on the composition and type of the membrane used. One of the basic characteristics of the membrane for the ISE sensor is that the membrane is adequate of being bypassed by the target ion to move toward the transducer surface. The presence of a target ion on the surface of the transducer will cause a change in the potential energy of the transducer surface [8]. In this study,
the membranes used is the hybrid membrane of the PVC/MB28 and also the PVC membrane as the comparative membrane. The magnitude of the potential value changes corresponds to the number of target ions that reach the surface of the transducer as shown in figure 1 below. Where this potential change will follow Nernstian’s response [2].

![Figure 1](image)

**Figure 1.** The response of the ISE-NH$_4^+$ sensor based on PVC/MB28 and PVC on the variation of the NH$_4^+$ concentration and temperature measurement

The ability of the membrane to be passed by the target ion is determined by the lower of the transition glass (Tg) properties of membranes. A low Tg will cause the membrane to be softer and more flexible and this will facilitate the process of transporting the target ion within the ISE membrane. Usually, a membrane that has a high Tg such as PVC will require a plasticizer material to reduce its tag value [5], which in this study is used DOS as a plasticizer. In addition, in order to facilitate the process of transfer of target ions such as NH$_4^+$ from the sample into the membrane, usually the membrane charge is manipulated by the addition of a lipophilic salt acting as an ion exchange [9] such as KTpClPB. The addition of a lipophilic salts of KTpClPB will cause the membrane to be rich in negative charges to attract positively charged ions such as NH$_4^+$. Seen from Figure 1, the lower the concentration of the NH$_4^+$ ions will cause the resulting potential value to decrease. This is because at low concentrations, the number of ions that arrive at the transducer surface is also less, making it difficult to affect the potential on the surface of the transducer [8].

Figure 1 also shows a phenomenon of the potential value of the membrane at a temperature of 40°C greater than 25°C. This corresponds to the Nernst equation phenomenon, where temperature changes cause changes in ionic motion and thermodynamic equilibrium [10]. This is inseparable from the MB28 membrane properties that have lower flexibility and Tg properties than PVC, so that with the presence of MB28 will increase the PVC flexibility [4]. The increasing flexibility of this PVC membrane will help the movement of the NH$_4^+$ ions in the membrane to be better. This is also supported by the data in the Table 1 which shows better Nersntian’s number for the hybrid of the PVC/MB28 membranes.

| Table 1. Performance of the ISE-NH$_4^+$ sensor at 25°C and 40°C |
|------------------|------------------|------------------|------------------|------------------|
| Membrane        | T(°C) | Slope(mV/dec) | Linear Range (M) | R$^2$       | LOD (M)         |
| PVC/MB28        | 25    | 55.4           | 0.1 – 10$^{-5}$   | 0.9989     | 5.43 x 10$^{-6}$ |
|                 | 40    | 58.7           | 0.1 – 10$^{-5}$   | 0.9999     | 5.01 x 10$^{-6}$ |
| PVC             | 25    | 54.2           | 0.1 – 10$^{-5}$   | 0.9990     | 4.79 x 10$^{-6}$ |
|                 | 40    | 35.3           | 0.1 – 10$^{-3}$   | 0.9293     | 1.51 x 10$^{-4}$ |
Apart from Tg, the membrane must have good adherence to the electrode surface. It is important to note that if the membrane fails to adhere properly to the surface of the electrode, it will cause the ions from the sample to move directly to the transducer surface without diffusing through the membrane. This condition will cause the sensor response to be disturbed [5-6]. This can be seen in figure 1 and table 1 above. It is seen that at the measuring temperature of 40°C, the response given by the ISE-NH₄⁺ sensor is limited within the range 0.1-10⁻³ M range wherein a Nersntian’s value of only 35.3 mV/dec, far from the ideal Nernstian’s number of 59 mV/dec [2]. This is inseparable from the fact that the PVC membrane on the surface of the transducer is detached as shown in Figure 2 below which is observed using an optical microscope. While the ISE-NH₄⁺ sensor using a hybrid PVC/MB28 membrane still shows good adhesive capability on the transducer surface.

![PVC membrane (detached)](image)

![PVC/MB 28 membrane (strong adhesive)](image)

**Figure 2.** The membrane conditions after measurement at 40°C, (a) PVC membrane and (b) the hybrid membrane of PVC/MB28

The hybrid membrane capability of PVC/MB28 remains viable even when measurements at high temperatures are inseparable from MB28 membrane membranes characteristics that have good adhesion to the transducer surface, thus retaining the PVC to adhere to the surface of the transducer [4]. Meanwhile, in the ISE-NH₄⁺ sensor using only PVC membrane, it fails to maintain its adherence. This cannot be separated from the plasticizer used will generally experience leaching when the sample temperature is increased. This effect in a higher Tg membrane value and causes the membrane to become more rigid, which brings consequences on the adhesive ability of the membrane to decrease [6].

Beside the Nernstian number, another important parameter that needs to be tested from an ISE is selectivity [11]. In this research, the selectivity testing is performed by using some interfering ions from the alkali and alkaline earth metals such as Li⁺, Na⁺, K⁺, Ca²⁺ and Mg²⁺. The test was performed using the SSM method [7], in which the test solution used had a concentration of 0.1 M. The result of selectivity testing can be seen in table 2 below. This selectivity test is carried out at 25°C and 40°C, which is specific to PVC membranes only at 25°C. This is because at a temperature of 40°C, the PVC membrane detaches from the transducer surface as can be seen in Figure 2 above.

| Interfering Ions | PVC/MB 28 (25°C) | PVC/MB 28 (40°C) | PVC (25°C) |
|------------------|-----------------|-----------------|-----------|
| Li⁺              | -3.82           | -3.75           | -3.89     |
| Na⁺              | -2.86           | -2.91           | -2.82     |
| K⁺               | -1.21           | -1.05           | -1.17     |
| Ca²⁺             | -4.13           | -3.98           | -4.20     |
| Mg²⁺             | -4.32           | -4.38           | -4.27     |

Based on table 2 above, it is seen that the value of selectivity coefficient is not much different for each measurement. This suggests that the presence of the MB28 membrane on the PVC membrane does not affect the value of selectivity. This is inseparable from MB28 membrane characteristics which have good flexibility properties, so the process of ion movement and also the recognition process between nonactine with the target ion in the ISE-NH₄⁺ sensor membrane is not inhibited. Based on the data
shown in Table 2, the measurement shows that the greatest interference is given by K⁺ ions. A large interference of the K⁺ ions is due to the size of the NH₄⁺ ions and the K⁺ ions is almost the same [5]. This almost equal ion size causes the ionic affinity to be almost the same [12]. This brings consequences to the interaction ability between the a K⁺ ions and nonactine as the recognition element in the membrane will be almost equal to the interaction ability between the a NH₄⁺ ions and nonactine.

4. Conclusion
Development of ISE-NH₄⁺ sensor based on the a hybrid membrane of PVC/MB28 has been successfully done. The developed ISE-NH₄⁺ sensor performs better than the PVC-based ISE-NH₄⁺ sensor. The addition of MB28 into the PVC membrane has been able to improve the mechanical strength of the PVC membrane without decreasing the performance of the ISE-NH₄⁺ sensors.

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6. References
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