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Plasticizer for Liquid Polymeric Membrane of Ion Selective Electrode Based on Thiazole Derivatives as Ionophore

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ABSTRACT. Ion selective electrode (ISE) is an electrode that has been designed to identify heavy metal ion in a solution. In this experiment, thiazole-4-carboxamide (Th) is used as ionophore and sodium tetraphenylborate (NaTPB) as an additive. Polyvinyl chloride (PVC) was used as a polymeric matrix in the membrane selective electrode. Different type of commonly used plasticizers is analysed to choose the one with the best response. There are four types of plasticizer used; dioctyl phthalate (DOP), dibutyl phthalate (DBP), benzyl acetate (BA) and nitrobenzene (NB). The ratio (w/w)% used for all plasticizers Th:PVC:NaTPB:Plasticizer is 5.0:30.0:2.0:63.0. ISE is used in a sample solution with different concentration to figure out the best plasticizer. Ion selective membrane using BA gives the best response with 19.3±1.4 slope value, while ion selective membrane using DOP gives the least response with 11.3±0.7 slope value.

Keywords: *Plasticizer, Polymeric membrane, Ion selective electrode, Ionophore;*

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1. INTRODUCTION

Ion Selective Electrode (ISE) has been widely used in many types of research for years. ISE is a sensor with a membrane that has potential to select specific ion and known as specific ion electrode. It indicates the activity of the ion dissolved in a solution and converts it into an electrical potential. There are four types of ISE which are glass membrane electrode, solid state electrode, liquid membrane electrode and gas sensing electrode. Liquid membrane electrode is designed using ion selective membrane as a main part of the electrode. The advantages of using liquid membrane are due to its high selectivity, efficient and effective.

In addition, specific molecular recognition can be achieved with the aid of suitable ion carriers for the transport mechanism [1]. Fig. 1 shows the components of ISE consist of four parts, which are the body, the electrode, inner solution and at the bottom which is the main part, the liquid membrane.

The liquid membrane is made of four components; polymeric matrix, ionic addictive, ionophore, and plasticizer. It is generally accepted that the components of the membrane, such as the carrier, ionic additives, and plasticizer influence the response and lifetime of the electrode [2]. Table 1 shows all of the membrane's component and its function.

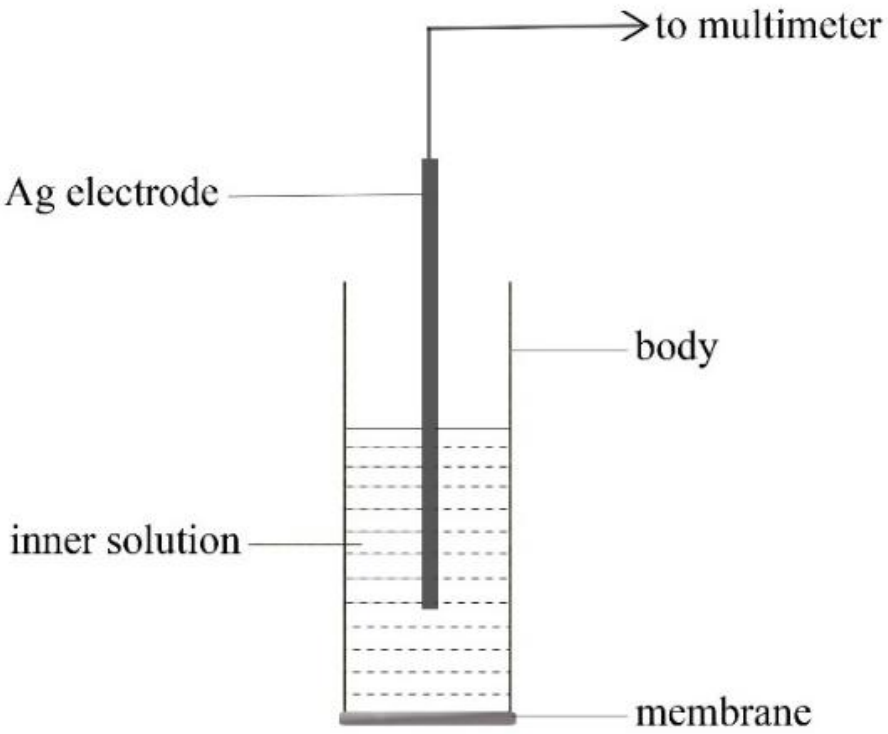

Fig. 1 Ion Selective Electrode (ISE)

Table 1 The component of the liquid membrane and its function

Component	Compounds	Function
Polymeric membrane	Polyvinyl chloride (PVC)	To provide elasticity properties in the membrane
Ionic addictive	Sodium tetraphenylborate (NaTPB)	To induce a selective response when there is insufficient ionophore amount is present [1]
Ionophore	Thiazole-4-carboxamide (Th)	As an ion exchanger
Plasticizer	Dioctyl phthalate (DOP), Dibutyl phthalate (DBP), Benzyl acetate (BA), Nitrobenzene (NB)	To increase the plasticity or fluidity of the membrane

Fig. 2 shows a structure of thiazole-4-carboxamide (Th) that act as ionophore in this experiment. The ideal plasticizer should have the following properties: softens the PVC membrane, solubilizes the ionophore, insoluble in water, and is inert with respect to ion exchange [3]. The plasticizers must have plasticity or fluidity properties to be physically compatible with the polymer, so as to give a homogeneous organic phase [4]. In contrast, the plasticizer must have solubility properties to be compatible with the chosen ionophore. These plasticizers must be fulfilled the four criteria such as high lipophilic, soluble with no crystallize formed,

no exudation and give a better selective behavior of ISE [5]. The appropriate plasticizer to use in the sensor membrane specifies that the lipophilicity of the plasticizer should be as close as possible to that of the ionophore [3].

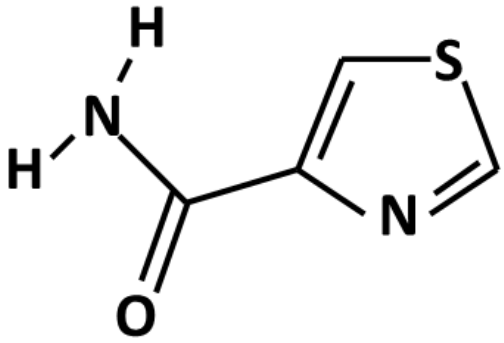

Fig. 2 Structure of thiazole-4-carboxamide (Th)

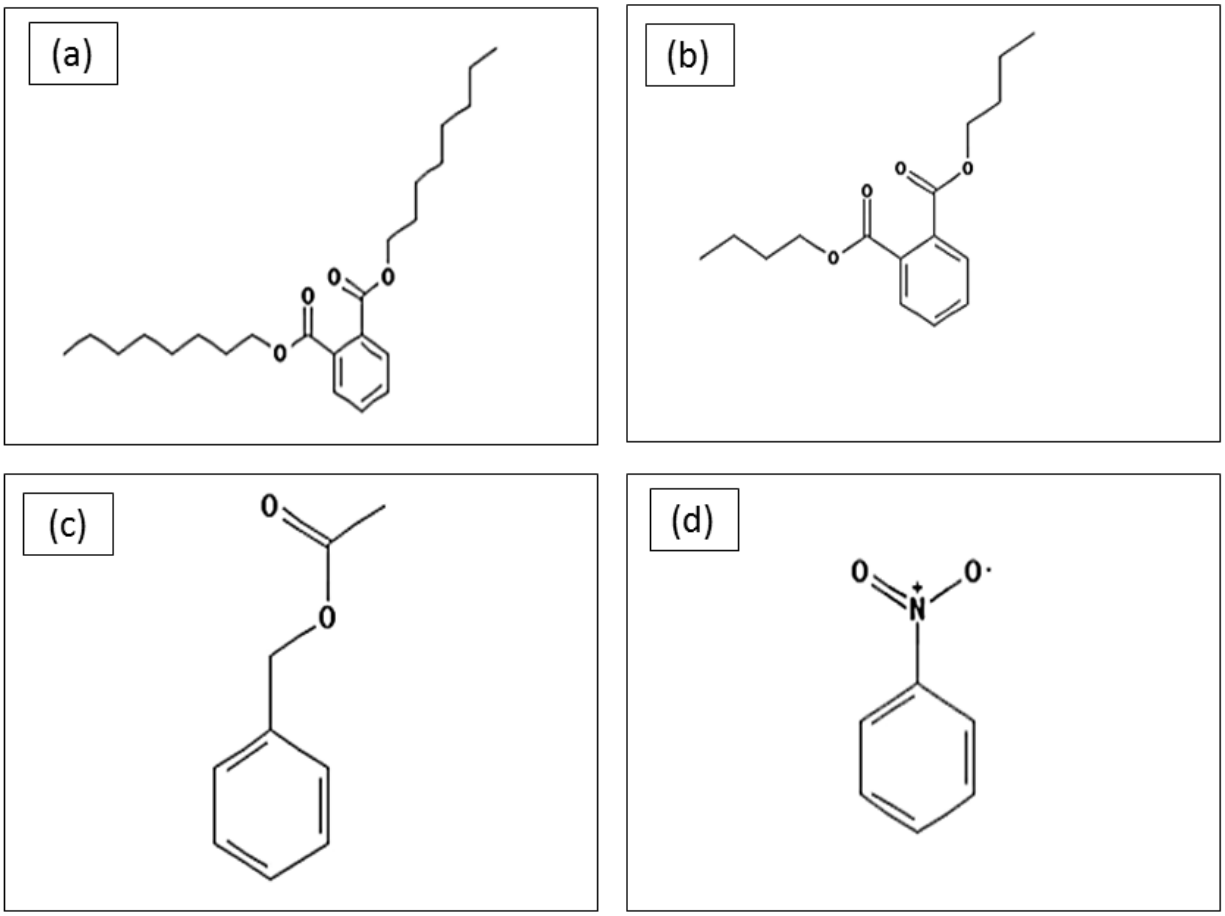

Fig. 3 The structure of plasticizer (a) Dioctyl phthalate (DOP), (b) Dibutyl phthalate (DBP), (c) Benzyl acetate (BA) and (d) Nitrobenzene (NB)

DOP is an ester of phthalic acid that appears as a light colored, odorless liquid and is used as a plasticizer for many resins and elastomers. DOP has good stability to heat and ultraviolet light, excellent resistance to hydrolysis and has a broad range of compatibility. DOP also insoluble in water and can be used as softening agent, because of its good plasticizing properties; can make long polymers molecules to slide against one another. DBP is in the same phthalate group with DOP, which is an ester and light colored, odorless liquid. DBP has the same properties with DOP; insoluble in water and can be used as softener mainly in adhesives, lacquers, varnishes and printing inks. DBP appears to have relatively low and chronic toxicity.

BA is an ester formed by condensation of benzyl alcohol and acetic acid. It from Benzyloxycarbonyls family; organic compounds that containing a carbonyl group substituted with a benzyloxyl group. BA can be found naturally in many flowers. It appears as a colorless liquid with an odor of pears and has a very low solubility in water. Whereas NB that emits toxic fumes of nitrogen oxides upon combustion is a yellowish, oily, aromatic nitro-compound with an almond-like odor. It's very slightly soluble in water but freely soluble in ethanol, ether, acetone and benzene. Fig. 3 shows the structure of each plasticizer. All these plasticizers are used in the experiment to choose the most suitable plasticizer for ISE. Although the rate ion exchange of plasticizer is small compared to the rate ion exchange of ionophore, the plasticizer is important in the membrane as it does not just soften the membrane but it also helps to increase the selectivity of ISE without interfering with ion exchange of ionophore. The plasticizer in the membrane also had a large effect on sensitivity, selectivity and useable service life [3]. The objective of this study is to select the best plasticizer from a various range of plasticizers (dioctyl phthalate (DOP), dibutyl phthalate (DBP), benzyl acetate (BA) and nitrobenzene (NB)) for ISE with thiazole-4-carboxamide (Th) as an ionophore using $Cd(NO_3)_2$ solution as analyte.

2. MATERIALS AND METHODS

2.1 Electrode Preparation. A 100 mg liquid membrane is prepared with a ratio 5.0:30.0:2.0:63 for Th:PVC:NaTPB:plasticizer. All of the components are measured respectively in 100 ml of beaker before completely dissolved in 5 ml of THF. Then, a PVC tube is dipped in the solution until a nontransparent membrane is formed at the bottom of the tube. The tube was kept for 24 hours at room temperature before finally conditioned it in the sample solution for 20 hours or until it gives a stable reading [6].

The membrane is conducted in cell assembly Ag/AgCl| KCl (3 mol/L)| internal solution (1.0×10^{-1} mol/L $Cd(NO_3)_2$)| membrane| sample solution| reference electrode to measure the potential difference of the electrode. An Extech EX420: 11 function professional multimeter was used to measure the potential at 21±1 °C.

***2.2 Sample Preparation*.** 7.71 g of $Cd(NO_3)_2$ powder is dissolved using deionized water in a 200 ml beaker and diluted to 250 ml volumetric flask labelled as A (1.0×10^{-1} mol/L $Cd(NO_3)_2$ solution). Pipette 25 ml solution A before diluted with deionized water in 250 ml volumetric flask and labelled as B (1.0×10^{-2} mol/L $Cd(NO_3)_2$ solution). The dilution process is accordingly to 1.0×10^{-3} mol/L $Cd(NO_3)_2$ solution, 1.0×10^{-4} mol/L $Cd(NO_3)_2$ solution, 1.0×10^{-5} mol/L $Cd(NO_3)_2$ solution, 1.0×10^{-6} mol/L $Cd(NO_3)_2$ solution, and 1.0×10^{-7} mol/L of $Cd(NO_3)_2$ solution and labelled as G.

3. RESULTS AND DISCUSSIONS

Four sensors have been prepared using same ratio and ionophore for the membrane, each sensor gives a different response behavior. The typical composition of solvent polymeric membranes is 30-33% (w/w) PVC and 60-66% of a plasticizer [1,4]. The sensitivity and selectivity of the ion selective electrodes depend significantly on the membrane compositions [7]. Addition of appropriate amount of plasticizer leads to

improve the electrochemical properties of conventional ISEs [6]. The right plasticizer leads to a better polymeric membrane and can form a high selectivity ISE. Fig. 4 shows a graph of the potential difference of ISE against log concentration of sample solutions

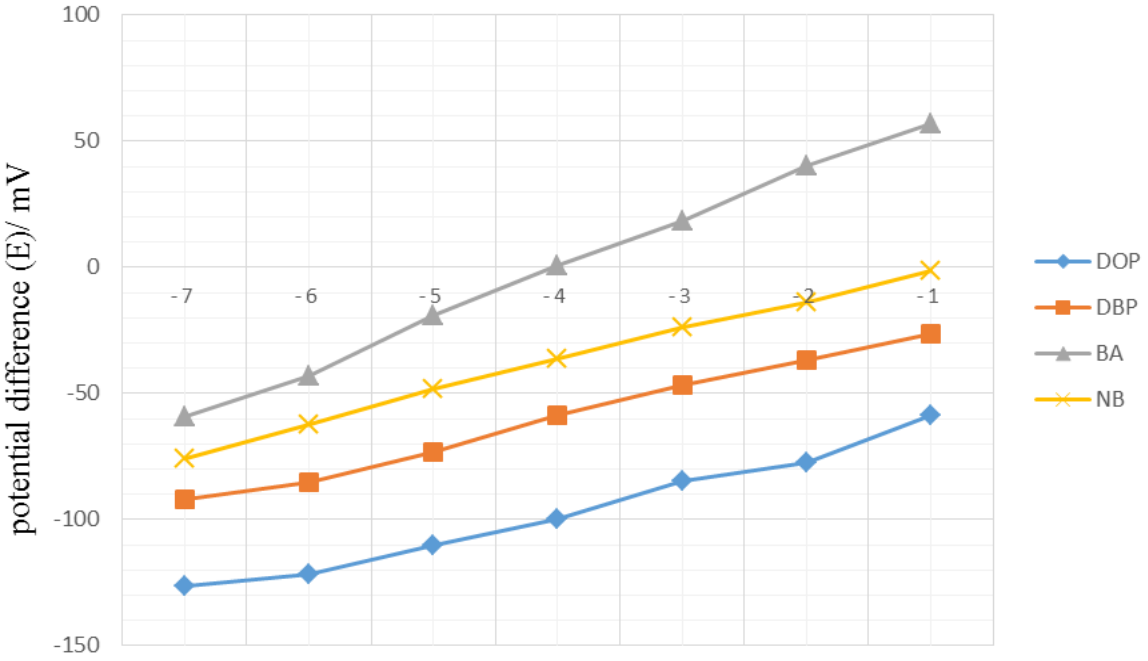

Fig. 4 Graph of E/mV vs log concentration

The graph shows four different slopes; DOP, DBP, BA and NB. The potential difference between the liquid membrane and the sample solution were plotted in the graph. The slope indicates the reaction of ion in the sample solution with the liquid membrane. Different slopes are patterned as a different content of liquid membrane are used. All ISE used was labelled as Sensor No.1 for Th:PVC:NaTPB:DOP; (5.0:30.0:2.0:63.0), Sensor No.2 for Th:PVC:NaTPB:DBP; (5.0:30.0:2.0:63.0), Sensor No.3 for Th:PVC:NaTPB:BA; (5.0:30.0:2.0:63.0) and Sensor No.4 for Th:PVC:NaTPB:NB; (5.0:30.0:2.0:63.0) in Table 2. The slope value and linear range are recorded.

Table 2 Optimization ratio of liquid membrane for $Cd(NO_3)_2$ solution ISE sensor

Sensor No.	Composition [wt.%]				Slope [mV/decade]	Linear range [M]
	PVC	Plasticizer	NaTPB	Th		
1	30	DOP, 63	2	5	11.3±0.7	1.0×10^{-6} to 1.0×10^{-4}
2	30	DBP, 63	2	5	11.7±0.8	1.0×10^{-6} to 1.0×10^{-3}
3	30	BA, 63	2	5	19.3±1.4	1.0×10^{-6} to 1.0×10^{-2}
4	30	NB, 63	2	5	12.4±1.2	1.0×10^{-7} to 1.0×10^{-3}

Sensor No.3 has the highest slope compared to others sensor. The highest slope is 19.3±1.4 with 1.0×10^{-6} to 1.0×10^{-2} of working range. While Sensor No. 1 has the lowest value, 11.3±0.7 with 1.0×10^{-6}

to 1.0×10^{-4} of working range. As the highest slope indicates the high response in the sensor, Sensor No.3 which is BA has the best response compared with other sensors.

The result clearly shows the effect of the plasticizer in ISE. When a plasticizer is added, the free volume of the polymeric chain is expanded, making penetration of an analyte easier, increasing its interaction with the sensing phase [8]. The nature of plasticizer affects the response characteristics of the electrode, due to its influence on the dielectric constant of the membrane phase, the mobility of ionophore molecules and the state of the ligand [4].

4. SUMMARY

A sensor that made up with a membrane containing ionophore is adequate to form a sensor that works properly. However, choosing a compatible plasticizer is important to get the best selective sensor. From the experiments, it is found that BA is the best plasticizers as it responded well as compared to the other plasticizers.

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REFERENCES

[1] F. Faridbod, M.R. Ganjali, R. Dinarvand, P. Norouzi, The fabrication of potentiometric membrane sensors and their applications, Afr. J. Biotechnol., 25 (2007) 2960-2987.

[2] E.M. Zahran, A. New, V. Gavalas, L.G. Bachas, Polymeric plasticizer extends the lifetime of PVC-membrane ion-selective electrodes, Analyst., 139 (2014) 757-763.

[3] C. Carey, Plasticizer effects in the PVC membrane of the dibasic phosphate selective electrode, Chemosensors, 3 (2015) 284-294.

[4] M.R. Pourjavid, M. Razaee, M. Hosseini, T. Razavi, Monitoring of praseodymium(III) ions in aqueous solutions, soil and sediment samples by a PVC membrane sensor based on a Furan-Triazole Derivative, Quim. Nova, 35 (2012) 1973-1980.

[5] R. Eugster, T. Rosatzin, Plasticizers for liquid polymeric membranes of ion-selective chemical sensors, Anal. Chimica. Acta, 289 (1994) 1-13.

[6] M.R. Pourjavid, T. Razavi, 2-amino-4-(4-aminophenyl) thiazole application as an ionophore in the construction of a Lu(III) selective membrane sensor, Chin. Chem. Lett., 23 (2012) 343-346.

[7] M.P. Mahmoodabadi, H.A. Zamani, S. Pasyar, Design of highly selective and sensitive pvc-membrane sensor for terbium ions based on Di(N-succinimidyl) carbonate as a neutral ion carrier, Int. J. Electrochem. Sci., 8 (2013) 4010-4022.

[8] O.V. Gurtova, L. Ye, F.A. Chmilenko, Effect of plasticizer on the characteristics of molecularly imprinted polymer based potentiometric sensor for propranolol, Bulletin of Dnipropetrovsk University: Series Chemistry, 21 (2013) 20-34.