COBALT(II) SELECTIVE MEMBRANE ELECTRODE BASED ON PALLADIUM(II) DICHLORO ACETYLTHIOPHENE FENCHONE AZINE

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DECLARATION

I hereby declare that the work in this dissertation is own except for quotation and summaries which have duly acknowledged.

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ABSTRACT

This study described the fabrication and characterisation of membrane based on palladium(II) dichloro acetylthiophene fenchone azine **(I)** as cobalt(II) ion-selective electrode. The ion-selective electrode was simple, inexpensive, good selectivities, shown a rapid respond and long-lasting. The membrane fabrication processes involved many different membrane compositions and the best membrane composition obtained was 10:60:5:21.12 (**I**)/PVC/NaTPB/DOP (w/w). The electrode exhibits a Nernstian response in the range of 1.0 x 10^{-1} to 1.0 x 10^{-6} M with a detection limit of 8.0 x 10^{-7} M and slope; 29.6 ±0.2 mV per decade respectively. The response time is within the range of 20-25 s and can be used for a period up to 4 months. The electrode showed good selectivity towards cobalt(II) ion in the presence of a number of interfering cations and could be used in pH range of 3-7. The proposed electrode also can be used for the determination of cobalt(II) ion in real samples. The results shown that the concentration of ion cobalt(II) obtained by the proposed membrane were in good agreement with those obtained by atomic absorption spectrophotometer.

ELEKTROD MEMBRAN PEMILIH KOBALT(II) BERASASKAN *PALLADIUM(II) DICHLOROACETYLTHIOPHENE FENCHONE AZINE*

ABSTRAK

Kajian ini menghuraikan penyediaan dan pencirian membran berasaskan palladium(II) dikloro asetiltiofen fencon azin **(I)** sebagai elektrod pemilih ion kobalt(II). Elektrod pemilih ion ini ringkas, murah, kepilihan yang baik, menunjukkan gerak balas yang pantas dan tempoh hayat yang panjang. Proses penyediaan membran melibatkan banyak komposisi membran yang berbeza dan komposisi membran terbaik yang didapati ialah 10:60:5:21.12 (**I**)/PVC/NaTPB/DOP (w/w). Elektrod ini menunjukkan gerak balas Nernstian dalam julat 1.0 x 10^{-1} hingga 1.0 x 10^{-6} M dengan had pengesanan 8.0 x 10^{-7} M dan kecerunan; 29.6 ±0.2 mV per dekad. Masa gerak balas elektrod adalah dalam julat 20-25 saat dan ia boleh digunakan dalam tempoh masa sehingga 4 bulan. Elektrod ini menunjukkan kepilihan yang baik terhadap ion kobalt(II) dalam kehadiran beberapa kation pengganggu dan boleh digunakan dalam julat pH 3-7. Elektrod yang dihasilkan ini juga boleh digunakan untuk menentukan ion kobalt(II) dalam sampel sebenar. Keputusan menunjukkan kepekatan ion cobalt(II) yang didapati oleh elektrod yang dihasilkan setara dengan yang didapati oleh spektrofotometer serapan atom.

TABLE OF CONTENTS

Page

CHAPTER 1 INTRODUCTION

CHAPTER 2 **LITERATURE REVIEW**

CHAPTER 3 **EXPERIMENTAL**

CHAPTER 4 **RESULT AND DISCUSSION**

CHAPTER 5 CONCLUSION

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrometry
Ag/AgCl	Silver/silver chloride
BA	Benzyl acetate
BBPA	Bis(1-butyl-pentyl) adipate
BD	α-benzil dioxome
BEHA	Bis 2-(ethylhexyl) adipate
BPPH	2-benzoylpyridine-2-pyridylhyrazone
BSOPD	Bis(salicylaldehyde)orthophenylenediamine
CMCPE	Chemically modified carbon paste electrode
CO_2	Carbon dioxide
CPE	Cloud point extraction
CWE	Coated-wire electrode
DBS	Dibutylsebacate
DEHA	Di-(2-ethylhexylexyl)adipate
DHMP	4,6-dihydroxy-2-mercaptopyrimidine
DLLME	Dispersive liquid–liquid microextraction
DMG	Dimethylglyoxime
DNP	Dinonylphthalate
DOP	Di-sec-octyl phthalate
DOPP	Dioctylphenylphosphonate
DOS	Dioctyl sebacate
DPASV	Differential pulse absorptive stripping voltammetry
DPTH	1,5-bis-(di-2-pyridylmethylene) thiocarbonohydrazine
ETAAS	Electrothermal atomic absorption
FAA	Flame atomic absorption
FAAS	Flame atomic absorption spectrometry
FET	Field effect transistor
FIE	Flow injection extraction

FIM	Fixed interference method
GF-AAS	Graphite furnace-atomic absorption spectrometry
H_3O^+	Hydronium ion
HCl	Hydrochloric acid
HIMH	Isonitroso-5-methy-2-hexanone
HPLC	High performance liquid chromatography
HPSAM	H-point standard addition method
ISE	Ion-selective electrodes
ISFET	Ion-sensitive field effect transistor
KCl	Potassium chloride
KTpClPB	Potassium tetrakis(4-chlorophenyl)borate
LaF_3	Lanthanum fluoride
LLE	Liquid–liquid extraction
MC	Microcolumn
MIBK	Methyl isobutylketone
MOImCl	1-methyl-3-octylimidazolium chloride
MPM	Matched potential method
MPT-AES	Microwave plasma torch-atomic emission spectrometric
NaCl	Sodium chloride
NaF	Sodium fluoride
NaOH	Sodium hydroxide
NaTFPB	Sodium tetrakis(4-fluorophenyl)borate dehydrate
NaTPB	Sodium tetraphenyl borate
NH_3	Ammonia
NN	1-nitroso-2-naphthol
NO	Nitrogen oxide
OA	Oleic acid
o-NPPE	2-nitrophenyl phenyl ether
OXCCD	1-(2-oxocyclohexyl)-1,2-cyclohexanediol
PAN	1-(2-pyridylazo)-2-naphthol
PVC	Poly(vinyl chloride)
SCE	Saturated calomel electrode
SPE	Solid phase extraction

SSM	Separate solution method
TBP	Tri-n-butyl phosphate
TDA_2CO_3	Tetradecylammonium carbonate
TEHP	Tris(2-ethylhexyl)phosphate
THF	Tetrahydrofuran
THTDPCl	Trihexyltetradecylphosphonium chloride
TLS	Thermal lens spectrometry
TMDP	Tetraethyl methylenediphosphonate
TOMACl	Trioctylmethylammonium chloride
Triton X-114	Octylphenoxypolyethoxyethanol
TS-FF-AAS	Thermospray flame furnace atomic absorption spectrometer
UV-VIS	Molecular absorption spectrometry

CHAPTER 1

INTRODUCTION

1.1 Introduction to Cobalt

Cobalt is a hard ferromagnetic, silver-white, hard, lustrous, brittle element. In the periodic table, it situated in Group VIII together with rhodium, iridium and unnilennium. It has a molecular weight of 58.9, atomic number of 27 and has four oxidation states (0, +2, +3 and +4) while the +2 and the ground state are the most (Chang, 2002).

Cobalt is active chemically and forming various compounds likes cobalt(II) hydroxide and cobalt(II) carbonate. Cobalt is stable in air and unaffected by water, but is slowly attacked by dilute acids (Boeck, Volders, & Lison, 2003). Cobalt(IV) is the highest oxidation state but it is far less important than cobalt(III) and cobalt(II).

Cobalt(I) and lower oxidation states are stabilised in organometallic species by π-acceptor ligands.

There are few binary compounds of cobalt(III) and only a limited number of cobalt(III) compounds commercially available. The only binary halide is brown cobalt(III) fluoride which is isostructural with iron(III) fluoride. It is used as fluorinating agent, in preparing perfluorinated organics, and is corrosive and an oxidant (Cotton, Wilkinson, Murillo, & Bochmann, 1999)

In the field of metallacarborane chemistry, cobalt(III) ion has been inserted into carborane anions in solution to prepare cobaltabisdicarbollide (Cotton, Wilkinson, Murillo, & Bochmann, 1999). Cobaltabisdicarbollide has been used as a model compound in the development of radiotransition-metal carriers for the antibodymediated y-imaging and P-therapy of tumour (Harwell, Nabakka, Knobler, & Hawthorne, 1995), development of ion-selective PVC membrane electrode for tuberculosis drug analysis (Stoica, Vinas, & Teixidor, 2008) and also in preparing membrane for enantiomer recognition with no chiral additives (Stoica, Vinas, & Teixidor, 2009).

Compared to cobalt(III), cobalt(II) forms a number of simple compounds. Reaction of anhydrous cobalt(II) chloride with hydrofuran at 570 K produce pink cobalt(II) fluoride while blue cobalt(II) chloride is made by combination of the elements and has a cadmium(II) chloride-type structure and it turns pink if expose to moisture and readily forms hydrates. The dark pink hexahydrate is an ordinary starting material in cobalt(II) chemistry and commercially available. The sparingly soluble cobalt(II) hydroxide may be pink or blue, with the pink form being the more stable, freshly precipitated blue cobalt (II) chloride turns pink on standing (Housecroft & Sharpe, 2008).

Cobalt is both a toxic and an essential element. In the form of Vitamin B12, cobalt is an essential component of the human diet and established treatment for anaemia. However, it has been recognised that side effects can occur, particularly toxicity to the thyroid (Bianci, Bertanza, Pietre, & Sabbioni, 1989). Polycytemia (an abnormal increase in the number of red blood cells in the blood) and hematopoiesis (the production of all types of blood cells generated by a remarkable self-regulated system) has also been observed in several intake of cobalt orally per day (Alexander, 1972). Cobalt known as one of the four most common contact allergens for the general population and it is often combined with sensitisation to nickel (Fisher & Rystedt, 1983; Cirla, 1994; Cugell, Morgan, Perkins, & Rubin, 1990; Forni, 1994; Lauwerys & Lison, 1994; Rizzato, 1997).

Exposure to cobalt can give rise to a number of adverse health effects such as pneumoconiosis, bronchoconstriction, cough and asthma which known as ‘hard metal diseases’ (Roto, 1980). Various organs and tissues like the respiratory organs, skin and myocardium are most likely to be infected by occupational exposure to cobalt or its inorganic compounds (Nordberg, 1994). In France, an increased occurrence of lung cancer has been noted in cobalt workers in an electrochemical plant (Coates and Watson, 1971; Mur, Moulin, Seinerra, & Lafitte, 1987; Hogstedt & Alexandersson, 1990). Obstructive ventilatory changes and/or asthmatic symptoms have been reported to occur at cobalt exposures of 10-150 g/m^3 for varying periods and irritation of mucous membranes may occur at an even lower concentration of cobalt in industrial air 5-10 g/m^3 (Roto, 1980).

However, cobalt is also known as an essential component of several enzymes and co-enzymes that has been shown to affect growth and metabolism of plants depending on the concentration. Cobalt has been shown to alter the sex of plants like cannabis sativa, lemna acquinoclatis, and melon cultivars.

Low concentration of cobalt(II) in medium stimulates growth from simple algae to complex higher plants but relatively higher concentrations are toxic. The toxic effects of cobalt include leaf fall, inhibition of greening, discoloured veins and premature leaf closure while the beneficial effects of cobalt include retardation of senescence of leaf, increase in drought resistance in seeds, regulation of alkaloid accumulation in medicinal plants, and inhibition of ethylene biosynthesis (Palit, Sharma, & Talukder, 1994) .

1.2 Introduction to Palladium

Palladium is one of the common precious metals. It is lustrous, corrosion-resistant, silver-white metal with a great ability to absorb hydrogen. Palladium is widely used in different areas. Palladium can resembles platinum’s character such as easy to form complex with others substances. Other than that, palladium also cheaper compare to platinum. Both metals widely used as catalyst because of its activities.

The importance of the palladium has grown many folds in recent years due to the increasing applications for the production of dental and medical devices, jewellery, automobile and catalytic converters (Rao & Reddi, 2000). Palladium is also finds an extensive use in the electrical industry as contacts in telephone relays and printed circuits, as grid for electronic tubes, electrodes for high quality spark plugs, very small multilayer ceramic capacitors and thick-film resistors or conductor (Daniel, Gladis, & Rao, 2003).

Palladium, rhodium and platinum are the platinum group metals (PGMs) that mostly used for producing catalytic converters for the treatment of pollutants. The production and recycling of catalytic converters in the metal finishing industry can cause toxicity to mammals, fish and higher plants (Raber, Kalcher, Neuhold, Talaber, & Kolbr, 1995; Schramel, et al., 2000; Limbeck, Rendl, & Puxbaum, 2003).

Palladium compounds have been reported as potential health risks to humans, causing asthma, allergy, rhino conjunctivitis and other serious health problems (Ketel & Ntebber, 1981; Merget & Rosner, 2001; Ravindra, Bencs, & Grieken, 2004; Liang, Zhao, & Li, 2009). The obvious paths of exposure are contact from use of dental appliances and jewellery. But other exposures pathways such as inhalation of palladium released from pollution caused by the mining also be considered (Kielhorn, Melber, Keller, & Mangelsdorf, 2002).

1.3 Introduction to Chiral Ligand

Since 1870’s, the concept of chiral ligand has been known in chemistry. However, chemists were started using this term after nearly hundred years later. The first edition of Eliel's "Stereochemistry of Carbon Compounds" in 1962 (Eliel, 1962), the word chiral is not mentioned but it was using in later editions (Eliel & Wilen, 1994). The usage of chiral ligands in pharmacology, industry and agriculture become prominent this day.

For example, the (R)-(+) enantiomer is the active enantiomer in killing the weeds, while the (S)-(-) enantiomer is inactive as an herbicide (Zipper, et al., 1999 ; Lewis, Garrison, Wommack, Whittemore, Steudler, & Melillo, 1999; Hegeman & Laane, 2002). In pharmacology, chirality is an important factor in drug efficacy (Rentsch, 2002). One of the earliest known uses of a chiral compound to cure a disease is the case of Quinine (vis-à-vis Cinchona alkaloids) (Arango, 1949). Another early use of a chiral compound to cure a disease is the case of Vitamin C.

1.4 Significance of Study

Some trace elements, such as cobalt, are essential to man, whose daily requirement is only a few milligrams. However, if ingested in high levels, this can be harmful to human health. The content of the element in water, sediment, plants and animals can also provide important information on levels of contamination in the environment (Teixeira, Costa, Assis, Ferreira, & Korn, 2001). The quantification of metal species in various matrices has been performed by a number of sophisticated methods such as flame atomic absorption (FAA) (Cadore, Goi, & Baccon, 2005), electrochemiluminescence (Zhang, Zhou, Hao, He, & Fang, 2005), thin film sequential injection (Staden & Talijaard, 2004), graphite furnace-atomic absorption spectrometry (GF-AAS) (Belarra, Crespo, Garbayo, & Resano, 2003), electrothermal-atomic absorption spectrometry and differential pulse anodic stripping voltammetry (Lu, Geng, Kang, & Gao, 2000).

However, these techniques apply sample manipulation which are time-consuming and use large amounts of high purity solvents that are expensive and toxic. Furthermore, these techniques not have adequate sensitivity and selectivity (Wen, Wu, Xu, Wang, & Hou, 2009).

A wide variety of chelating agents have been reported for the spectrophotometric determination of cobalt (More & Sawant, 1992; Reddy & Sarma, 1994; Kamburova, Alexandrov, & Trifonov, 1994). Nevertheless, these methods suffer from limitations such as critical pH (Silva & Martins, 1992; Maheshwari & Balasubramanian, 1995; Pillai & Shinde, 1995), long extraction time (Belarra, Crespo, Garbayo, & Resano, 2003), long colour development time (Umebayashi & Ishiguro, 1996) and interference from some ions (Silva & Martins, 1992; Maheshwari & Balasubramanian, 1995; Pillai & Shinde, 1995; Umebayashi & Ishiguro, 1996; Lu, Geng, Kang, & Gao, 2000; Cadore, Goi & Baccon, 2005; Zhang, Zhou, Hao, He, & Fang, 2005). In addition, procedures of separation or preconcentration may be required before the spectrometric determination of trace elements (Lemos, Gama, & Lima, 2006). Techniques such as liquid–liquid extraction (LLE), flow injection extraction (FIE), cloud point extraction (CPE), solid phase extraction (SPE), dispersive liquid–liquid microextraction (DLLME), new liquid-liquid extraction

(LLE) methods based on liquid membranes (Ribeiro , Costa, Lopes, Campos, Ferreira, & Salum, 2004; Kakoi, Ura, Kasaini, Goto, & Nakashio, 1998) and hollow fiber contactors (Soldenhoff, Shamieh, & Manis, 2005) were used for extraction and preconcentration of cobalt.

Selective analytical methodologies, which are easily operated and involve harmless reagents, cost effective equipment, have therefore been proposed as alternative to standard methods. Potentiometric sensors based on ion-selective electrodes are especially suited for such determination because they offer advantages such as selectivity, sensitivity, good precision, simplicity and low cost (Wipf, Pioda, Stefanac, & Simon, 1968; Hutchins & Bachas, 1995).

A literature survey revealed that the sensors developed for cobalt make use of chelates, macrocycles (Jain, Gupta, Singh, & Khurana, 1997), extractants, organic resins, mercapto compounds (Mashhadizadeh, Momeni, & Razari, 2002), OXCDD (diamide) (Ganjali, Mizani, Emami, Darjezini, Darvich, & Yousefi, 2004), Schiff base, isothiazole , calixarenes and variety of other ligands (Kumar & Shim, 2009) . However, most of these sensors suffer from disadvantages such as narrow working concentration range. With a near or non Nernstian response, exhibit high response time, poor reproducibility.

1.5 Electrochemistry

Electrochemistry is the measurement of an electrical signal generated by a chemical system in an electrochemical cell. An electrochemical cell is a device capable of either deriving electrical energy from chemical reactions, or facilitating chemical reactions through the introduction of electrical energy.

Electrochemical sensors are used to determine the concentrations of various analytes in testing samples such as fluids and dissolved solid materials. Electrochemical sensors are frequently used in occupational safety, medical engineering, process measuring engineering, environmental analysis and many more. Electrochemical sensors have electrode arrays with two, three or more electrodes, which are called auxiliary electrode, reference electrode, and working electrodes. The electrodes of an electrochemical sensor provide a surface at which an oxidation or a reduction reaction occurs to provide a mechanism whereby the ionic conduction of an electrolyte solution in contact with the electrodes is coupled with the electron conduction of each electrode to provide a complete circuit for a current. Electrochemical sensors, such as pH sensors, ion-selective sensors, and redox sensors, are equipped with electrical conductors to allow electrical signals to be transmitted to and from electrodes contained within the sensor.

There are three types of electrochemical techniques: voltammetric, potentiometric and coulometric. Potentiometry is the most commonly used of the electrochemical technique and involves the measurements of a potential generated by a cell under essentially equilibrium conditions (Frant & Ross, 1970).

1.5.1 Voltammetry

Voltammetry is an electrochemical technique that apply a time-dependent potential excitation signal to the working electrode, changing its potential relative to the fixed potential of the reference electrode and measure the current that flows between the working and auxiliary electrodes. The auxiliary electrode is generally a platinum wire, and the reference electrode is usually a saturated calomel electrode (SCE) or a silver/silver chloride (Ag/AgCl) electrode (Harvey, 2000). The resulting plot of current versus applied potential is called voltammogram (Maloy, 1983).

Voltammetry developed from discovery of polarography in 1922 by the Czech chemist Jaroslav Heyrovsky which he received the 1959 Nobel Prize in chemistry. The early voltammetric methods undergo a number of difficulties, making them less than ideal for routine analytical use. Yet, during 1960s to 1970s, meaningful advances were made in all areas of voltammetry which improved the sensitivity and expanded the repertoire of analytical methods. These advances and the occurrence of low-cost operational amplifiers promoted the rapid commercial development of relatively inexpensive instrumentation.

Analytical chemists typically use voltammetric techniques for the quantitative determination of a variety of dissolved inorganic and organic substances. Inorganic, physical and biological chemists use voltammetric techniques for variety of purposes, including fundamental studies of oxidation and reduction processes in various media, adsorption processes on surfaces, electron transfer and reaction mechanisms, kinetics of electron transfer process and thermodynamics properties of solvated species. Voltammetric methods are also applied to the determination of compounds of pharmaceutical interest. It can be effective tools for analysis of complex mixtures when coupled with high performance liquid chromatography (HPLC) (Kounaves, 1997).

1.5.2 Potentiometry

Potentiometry is the measurement of the electrical potential generated by an electrolytic cell without drawing appreciable current. In early years, potentiometric techniques have been used to locate end points in titrations (Hutchins & Bachas, 1997).

In mid 1960s, different independent achievements marked the starting point of modern potentiometry (Buck & Lindler, 2001). In more recent methods, ion concentrations are measured directly from the potential of ion-selective membrane electrodes. In 1967, Ross described the first membrane electrode based on a liquid ion exchange (Ross, 1967) while Bloch and co-workers introduced the first ionophore-based solvent polymeric membrane based on PVC, a matrix still widely used today (Bloch, Shatkay, & Saroff, 1967). Tremendous results were achieved by a number of research groups worldwide and microelectrodes were pioneered for in vivo measurements (Thomas, Simon, & Oehme, 1975).

Potentiometry has become the standard technique in the clinical analysis of ions, because of the equipment is simple and inexpensive (Pretsch, 2007). Figure 1.1 shows the schematic diagram of a simple electrochemical cell for potentiometric measurements.

Figure 1.1 Schematic Diagram of An Electrochemical Cell for Potentiometric Measurements

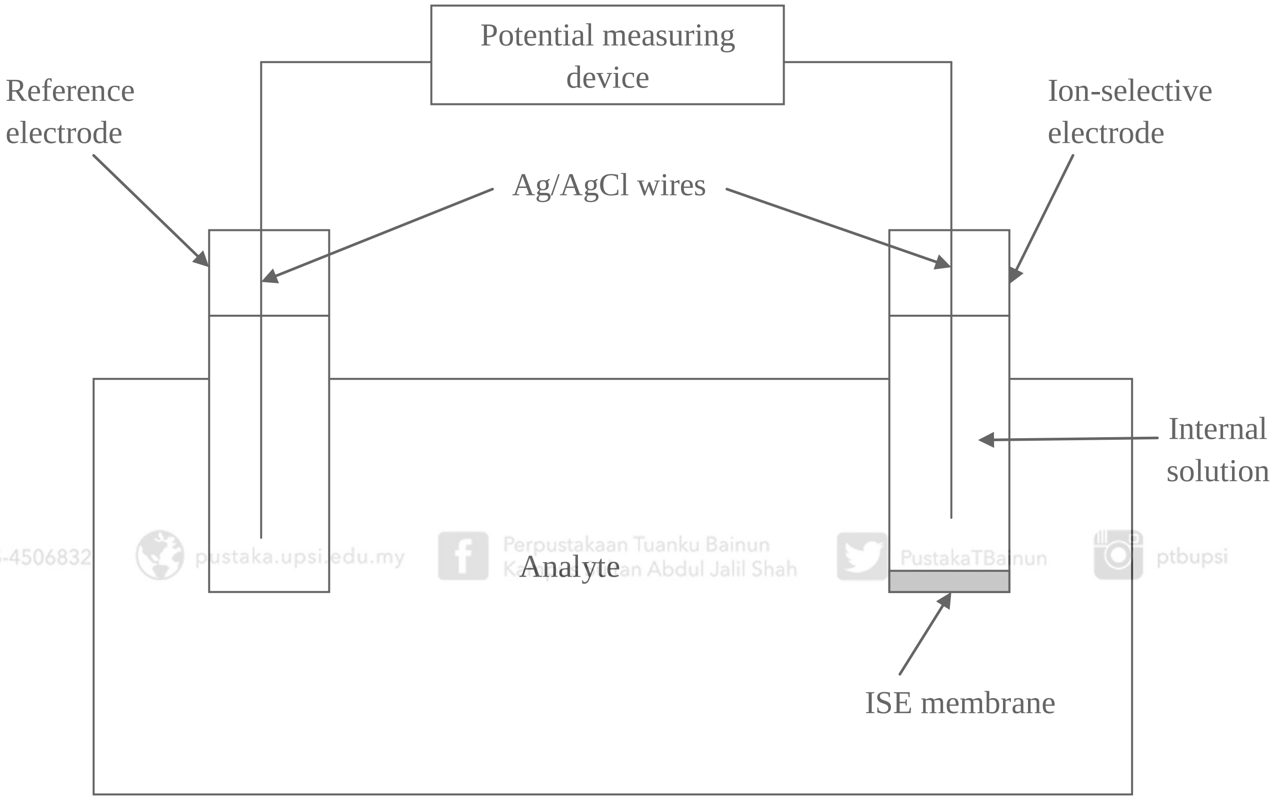


Figure 1.1 Adapted from "*Analytical Electrochemistry, 2nd Edition*" by Wang (2002)

1.5.3 Coulometry

Coulometry is an analytical method based on Faraday’s law of electrolysis and used for measuring the quantity of electrical charge required to convert a sample of an analyte quantitatively to a different oxidation state (Skoog, West, Holler, & Crouch, 2004). The measuring results depend directly on the reliability of measuring physical quantities and constants expressed in SI units and are accepted without reference to the chemical standards (Ford, 1960).

1.6 Introduction to Ion-Selective Electrodes (ISEs)

Ion-selective electrodes (ISE) are membrane electrodes that respond selectively to ions in the presence of others (Covington, 1979). ISE are mainly membrane-based devices, consisting of permselective ion-conducting materials, which separate the sample from the inside of the electrode. The membrane is usually nonporous, water insoluble and mechanically stable. The membrane mechanically prevents mixing of two electrolytes without hindering the diffusional transport of any species across the interface (Koryta, 1983). On the inside is a filling solution containing the ion of interest at a constant activity. The potential of the reference electrode is rigid and the activity of the ion in the internal solution is constant, the measured cell potential reflects the potential of the ion-selective electrode (Wang, 2000).

1.6.1 Classifications of ISEs

ISEs are classified depending on the nature of the membrane material. Classes of ISEs may be divided into six groups: glass electrode, liquid membrane electrode, solid state membrane electrode, gas sensing probe electrode, enzyme-based electrode and miscellaneous electrodes.

1.6.1.1 Glass Electrode

Over the years, several attempts have been made at constructing glass electrodes (Portnoy, 1967).Various types of glass electrodes are now available such as phosphate glasses (Truesdell & Pommer, 1963), alkali metal silicate (Sprokholt, Maas, Rebel, & Covington, 1982; Kennedy, 1983) and chalcogenide (Vlasov, Bychkov, & Medvedev, 1986).

Glass was included in voltaic piles by Ritter as early as 1802 and during the 19th century several researchers studied conduction through glass. Thomson was the first to make experiments in which the possibility of surface conduction had been excluded, and he showed that glass behaved as an electrolytic conductor.

According to Eisenman (1962), if the four-coordinated silicon atom could be replaced by another more coordinated atom which carries a larger positive charge, a positively charged site would appear, which would be expected to lead to anion-exchange properties. In conventional glass electrodes, the electrical contact between the external circuitry and the ion-sensitive glass membrane is made by means of an internal contact solution.

An glass electrode construction has obvious advantages in terms of ruggedness and application range (temperature, pressure), and is more compatible with modern manufacturing techniques. Almost all commercial glass electrode responsive to univalent cations such as hydrogen ion, sodium ion, silver ion, ammonium ion and potassium ion. Yet, several chalcogenide glass electrodes are selective towards double-charged ions such as lead ion and cadmium ion. The most common glass electrode is the pH-electrode that widely used for pH measurements (Bailey, 1980).

1.6.1.2 Liquid Membrane Electrode

Liquid membrane electrodes are widely used for direct potentiometric measurements because of their performance is good and covering a wide range of compounds compare to glass electrode or solid state electrode. However, the lifetime is not as good as the glass electrodes.

The test solution must be separated from the inner solution and an inert polymeric membrane such as PVC is used for that purpose. The membrane active component (ionophore) can be a liquid ion exchanger or a neutral carrier (Gupta & Agarwal, 2005; Syarma & Goel, 2005). The liquid ion exchanger should have a viscosity high enough to prevent its rapid loss by flow across the membrane (Moody & Thomas, 1971). The membranes are prepared by dissolving the ionophore, a plasticiser such as bis(1-butyl-pentyl) adipate (BBPA) (Schulthess, Ammann, Kraeutler, Caderas, Stepanek, & Simon, 1985) and PVC in a suitable solvent (Gupta & Agarwal, 2005; Syarma & Goel, 2005). All the membrane constituents are hydrophobic because ion activity measurements are conducted in aqueous media.

The carrier for liquid membrane electrode could be natural macrocyclic compounds or synthetic crown ethers. A few decades ago, a considerable effort has been grown in the synthesis and characterisation of ionophores or neutral carrier with high selectivities for specific ions. For example, crown ethers as a neutral carrier has been used to detect cations such as strontium ion (Aghaie, Giahi, Monajjemi, Arvand, Nafissi, & Aghaie, 2005), beryllium ion (Singh, Ganjali, Daftari, Rastegar, & Moghimi, 2003) and anions like chromate ion (Singh, Bhatnagar, Tanaka, Tsue, & Mori, 2005).

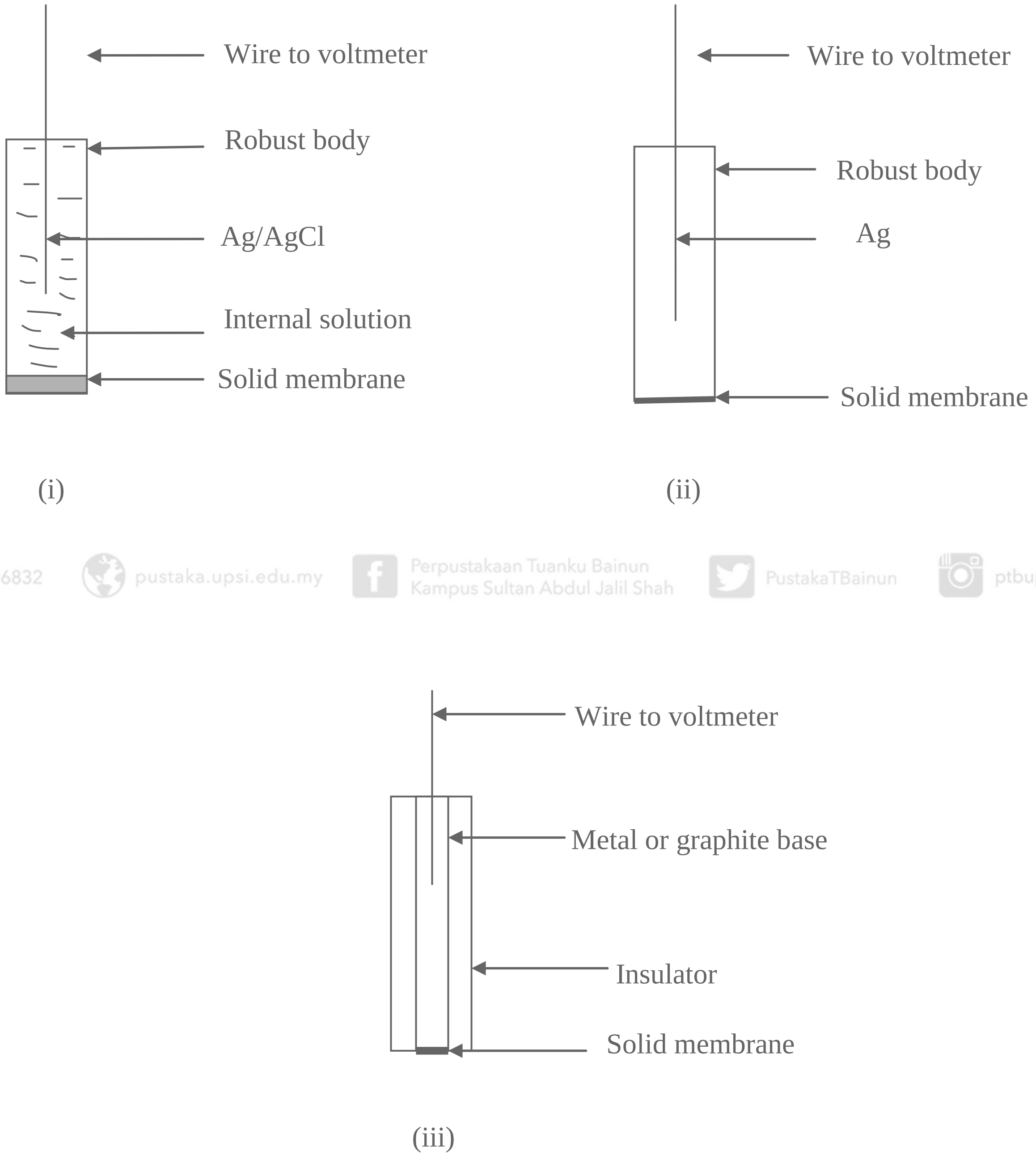
Liquid anion exchanger membrane electrodes ordinarily prepared with established ion exchanger such as lipophilic ammonium salts or phosphonium salts (Arnold & Solsky, 1986). They interact with the target anion through electrostatic attraction and induce a selectivity sequence governed by an anion’s enthalphy of hydration.

1.6.1.3 Solid State Membrane Electrode

Solid state membrane can be made of single crystals, polycrystalline pellets or mixed crystals. The crystal is fragile and indeed suffering from the problem of cracking during usage. A non-active material such as PVC or poly(ethane) that act as a binder usually blend with the crystal ionophore to enrich the mechanical strength. Membrane containing binders are referred as heterogeneous membrane.

Solid state membrane electrodes can be grouped based on how an internal reference is formed. One is solid state membrane electrode with internal reference solution while the other is solid state membrane electrode without reference solution and coated wire electrode as shown in Figure 1.2.

Figure 1.2 Solid State Membrane ISEs. (i) with Internal Reference Solution; (ii) Solid State Configuration Electrode; (iii) Coated Wire Electrode.



(i) (ii) (iii)

1.6.1.3.1 Solid State Membrane Electrode With Internal Reference Solution

Figure 1.2 (i) shown the solid state membrane membrane electrode with internal reference solution. The internal reference is form by an internal solution and electrode, likely as in the glass electrode. An example of a very successful solid-state sensor is the fluoride ion-selective electrode. This single-crystal device is by far the most successful anion-selective electrode. It consists of a lanthanum fluoride (LaF_3) crystal and an internal electrolyte solution that consisting of 0.1M sodium fluoride (NaF) and 0.1M potassium chloride (KCl) and containing the silver/silver chloride wire.

1.6.1.3.2 Solid State Membrane Electrode Without Internal Reference Solution

Solid state membrane electrode without internal reference solution can be divided into two categories. One is solid state configuration electrode, Figure 1.2 (ii) while the other is coated wire electrode, Figure 1.2 (iii).

For solid state configuration electrode, the cable from the voltmeter is connected directly to the membrane that commonly containing silver salt. A silver wire is attached by gluing it to the surface of the membrane using epoxy resin containing divided silver to furnish the required electrical contact. The main advantage for this kind of electrode is no solution will leak away or evaporate.

Coated-wire electrodes (CWEs) introduced by Freiser in the mid-1970s, are prepared by coating an appropriate polymeric film directly onto a conductor. The ion-responsive membrane is normally based on PVC with an ionophore, while the conductor can be either platinum, silver or graphite-based. A couple of reports state the usage of platinum (Dastjerdi & Alizadeh, 2004), silver (Sil, Ijeri, & Srivastava, 2001) and graphite (Ganjali, et al., 2002) as conductor have been published. The conductor is usually dipped in a solution of PVC with ionophore and the resulting film is allowed to air-dried.

CWEs are particularly simple, inexpensive and easy to prepare and function well over 10^{-5}M to 10^{-1}M concentration range. However, CWEs may suffer from reproducibility and long-term stability problems (Wang, 2000).

From the Figure 1.2, the difference between (i) and (ii) is the thickness of the membrane. In (i), the membrane is relatively thick, while in (ii), it is merely a surface coating. Nevertheless, the third type (iii) is much easier to construct and very tough.

1.6.1.4 Gas Sensing Probe Electrode

The basic design of a gas-sensing electrode is consisting of a thin membrane that separates the sample from an inner solution containing an ion-selective electrode. The membrane is permeable to the gaseous analyte, but impermeable to nonvolatile components in the sample’s matrix. The gaseous analyte passes through the membrane where it reacts with the inner solution, producing a species whose concentration is monitored by the ISE (Harvey, 2000).

The Severinghaus-type gas sensors have been used widely for measurement of carbon dioxide (CO_2), ammonia (NH_3) and nitrogen oxide (NO_x) gases. For example, in a CO_2 electrode, CO_2 diffuses across the membrane where it reacts in the inner solution to produce hydronium ion (H_3O^+). The change in the activity of H_3O^+ in the inner solution is monitored with a pH electrode (Ma & Hassan, 1982).

1.6.1.5 Enzymes-Based Electrode

Enzyme electrodes are based on the coupling of a layer of an enzyme with appropriate electrode. As a results of the coupling, enzyme electrodes have been shown to be extremely useful for monitoring a wide variety of substrates of analytical importance in clinical, environment and food samples. For example, glucose oxidase has been used to detect glucose (Delvaux & Champagne, 2003; Fang, Ng, & Li, 2003).

Yet, the enzyme electrodes have its own defects. Their response times are long, low in sensitivity and their lifetime can be quite short due to the short lifetime of the enzyme. Besides that, the main source of interference is from ions diffusing through the enzyme from the bulk of the solution to the surface of the inner ISE (Tsuchida & Yoda, 1983)

1.6.1.6 Miscellaneous Electrode

The field of microfabricated chemical sensors research based on ion-sensitive field effect transistors (ISFETs) and related sensors has been dynamic since Bergveld introduced the ISFET concept in 1970 (Bergveld, 1970). ISFETs sensitive to different ions can be made by depositing appropriate ion selective membranes on the field effect transistor (FET). The centre of an ISFET is the gate. A chemically sensitive layer is replaced the metal gate and the electrical path is closed with a reference electrode and the conducting solution. The device is protected by a suitable encapsulant (Wang, 2000).

The output signal of the ISFETs is usually a potential difference the magnitude of which varies with the change of logarithm of sensed ion activity or concentration in the same way as the corresponding ion-selective electrode. It is proposed that the output potential difference be plotted versus logarithm of ion activity or concentration, so that the slope of the plot is positive for cation responsive devices and negative for anion-responsive ones.

ISFETs present some advantages over conventional ISEs. They show a very fast response and they are miniature devices. These features facilitate their in vivo applications and working with small sample volumes. ISFETs are mass-fabricated using photolithographic techniques which lower their cost and open the possibility of disposable devices. Furthermore, an added advantage versus conventional sensors is that several ISFET devices can be integrated in a single chip producing single piece multi-parametric sensors (Sanchez & Valle, 2001).

However, there are a number of problems that have to be overcome to permit ISFETs to become widely used devices. For instance, a good anchoring of the polymer membranes to the transducer surface has to be ensured. Like typical PVC membranes ISFETs provide good response characteristics (selectivity and sensitivity) but limited lifetime due to their poor adhesion and progressive leaking of membrane components towards the solution (Sanchez & Valle, 2001).

1.6.2 Ion-Selective Electrode (ISE) Membrane Components

Each polymeric membrane ion-selective electrode (ISE) comprises four basis components; the polymeric matrix, the ionophore, the membrane solvent and ionic additives. The ISE nature and characteristics are considerably influenced by the nature and the amount of each component. As far as the polymeric membrane is concerned, it separates the test solution from the inner compartment, containing the target ion solution (Ganjali, Norouzi, Rezapour, Faridbod, & Pourjavid, 2006).

1.6.2.1 The Polymeric Matrix

Polymers have been utilised as homogeneous membrane matrices. A typical composition for the preparation of a sensing membrane is 33% (w/w) PVC as the polymeric matrix, 66% (w/w) plasticiser for the matrix homogenisation and 1% (w/w) ionophore (Ganjali, Norouzi, & Rezapour, 2006). In polymeric membranes, the polymer could provide the required physical properties likes elasticity and mechanical stability. The most favourable polymer used for ISE membranes is PVC because of good mechanical properties, amenability to plasticisation and relatively cheap cost (Bakker, Buhlmann, & Prestch, 1997).

Apart from PVC, other polymers such as silicon rubber, epoxy polyurethanes, polysulfone and modified PVC (Moody, Saad, & Thomas, 1987; Cha, et al., 1991; Lindner, et al., 1994) also can be employed in membrane fabrication. Generally, those membranes were prepared by dissolving the polymer and other components in an organic solvent such as tetrahydrofuran (THF), then pouring the resulting solution into a glass mold or dip-coating the cocktail onto a support, and followed by evaporating the solvent. A number of photocurable and solvent-free polymers such as methacrylates have been demonstrated as ISE matrices as well when the use of a solvent is undesirable. (Ambrose & Meyerhoff, 1997; Ambrose & Meyerhoff, 1999; Malinowska, Gawart, Parzuchowski, Rokicki, & Brzozka, 2000; Heng & Hall, 2000).

When the physical requirement like glass transition temperature is satisfy, the membranes are sufficiently fluid under ambient conditions to allow reasonable ionic conductivities, diffusion of membrane components and have mechanical properties amenable to routine processing and handling (Armstrong & Horvai, 1990). Nonetheless, most polymers employed do not meet this physical requirement and must be plasticised.

1.6.2.2 The Plasticiser

Addition of plasticiser able to create desired physical properties of the membranes and acting as a solvent. For PVC-based ISEs, typical weight ratios of polymer to plasticiser are approximately 1:2 (Moody, Oke, & Thomas, 1970). The plasticiser are significantly influenced the selectivity and the performance of the ISEs.

A study of the effect of plasticisers on the selectivity of ISEs constructed from same ionophore demonstrated a relationship the character of the plasticising molecules and observed selectivity (Sakaki, Harada, Kawahara, & Shinkai, 1994). For example, cation-exchanger-based membranes based on the nitrophenyl octyl ether (NPOE) demonstrate much higher affinity for divalent cations than do membranes of the same composition except containing dioctyl sebacate (DOS) (Bakker, Buhlmann, & Prestch, 1997). Another parameter have been known for being dependent on the nature of the plasticiser employed are detection limits and degrees of ion pairing (Armstrong, Covington, & Proud, 1988; Armstrong & Todd, 1988).

In spite of these facts, the plasticiser commonly selected based on compatibility with the ionopore because of solubility reasons and the ultimate application of ISE (Bakker, Buhlmann, & Prestch, 1997). A few names of the most common plasticisers employed in the ISE fabrication are as follow: di-sec-octyl phthalate (DOP) (Ganjali, et al., 2004), tri-n-butyl phosphate (TBP) (Gupta, Jain, Ishtaiwi, Lang, & Maheshwari, 2007), 2-nitrophenyl phenyl ether (o-NPPE) (Peper, Gonczy, & Runde, 2005), dipropylene glycol dibenzoate (D(PG)DB) (Kermanshahipour, Cooper, Mamer, Maric, & Nicell, 2009), di-(2-

ethylhexylexyl)adipate (DEHA) (Goulas, Anifantaki, Kolioulis, & Kontominas, 2000), bis(1-butyl-pentyl) adipate (BBPA) (Schulthess, Ammann, Kraeutler, Caderas, Stepanek, & Simon, 1985), tris(2-ethylhexyl)phosphate (TEHP) (Miguel, Aguilar & Gyves, 2008), bis 2-(ethylhexyl)adipate (BEHA) (Isa & Ghani, 2007), 1-methyl-3-octylimidazolium chloride (MOImCl), trihexyltetradecylphosphonium chloride (THTDPCl) (Peng, Zhu, Liu & Qin, 2008), dibutylsebacate (DBS), dinonylphthalate (DNP) (Hassan, Mahmoud & Othman, 1997), dioctylphenylphosphonate (DOPP) (Oohira & Toko, 1996) and benzyl acetate (BA) (Singh, Mehtab, & Jain, 2006).

1.6.2.3 The Ionophore

The ionophore or the ion carrier is the most essential component in a polymeric membrane sensor in terms of selectivity. The ionophore or the membrane-active recognition can be an ion exchanger or a neutral macrocyclic compound (Ganjali, Norouzi, Rezapour, Faridbod, & Pourjavid, 2006).

The ionophore has molecule-sized dimensions and it contains cavities or semi-cavity to surround the ion of interest. The binding between the ionophore and ion of interest is the molecular-level phenomenon, sensed by the ISE. Hence, the selectivity of an ISE towards the other ions are reckon to derive from the difference in the binding strengths between various ions and the ionophore from which the ISE is constructed. Ion-ionophore interaction strengths also can be studied via NMR, where the differences in chemical shift patterns between free and complexes ionophore can be used to estimate or explain observed selectivities (Badr, Diaz, Hawthorne, &

Bachas, 1999). Other than that, mass spectrometry also can be used to evaluate selectivity by combining a number of ions and ionophore in the same solution and looking at the distribution of ion-ionophore complexes in a mass spectrum (Brodbelt, 2000).

Many ionophores have been identified by trial and error, often with compounds designed for other uses like antibiotics such as valinomycin, monensin and nonactin have been identified as useful ionophores for potassium, sodium and ammonium ions (Johnson & Bachas, 2003).

Two general approach; rational design and biometric design have been considered in designing and synthesising ionophores. In rational design, parameters that are normally considered include structural flexibility, binding site geometry, molecular topology and binding and stabilising interactions such as Lewis acid/base chemistry, hydrogen bonding, charge and π-electron interactions. Biomimetic ionophore design incorporates similar concerns but this strategy is based on learning what the optimal design features should be from natural systems. (Bochenska, 1998).

According to Buchlmann, Pretsch and Bakker (1998), more than 1000 reports have been published pertaining to various ionophores and their selectivities. While approximately third quarter are concerned with the development of cation-selective sensors. Cation-selective ionophore designs are usually mononuclear and roughly spherical in shape. Most highly selective ionophores for these species are macrocyclic compounds due to the overwhelmingly spherical geometry of inorganic cations. Most macrocycles feature a geometry that is similar to that of a ring, cylinder or “open barrel", or hemisphere. Ring-shaped ionophores consist mostly of cyclic antibiotics/peptides like the potassium ion-selective ionophore and crown compounds like 12-crown-4 and 14-crown-4 derivatives, which exhibit selective binding toward lithium ion (Pioda, Stankova & Simon, 1969). The primary representatives of the cylindrically shaped ionophores are calixarenes, which possess a cyclic scaffold comprised of repeating substituted phenyl groups as in the sodium-selective calix[4]arene group of molecules (Diamond, Svehla, Seward, & McKervey, 1988). Hemispherands have been identified as useful ionophores which are similar to crown compounds yet contain an extra bridge to enhance preorganization and geometric stability, (Lein & Cram, 1985).

Interactions between cations and macrocyclic ionophores occur through the Lewis base centers in the macrocycle's backbone such as carbonyl oxygens or ether oxygens. Therefore, different selectivities can be obtained when different Lewis bases are introduced into the structure due to the "hard-soft, acid-base" concept which is the hard acid (the electron acceptor) is complexed by a hard base (the electron donor) or otherwise (Pearson, 1995). Most macrocycles containing hard oxygen centres exhibit selectivity towards alkaline and alkali earth cations, crowns containing softer sulphur atoms tend to interact with softer species like transition-metal ions.

Cation binding to basically all macrocycles is often described by the best-fit concept, which defines the preference of a given ionophore for a certain ion based on the relationship between binding cavity size and ionic radius (Weber, et al., 1989). If the ionic diameter of a given cation is much larger than the macrocycle diameter, the cation cannot fit into the binding cavity and does not enter into significant interactions with the ionophore. Yet, if cation’s diameter is small relative to that of the cavity, the ion will not possess the size required to take advantage of the numerous binding interactions that may be available simultaneously (Buchlmann, Pretsch, & Bakker, 1998).

1.6.2.4 Ionic Additives

The other important component of ISE membrane is ionic additive that is sufficiently lipophilic to remain solely in the organic membrane phase when in contact with aqueous solution. There are two primary types of those additives, where cationic sites are desired, a quaternary ammonium salt is typically used, while tetraphenylborate salts are incorporated into the membrane when anionic sites are needed (Bakker, Buhlmann, & Prestch, 1997). Ionic additives are employed to ensure that the ISE membranes are permselective. The permselectivity ensures that no significant amount of the counter ions may enter the membrane phase.

If the ionophore employed is a neutral carrier, the lipophilic additive employed is opposite in sign from the ion of interest. This concept assured that a sufficient amount of analyte ions can be excluded. The presence of ionic sites in the membrane will stabilise charged complexes between ion and ionophore (Meier, Morf, Läubli & Simon, 1984). Moreover, ionic sites will scale down the electrical resistance of the membranes and allow greater ion mobilities within the organic layer (Ammann, Pretsch, Simon, Lindner, Bezegh, & Pungor, 1985).

If the employed ionophore is charged, the membrane no longer requires ionic additives to obtain the desired behaviour (Bakker, Buhlmann, & Prestch, 1997). However, some ionic additives are normally included in the membrane. This inclusion results from the fact that the addition of ionic sites in ISE membranes can have an influence on the selectivity of such sensors (Schaller, Bakker, Spichiger, & Pretsch, 1994; Schaller, Bakker, & Pretsch, 1995).

A few names of the most common ionic additives employed in the ISE fabrication are as follow: oleic acid (OA) (Poursaberi, et al., 2001), sodium tetraphenylborate (NaTPB), trioctylmethylammonium chloride (TOMACl), carboxylated-PVC (Khorasani, Amini, Motaghi, Tangestaninejad, & Moghadam, 2002), tetradecylammonium carbonate (TDA_2CO_3), potassium tetrakis(4-chlorophenyl)borate (KTpClPB) (Levitchev, Smirnova, Khitrova, Lvova, Bratov, & Vlasov, 1997; Singh, Singh, & Bhattacharjee, 2009) and sodium tetrakis(4-fluorophenyl)borate dehydrate (NaTFPB) (Salleh, Gaber, Khalaf, & Tawfeek, 2006).

1.6.3 ISE Characterisation

1.6.3.1 Membrane Potential

Changes in the potential of the ISE membrane are measured against the constant potential of a reference electrode immersed in the same sample solution. In normal practice the ISE membrane is placed between the sample solution and a reference electrolyte which connects the membrane to a usually silver/silver chloride

(Ag/AgCl) internal reference electrode. In some cases, for coated wire electrode the internal filling electrolyte is absent, although sensors with this type of configuration often have drifting potentials owing to an ill-defined phase boundary potential at the membrane/wire interface.

The response of ion-selective electrodes toward a single analyte ion typically occurs under the condition of thermodynamic equilibrium at the sample/membrane interface and is described by the Nernst equation (Diamond, 1998).

$$\mathrm{EMF} = \mathrm{E}^0 + \frac{\mathrm{RT}}{\mathrm{ZiF}} \ln \mathrm{ai}$$

where E^0 is a constant potential, R is the universal gas constant, T is the absolute temperature, F is the Faraday constant, z is the charge on ion i, and ai is the activity of ion i. Response characteristics of ion-selective electrodes are evaluated by monitoring the potential of the electrodes at varying concentrations of different ions. The calibration curve generated for each ion measured is constructed by plotting log [ion] or log a i versus potential and takes a form similar to that displayed in Figure 1.3.

Figure 1.3 Response Profile of A Hydrogen Sulphite-Selective Electrode Based On A Biomimetic Guanidinium Ionophore

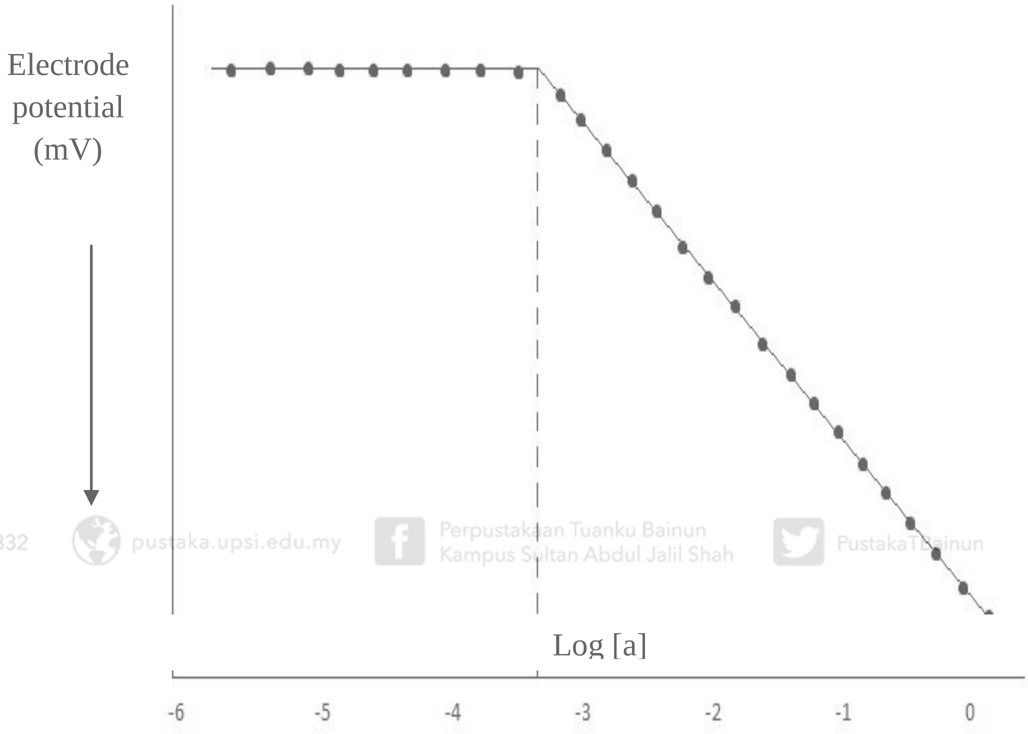


Figure 1.3 Adapted from “Use of a guanidinium ionophore in a hydrogen sulfite-selective electrode” by Hutchins,Molina, Alajarin, Vidal & Bachas (1994)

Since the potential is actually dependent on activity rather than concentration, Debye–Hückel theory is normally employed to convert between these two values (Bakker, Buhlmann, & Prestch, 1997). However, in many cases, ionic strengths in aqueous sample solutions are at values such that ion activity coefficients are nearly constant, hence concentrations are used rather than activities (Klotz & Rosenberg, 1994).

The functional potential of any selective ion-sensitive membrane electrode depends on a number of factors including potential-activity responses, selectivity in the presence of various interferants, operative pH range, response times, temperature and operative life. With few exceptions, the electrodes follow a Nernstian potential-activity pattern within working range as given by the relation

$$\mathrm{E} = \mathrm{E}^{\circ} + \frac{2.303\,\mathrm{RT}}{\mathrm{zF}} \log \mathrm{a}$$

If concentration assessment is to depend on the convenient linear relationship between response and log activity, then knowledge of the activity/concentration relationships as given by the Debye-Hückel relationship

$$\frac{\mu^{\,1/2}}{1 + 1.5\,\mu^{1/2}} - 0.2\mu$$

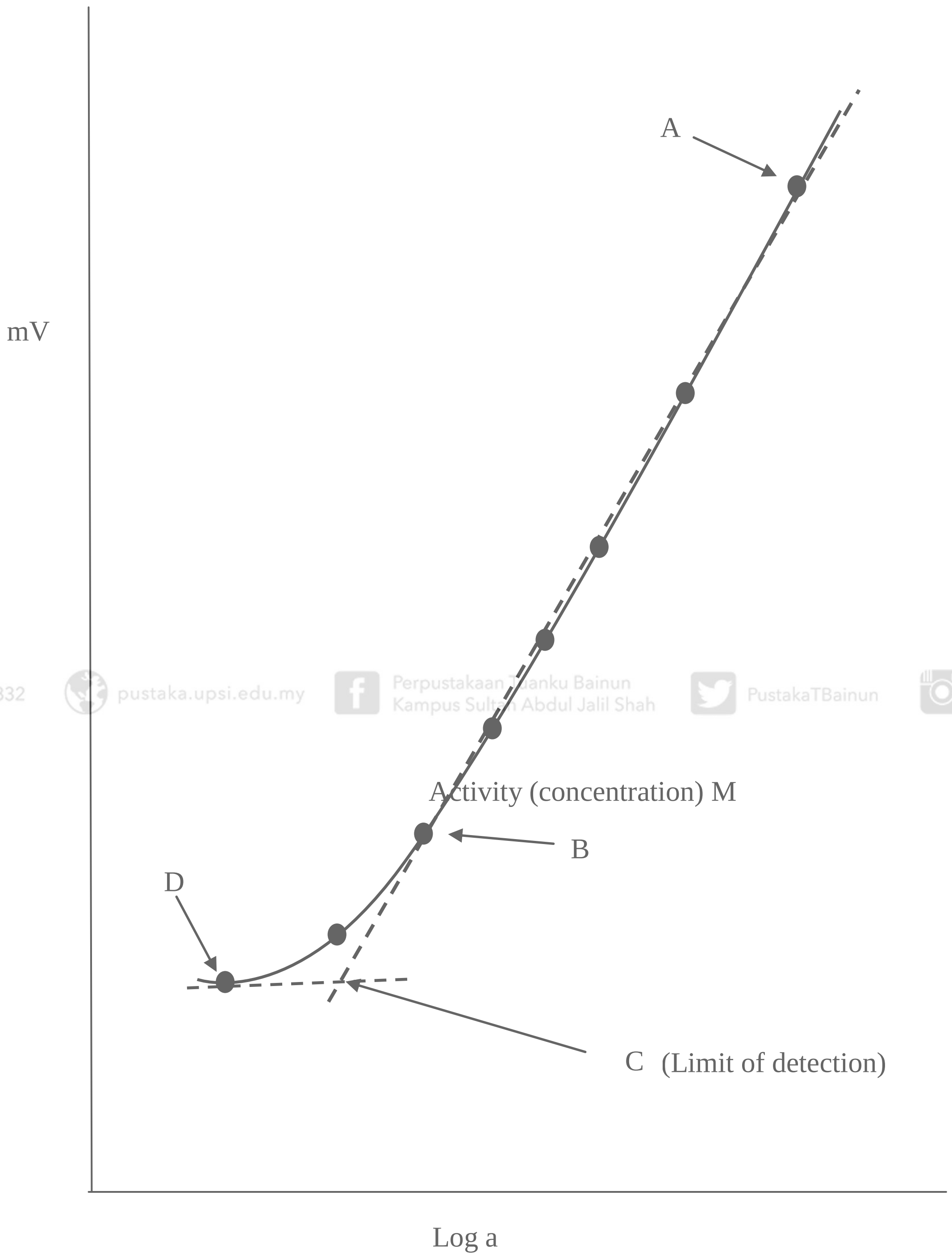
is demanded, otherwise concentration has to be assessed from a carefully plotted direct response/concentration curve known as a working curve.

The working curve is not straight line and does not have a Nernst slope. Besides, it will be in error if the level of the ions in the sample solution is high, this is because the activity depends on the total ionic strength.

1.6.3.2 Linear Concentration Range and Limit of Detection (LOD)

The Nernstian response range/ linear concentration range can be used to characterise an ion-selective electrode. An ion-selective electrode is said to have a Nernstian response over a given range of activity or concentration in which a plot of the potential of such electrode in conjunction with a reference electrode versus the logarithm of the ionic activity of a given species (a_A) is linear with a slope according to Nernstian equation (Guilbault, et al., 1976). According to Figure 1.4, AB is the linear concentration range. On the other hand, the limit of detection can be defined as the activity or concentration of A at the point of intersection of the extrapolated linear segments of the calibration curve. Hence, the lower of detection limit is betoken by point C. The lower limit of measurement is not the same as the lower of detection limit. At point B, the straight line of calibration plot starts to curve. Therefore, that the lower limit of Nernstian response.

Figure 1.4 Typical Activity (Concentration) Calibration Graph



1.6.3.3 Response Time and Lifetime

The response time is the time taken for the potential of the cell to reach a value 1 mV from final equilibrium potential. The experimental conditions such as the stirring rate, the composition of solution of which the response time is measured, the composition of the solution to which the electrode was exposed prior to this measurement, the history and preconditioning of the electrode, the temperature and the type of membrane should be stated clearly (Guilbault, et al., 1976). Glass and solid state membranes tend to respond more quickly than do liquid ion exchange membranes or gas sensing probes (Evans, 1987).

The fact that the slope of the response of ISEs remain fairly constant during experimental is widely accepted. Hence, the lifetime of the membrane electrode depends on the Nernstian slope of the membrane. Changes in the membrane composition as a consequence of ion exchange process, decomposition of the ionophores and leaching membrane components can cause drifting of the voltage.

The lifetime or stability of a potentiometric sensor is defined as “the time interval between the conditioning of the membrane and the moment when at least one parameter of the functionality characteristics of the device changes detrimentally” (Dinten, et al., 1991). The leaching of the ionophore from the membrane can cause loss of sensitivity and selectivity and also shorten the life time of the membrane (Meier, Morf, Laubli, & Simon, 1984; Eugster, Gehrig, Morf, Spichiger, & Simon, 1991).

1.6.3.4 Selectivity

The potentiometric selectivity coefficient (K^{pot}) is perhaps the most important characteristic of an ion-selective electrode (Segui et al., 2007). K^{pot} can be determined experimentally in a number of ways, although three methods have been widely accepted: the separate solution method (SSM), fixed interference method (FIM), and matched potential method (MPM) (Umezawa, Umezawa, & Sato, 1995; Bakker, Pretsch, & Buhlmann, 2000). The SSM and MPM involve creating calibration curves of ISE response toward the primary and interfering ions individually. However, MPM selectivity coefficients are empirical numbers that are expressive of the relative magnitudes of ion responses, while SSM are calculated from an expression that is derived from the Nicolskii equation.

$$E = \text{constant} + \frac{2.303\ RT}{zAF} \log\ (a_A + K^{pot}_{A,\,B}\ a_B{}^{zA/zB})$$

The FIM relies on the calibration of ISE response toward the primary ion in the presence of a fixed background of interfering ion in the sample solution. The selectivity coefficient in the FIM is then calculated from the detection limit of the calibration (Bakker, 1997).

The magnitude of selectivity coefficient ($K^{pot}_{A,B}$) depends on the ionic charges. $K^{pot}_{A,B}$<1, indicates that the ISE responds more to the primary ion and on the other hand, if $K^{pot}_{A,B}$>1, the ISE responds more to the interfering ion, B.

1.6.3.4.1 Separate Solution Method (SSM)

In the separate solution method, the electrode will be calibrated in two different solutions. Example, primary ion solution and followed by the interfering ion solution. A graph for EMF versus log activity for each calibration are then compared and the value for the K_{AB}^{pot} can be calculated by the given equation (Umezawa, 1990);

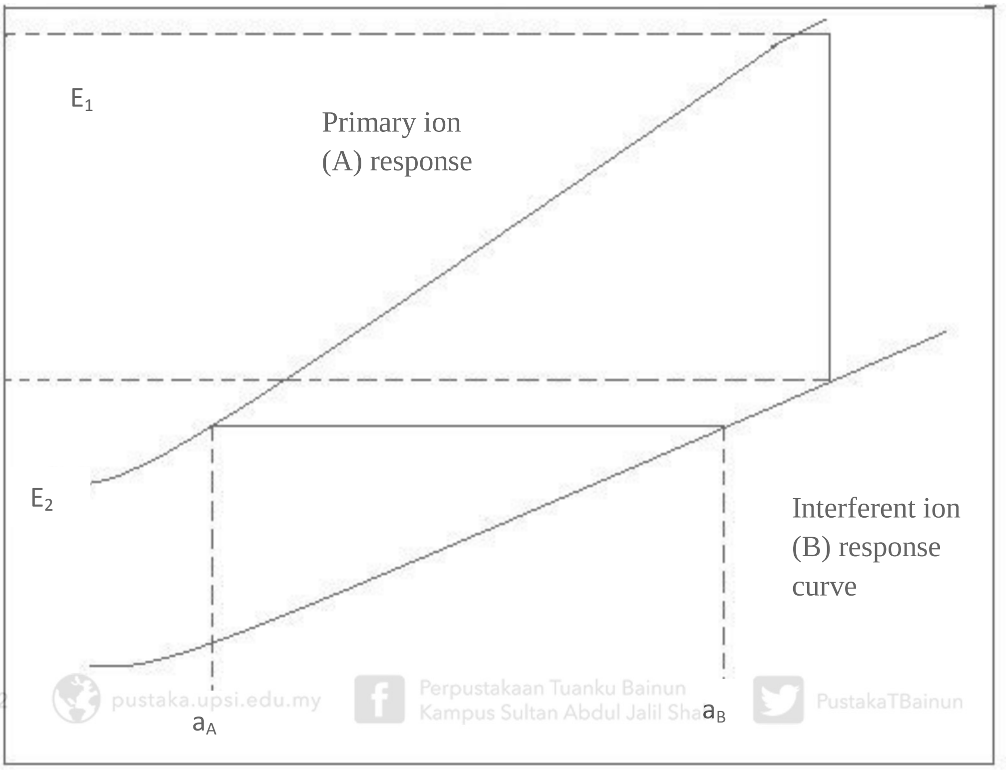
$$\frac{E_B - E_A}{S} = \log K_{A,B}^{pot} + \left[\left(\frac{Z_A}{Z_B}\right) - 1\right] \log a_A$$

Where E_A and E_B are the EMFs developed by the primary ion and interfering ion respectively at the same activity (Figure 1.5) and S is the slope of the calibration curve. Alternatively, K_{AB}^{pot} is given by:

$$K_{AB}^{pot} = \frac{a_A}{a_B}$$

Value for a_A and a_B respectively exert the same EMF, E_c.

Figure 1.5 Selectivity Constant, K_{AB}^{pot} Calculations Using Separate Solution Method

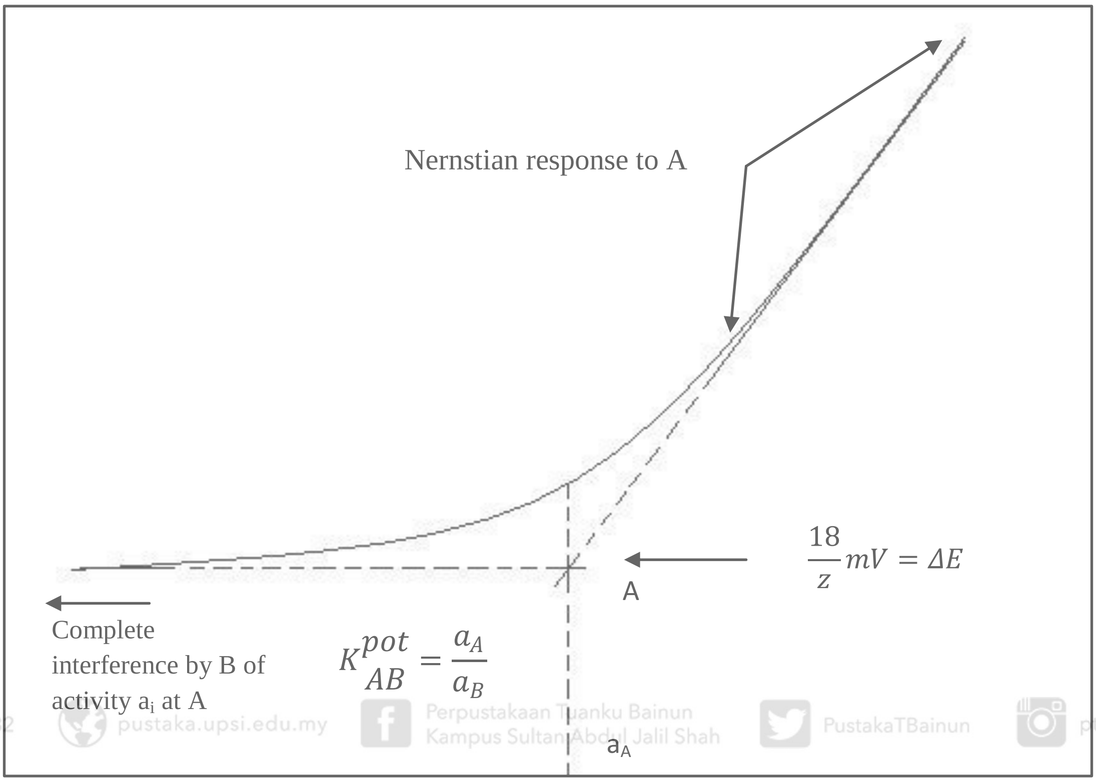


1.6.3.4.2 Fixed Interference Method (FIM)

A very common procedure in fixed interference method is to measure potentials in solutions containing a fixed initial amount of interferent ion, B, varying the activities of that ion, A for which the electrode is designed. Figure 1.6 illustrates the general idealised pattern. A, the activity of the primary cations falls, there is gradual onset of interference until eventually complete interference sets in along the horizontal plateau, when the potential is constant. The intercept of the extrapolated Nernstian response line with that of the horizontal total interference defines a particular intercept activity for the primary cation a_A (Umezawa, Umezawa, & Sato, 1995). The selectivity constant is then readily calculated using this equation;

$$K_{AB}^{pot} = \frac{a_A}{a_B}$$

Figure 1.6 Selectivity Constant Evaluating Using Fixed Initial Amount of Interference



Under condition of high interference, the potential measurements in the plateau region are subject to drift and irreproducibility. In such cases, the required a_A value is better located by taking the point on the experimental potential curve where ΔE between that curve and the extrapolated Nerstian line is exactly 18/z mV. The activity at this point will be required a_A value as before. Many of published selectivity values for glass and liquid ion exchange electrodes seem to have been evaluated by this simple mixed solution method.

The technique employed in an alternative method is varied the interference ion against the constant level of primary ion. In general, cations do not interfere with anion selective electrodes, and conversely, anions do not interfere with cation selective electrodes.

1.7 Objective of Study

Regarding to the various standard methods such as AAS and GC-MS, the identification of cobalt(II) ion can be expensive and time-consuming because involving sample manipulation and sometimes required separation or preconcentration procedures. Therefore, objective of this study is to develop the cobalt(II) ion-selective electrode (ISE) that simple, inexpensive, sensitive, having a rapid respond and withstand without divergence in potential for a few months by using palladium(II) dichloro acetylthiophene fenchone azine as the ionophore. A close literature survey reveals that palladium(II) complex has so far not been employed as ionophore for cobalt(II) ion-selective electrode. The first step in the developing this

ISE is the fabrication of homogeneous membrane using different ratio of ionophore and poly(vinyl chloride) (PVC).

Then, the best ratio that were obtained through several trials are added with plasticiser such as di-sec-octyl phthalate (DOP) and tetraethyl methylene diphosphonate (TMDP). The membranes are then characterised for slope, pH range, lifetime, detection limit, linear range, response time and selectivity. For the real sample analysis, the proposed cobalt(II) ion-selective electrode are applied for the analysis cobalt(II) in various water samples.