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CHITOSAN AS AN IONOPHORE IN A POLYVINYL CHLORIDE BASED ELECTRODE FOR pH DETECTION

MOHD HIZUAN BIN HAMZAH

UNIVERSITI PENDIDIKAN SULTAN IDRIS

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CHITOSAN AS AN IONOPHORE IN A POLYVINYL CHLORIDE BASED ELECTRODE FOR pH DETECTION

MOHD HIZUAN BIN HAMZAH

THESIS SUBMITTED IN FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE ANALYTICAL CHEMISTRY (MASTER BY RESEARCH)

FACULTY OF SCIENCE AND MATHEMATICS UNIVERSITI PENDIDIKAN SULTAN IDRIS

2014

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APPRECIATION

Alhamdulillah, finally I have completed this dissertation. First and foremost, I would like to express my gratitude to my parent Hj Hamzah Bin Abdullah and Hjh Hamidah Binti Awang Lah for their understanding, encouragement, advices and great supports during these years of study.

My gratitude and sincere thanks to my supervisor Associate Professor Dr. Illyas Bin Md Isa, whose total support, assistance, guidance patient and understanding made this thesis possible and also for giving me opportunity to take part in invention and publishing the journal article. It must be mentioned that I feel blessed and very much honour to have been able to work with a supervisor whose integrity and dedication to his profession and exemplary.

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ABSTRACT

A heterogeneous membrane pH sensor based on chitosan, polyvinyl chloride (PVC) and a suitable plasticizer was developed. The best overall performance was shown by a membrane with composition ratio of chitosan (ionophore) : PVC (binder) : 2-nitrophenyl octyl ether (2-NPOE) (plasticizer) at 20 : 30 : 30 (w/w) respectively. The potentiometric responses were linear within pH 2 to 9, limit of detection at pH 9.5, slope 56.6 ± 0.4 mV per decade at 25.0 ± 1.0 ^{o}C and response time of 20.0 ± 5.0 seconds. A life time of more than 3 months was obtained. The sensor showed good selectivity and reproducibility towards hydrogen ion in the presence of a number interfering cations. Results were in agreement with a commercial pH electrode for pH measurement in fruit juice samples. The sensor has been utilized in the flow injection analysis (FIA) of pH at standard solution. The slope of 57.1 ± 0.2 mV per decade was linear at pH range of 2 to 7 at 25.0 ± 1.0 ^{o}C was obtained.

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KITOSAN SEBAGAI INOFOR DALAM ELEKTROD BERASASKAN POLIVINIL KLORIDA BAGI PENGESANAN pH

ABSTRAK

Membran heterogen pengesan pH berasaskan kitosan, polivinil klorida (PVC) dan pemplastik yang sesuai telah dibangunkan. Keupayaan keseluruhan yang terbaik telah ditunjukkan oleh membran dengan nisbah komposisi masing-masing kitosan (inofor): PVC (pengikat): 2-nitrofenil oktil eter (2-NPOE) (pemplastik) pada 20: 30: 30 (w/w). Gerak balas potensiometrik adalah linear di antara pH 2 hingga 9, had pengesanan pada pH 9.5, kecerunan 56.6 ± 0.4 mV per dekad pada 25.0 ± 1.0 ^{o}C dan masa gerak balas adalah 20.0 ± 5.0 saat. Jangka hayat melebihi 3 bulan telah diperolehi. Pengesan menunjukkan kepilihan yang baik dan kebolehasilan terhadap ion hidrogen dalam kehadiran beberapa kation pengganggu. Keputusan adalah setara dengan elektrod pH komersial bagi pengukuran pH sampel jus buah-buahan. Pengesan telah digunapakai dalam analisis suntikan aliran (FIA) pH bagi larutan piawai. Kecerunan 57.1 ± 0.2 mV per dekad adalah linear pada julat pH 2 hingga 7 pada 25.0 ± 1.0 ^{o}C telah di perolehi.

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N IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI P

TABLE OF CONTENTS

		Page
DECLARATION		ii
APPRECIATION		iii
ABSTRACT		iv
ABSTRAK		v
TABLE OF CONTENTS		vi
LIST OF TABLES		x
LIST OF FIGURES		xi
LIST OF ABBREVIATIONS		xiii
CHAPTER 1	INTRODUCTION	
1.1	Electrochemical Sensors	1
1.2	Potentiometric Sensors	3
1.3	Ion Selective Electrodes (ISEs)	4
1.3.1	Background of ISEs	6
1.4	ISEs Membrane Composition	10
1.5	Membrane Potential	18
1.6	Selectivity of Membrane	22
1.6.1	Mixed Solution Methods	24
1.6.1.1	Fixed Interfernce Method	24
1.6.1.2	Fixed Primary Ion Method	24

UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKA
DRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PEN

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N IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI P

1.6.1.3 Two Solution Method 25

1.6.1.4 Matched Potential Method 25

1.6.2 Separate Solution Methods 26

1.6.2.1 Separate Solution Method ($a_A = a_B$) 26

1.6.2.2 Separate Solution Method ($E_A = E_B$) 26

1.7 Response Time 27

1.8 Lifetime 27

1.9 Detection Limit of ISEs 29

1.10 Chitosan 31

1.11 Analytical Determination of pH 33

1.12 Flow Injection Analysis (FIA) 35

1.13 Objectives of Study 38

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction 41

2.2 Glass Electrode 42

2.3 Optical pH Sensor 45

2.4 Fluorescence pH Sensor 48

2.5 Metal Oxide pH Sensor 49

2.6 Polymeric Membrane pH Sensors 51

2.7 Flow Injection Analysis (FIA) 53

UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKA
DRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PEN

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N IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI P

CHAPTER 3 EXPERIMENTAL

3.1	Chemicals and Reagents	55
3.2	Instrumentations	56
3.3	Fourier Transform Infrared (FTIR)	57
3.4	Preparation of Membrane and Electrode	57
3.5	Potentiometric Measurements	59
3.6	Response Time	60
3.7	Lifetime	60
3.8	SelectivityCoefficient, K^{pot}	61
3.9	Characterization of Membrane	61
3.9.1	Conditioning of Membrane	62
3.9.2	Water Content	62
3.9.3	Porosity	63
3.9.4	Thickness and Swelling	63
3.10	Analysis of Real Samples	64
3.11	Flow Injection Analysis Method	64

CHAPTER 4 RESULTS AND DISCUSSION

4.1	Characterization of Chitosan	66
4.2	Selection of Electrode	68
4.3	Selectivity Coefficient of the pH Electrode, K^{pot}	74
4.4	Response Time and Lifetime of the Electrode	74

UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKA
DRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PEN

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N IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI P

	4.5	Membrane Characterization	77
	4.6	Analysis of Real Samples	80
	4.7	Sample Analysis with FIA	80
CHAPTER 5	CONCLUSION		
	5.1	Conclusion	85
REFERENCES			87
PUBLICATION			99
AWARD			100

UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKA
DRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PEN

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N IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI P

LIST OF TABLES

Tables		Page
4.1	Optimised membrane composition and their potential response	72
4.2	Selectivity coefficients of chitosan membrane electrode(no.8) towards various interfering cations	75
4.3	Characterization of chitosan membrane no.8	79
4.4	pH determination of fruit juice samples using proposed electrode (no.8) and glass electrode	81

UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKA
DRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PEN

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N IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI P

LIST OF FIGURES

Figures		Page
1.1	A classical electrochemical cell of ion selective electrode, ISE	5
1.2	Common used conducting polymers as ion to electron transconducers in concstruction of all solid state potentiometric sensors	11
1.3	Different types of conducting polymeric based ISE; (a) conductor, (b) electronic conductor with a high work function (the work function is the minimum energy needed to remove an electron from a solid to a point close to the solid on the macroscopic scale outside the solid surface), (c) conducting polymer, (d) ion selective membrane, (e) ion selective membrane containing conducting polymer, (f) conducting polymer doped with ionophores	12
1.4	Typical activity (concentration) calibration graph for ISE	30
1.5	Molecular tructure diagram of chitosan	32
1.6	Manifold of the flow injection analysis system	37
1.7	The analog recording response peaks for proposed sensor; S is the time span between the sample injection, H is peak height, W is peak width, A is peak area, T is residence time to the peak height measurement, and t_b is the peak width at the baseline	39
2.1	Typical glass electrode pH	44
2.2	General arrangement of spectroscopic absorption/ fluorescence measurement: λ is a wavelength selector, X is a light sourse, D is a detector, R is a recorder. Intensity of initial (Io), or fluorescent (IF) light is related to the concentration of the sample C	46
3.1	Casting of the membrane mixture	58
3.2	Heterogeneous chitosan membrane electrode	58
4.1	FTIR spectrum for chitosan membrane	67

UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKA
DRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PEN

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N IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI P

4.2	Possible mechanism at membrane solution interface	69
4.3	Calibration plots of chitosan membrane electrode with composition ratio of chitosan (20), PVC (30) and different plasticizer (30): (●) NPOE, no.8;(▲) DOP, no.9; (■) BEHA, no.10; (×) TEHP, no.11; (◆) DBP, no.12 and (⁎) without plasticizer, no.7	73
4.4	The lifetime of chitosan membrane electrode: (◆) NPOE, no.8; (■) DOP, no.9; (▲) BEHA, no.10; (⁎) TEHP, no.11; (×) DBP, no.12 and (●) without plasticizer, no.7	78
4.5	Recording chart graph at FIA conditions	83
4.6	The corresponding calibration curve at FIA conditions	84

UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKA
DRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PEN

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LIST OF ABBREVIATIONS

ATR	Attenuated total reflectance
BA	benzyl acetate
BBPA	bis(1-butylpentyl) adipate
BEHA	bis(2-ethylhexyl) adipate
BEHP	bis(2-ethylhexyl) phthalate
BEHs	bis(2-ethylhexyl) sebacate
CPISEs	Conducting polymer ISEs
CWEs	Coated wire electrode
DBE	dibenzyl ether
DBP	dibutyl phthalate
DBS	dibutylsebacate
DDP	didecyl phthalate
DOP	dioctylphthalate
DOPP	dioctyl phenyl phosphonate
E	Membrabe potential
E_{cell}	Cell potential

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E^o	Standard cell potential
FIA	Flow injection analysis
FTIR	Fourier transform infrared
HDPB	Hexadecylpyridinium bromide
HTAB	Hexadecyltrimethylammonium bromide
IrO_2	Iridium dioxide
ISFETs	Ion-sensitive field-effect transistor
IUPAC	International Union of Pure and Applied Chemistry
$K_{A,B}^{pot}$	Selectivity coefficient of primary ion, A and interference ion, B
KTPClPB	Potassium tetrakis(*p*-chlorophenyl) borate
NaHFPB	Sodium tetrakis-[3,5-bis(1,1,1,3,3,3-hexafluoro-2-methoxy-2-propyl)phenyl] borate
OsO_2	Osmium dioxide
PET	Photoinduced electron transfer
PTFE	Polytetrafluoroethylene
PtO_2	Platinum dioxide
RhO_2	Rhodium dioxide

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RuO_2	Ruthenium dioxide
SCEs	Solid contact electrode
SCISEs	Solid contact ISEs
SiO_2	Silicon dioxide
SnO_2	Tin dioxide
SPISEs	Single piece ISEs
Ta_2O_5	Tantalum pentoxide
TBP	tri-*n*-butyl phosphate
TEHP	tris(2-ethylhexyl) phosphate
TFPB	Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
Tg	Glass transition temperature
THF	Tetrahydrofuran
TiO_2	Titanium dioxide
TOMACl	Trioctylmethylammonium chloride
w/w	Weight per weight
2-NPOE	2-nitrophenyl octyl ether
ΔE	Potential change

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CHAPTER 1

INTRODUCTION

1.1 Electrochemical Sensors

Electrochemical sensors are the largest and oldest group of chemical sensors and have been used extensively either as a whole and an integral part of chemical and biochemical sensing element. Many members of this group have reached commercial maturity while many are still in various stages of development (Janata, 2009). Electrochemical sensor represents an important subclass of chemical sensor in which an electrode is used as the transduction element. Such devices hold a leading position among sensors presently available, have reached the commercial stage, and have found a vast range of important applications in the fields of clinical, industrial, environmental and agricultural analyses (Wang, 2006).

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There will be discussed within the broadest framework of electrochemistry, the interaction of electricity and chemistry. Electrochemical sensor generally can be categorised by their mode of measurements, i.e, into potentiometric (measurement of potential different), amperometric (measurement of current) and conductimetric (measurement of conductivity) sensors (Liu, 1995). Potentiometric are the electrochemical sensor with the longest and probably the most frequent routine application.

Electrochemical sensor measurement can be made at steady-state or transient, its means electrochemistry implies the transfer of charge from an electrode to another phase, which can be a solid or a liquid sample. During this process, chemical changes take place at the electrode surface and the charge is conducted through the bulk of sample phase. Both the electrode reactions and/or the charge transport can be modulated chemically and serve as the basis of the sensing process (Janata, 2009).

Another important general aspect of electrochemical sensors is that the charge transport within the transducer part of the sensor and/or inside the supporting instrumentation, which is part of the whole circuit, is always electronic. On the other hand, the charge transport in the sample can be electronic, ionic, or mixed. In the latter two cases electron transfer and sometimes electrolysis take place at the electrode – sample interface and its mechanism becomes one of the critical aspects of the sensor performance.

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1.2 Potentiometric Sensors

Potentiometric sensor have become a well established routine analytical technique in biochemical analysis and environmental monitoring for many years (Liu, Peng, Liu, & Qin, 2007). Potentiometric technique is most commonly used especially for determination of ionic species. This is because this sensor can provide a direct, fast response and an inexpensive way of performing ion measurements (Gupta, 2010).

Potentiometric measurements are based on monitoring potential values under a zero current flow regime, in order to determine the analytical concentration of the desired analyte. The potential difference between an indicator electrode (i.e. ion-selective electrode, redox electrode, metal-metal oxide electrode) and the reference electrode is measured. The potential of an electrochemical cell is due to the changes in the free energy that occurs if the chemical phenomena reach equilibrium; which is a concept that is typically applied in quantitative analysis in relation to electrochemical cells, in which case, the difference between the cathodic and the anodic potentials is the potential of the electrochemical cell. The potential is calculated using the so-called Nernst equation (Koryta, Dvorak, & Kavan, 1993).

Another source of potential may be physical phenomena not involving explicit redox reactions but having non-zero free energy initial conditions. For instance, ion concentration gradient across a semi-permeable membrane is one such phenomena (Janata, 2009). This can also be potentiometric phenomena, and is the basis of

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measurements that use ion-selective electrodes (ISEs), according to which the equation 1.1 below is used to determine the concentration of the analyte:

$$E = \text{Constant} - RT/zF \ln a \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.1)$$

where **z** and **a** represent the charges and the activity of the ion of interest respectively. As indicated in Nernst, a linear relation exists between the measured potential, E and the natural logarithm of the ratio of the activities of the reactant and product. If the number of electrons transferred, z is one, at ambient temperature (25.0°C or 298°K) the slope is approximately 60.0 mV/decade. This slope value governs the sensitivity of the potentiometric sensor.

The equipment required for direct potentiometric measurements includes an ion selective electrode, a silver-silver chloride (Ag/AgCl) reference electrode and a potential measuring device (a pH/millivolt meter). Figure 1.1 showed the schematic diagram of a simple electrochemical cell for potentiometric measurements.

1.3 Ion Selective Electrodes (ISEs)

The field of ISE has matured over more than three decades. ISEs are chemical sensors with the longest history, and still probably have the largest number of applications (Ammann, Lanter, Steiner, Schulthess, Shijo, & Simon, 1981). The ISE is an indicator electrode capable of selectively measuring the activity of a particular ionic species.

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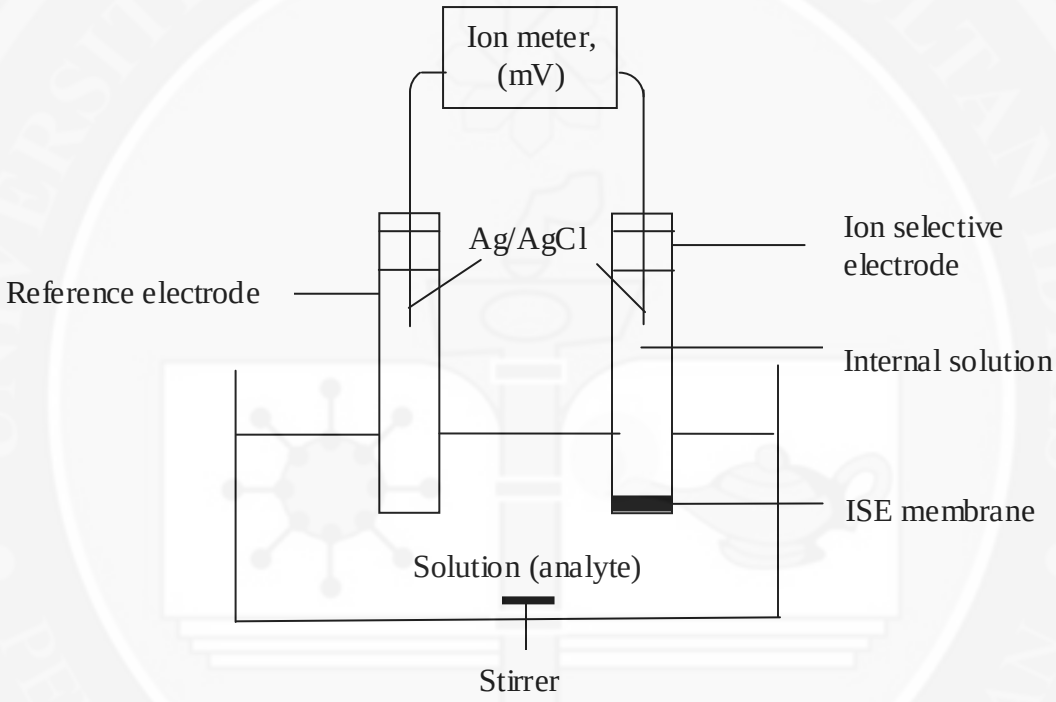


*Figure 1.1.*A classical electrochemical cell of ion-selective electrode, ISE

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Normally, the ISEs have criteria such as fast response, wide linear range, are not affected by colour or turbidity, are not destructive, and very cheap (Kemer & Ozmdemir, 2008). The specially design cells of ISE (flow injection) allow a microliter volume of sample to be analysed.

ISEs are mainly membrane based devices and consist of permselective (only one type of ion can pass through) ion conducting materials, which separate the sample from the inside of the electrode. Normally, the ion of interest is at a constant concentration or saturated is filled inside the electrode. The membrane is usually nonporous, water insoluble and inert or mechanically stable. In order to satisfy the crossing of the ion, the condition of membrane must have a minimum thickness, which is related to its dielectric constant and conductivity. On the other hand, the composition of the membrane is designed to yield a potential that is primary due to the ion of interest.

1.3.1 Background of ISEs

Electroanalytical methods have a long history of development. Researchers aimed at exploring and understanding how to use the materials of Faradaic electrochemistry as electronic, ionic and sometimes mixed conductors has been carried out since early 1900s. Today, studies of the ion transfers energetics and kinetics at interfaces of mobile and fixed site plasticitized polymer, insoluble ionic crystalline and immiscible liquid-liquid electrolytes are the vanguard of physical and electroanalytical chemistry research. This knowledge is also a cornerstone of selective interface design.

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Synthetic membranes can be tailored to choose and transport ions with a selected charge sign or a particular ion among others of the same charge. Discoveries such as these have led to exciting opportunities for theory and experiment, including the synthesis of neutral and charged ion carriers or ionophores. Faradaic ionic process membranes have also lent themselves to the development of ISEs.

During 1900 – 1930, four aspects of electrochemistry grew. First, the design of electrodes (half – cells), M|MX|NX|N^+were explored (M is metal, N^+ is cation and MX and NX are barely soluble salts of the respective cation and anion). Secondly, the use of these cells without electrolyte junctions to calculate the thermodynamic properties captured the interest of scientists. Third is the perturbation of cells with small currents. Transport studies were formulated using DC or AC through regions of uniform electrolyte, which were well isolated from the working electrodes and transference numbers were determined. The fourth and the most important electrochemical lesson learned was relationship between the space charge, electrode potential difference and capacitance of the phase boundary between solid conductors and electrolyte solutions. It is widely known that two parallel metals sheets form a capacitor, but the proof that metals in electrolytes also have this property came by studying the change of surface tension of liquid metals upon charging. The metal carries the surface electronic charge; the electrolyte carries the opposite charge by ion accumulation near the metal surface. This is the double layer, and the ionic side is called the space charge because it spreads out into the solution via thermal motion. It was somehow not recognized that the excess of charge on a metal tracks the electrode potential difference relative to the adjacent electrolyte solution. This principle applies to all interfaces of metals, electronic semiconductors, ionic crystals, synthetic ion

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exchangers, and other immiscible electrolyte phases in contact with electrolytes. The absolute electronic charge on solid electrodes in electrolytes is not known, but the changes in charge can be measured.

During 1935 – 1980 the sensing membranes was discovered. Many of fixed site ion exchange membrane contain covalently attached, functionalized groups that were developed in the 1930s, followed by the discovery of the first sulfonated polystyrene. These membranes include sulfonated poly(tetrafluoroethylene) with SO_3 sites and plasticized, functionalized poly(vinyl chloride) (PVC) with COO^-, SO_3^-, $(P{=}O(OH)_2(O)$, and NR_3^+ sites. Those with negative sites are permeable to cations and those with positive signs are permeable to anions. ISEs technology use ion conductors such as membranes, with four characteristics that determine their electrical behavior. First, there is a built in site density of fixed or mobile hydrophobic ion site. The site density determines by a membrane is permselective and allows only sample counterions with the opposite charge sign into the membrane. The counterions can move through the membrane by diffusion. An electric field can facilitate or impede the counterion transport. Low site density membrane, on the other hand, are not permselective and contain a significant concentration of co–ions (ions of the same sign as sites) from the bathing electrolyte. Second, the inherent site density changes because of water adsorption and membrane swelling. Third, water spontaneously diffuses across membranes because of the osmotic pressure differences. Many plasticized, synthetic, functionalized ISE membranes transport very small amounts of water but they are basically non–osmotic. Finally, the macroscopic electroneutrality in permselective membranes requires that very few co–ions be present in the membranes, causing what is known as the Donnan exclusion of co–ions.

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The subsequent development of liquid ion exchanger, crystalline and press pellet membrane ISE is the culmination of the work of many scientists because of their simplicity, low cost, improved accuracy, applicability to unusual or extreme conditions and timeliness. ISEs were rapidly recognized as novel analytical tools. James Ross and Martin Frant of Orion Research were the founding fathers of ISEs. They developed calcium and fluoride ISEs in the mid 1960s started a new era in potentiometric analysis (Frant, 1994). In the early 1960s, Pungor and Toth (1969) published his first paper on AgI based electrodes and filed a patent on the heterogeneous selective membranes with his coworkers Klara Toth, Jeno Havas and Geza Madarasz, which were the basis for the first commercial solid state ISEs. Wilhelm Simon, a chemist at the Swiss Federal Institute of Technology in Zurich, Switzerland studied on the structure selectivity relationship of many synthetic ionophores, plasticizers and additives, thus allowing his group to fabricate a novel ISEs (Ammann, Morf, Anker, Meier, Pretsch, & Simon, 1983). To make ionophore based electrodes successful, a user friendly, robust membrane matrix was also needed. The unique features of PVC (it can be plasticized with polar and nonpolar water immiscible solvents) made it the best candidate.

Surface coated membrane systems were applied during 1970 – 2000. There have been huge developments in ISEs research over the past 40 years. The configurations of ISEs were moved from the traditional barrel configuration to wire type electrode such as solid contact electrode (SCEs) and coated wire electrode (CWEs) (Han, Park, Chung, Cho, & Hong, 2000). The variety of analytes that can be assessed with potentiometric devices grew when thin. Inert or reactive layers were placed over the sensor surfaces.

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1.4 ISEs Membrane Composition

The ISEs membrane component can be conducting polymer (conjugated polymer) with or without ionophore or non-conducting polymer with the ionophore. A few sensors for inorganic cations and anions with different characteristics based on conducting polymers have been reported (Bobacka, Ivaska, & Lewenstam, 2003; Bobacka, 2006; Janata & Josowicz, 2003; Ramanaviciene, Ramanavicius, & Malinauskas, 2006). Conducting polymers are electroactive materials of mixed electronic and ionic conductivity, which gives them the unique potential to transducer ionic signals into electronic ones. Common conjugated polymer are poly(acetylene), poly(pyrrole), poly(thiophene), poly(terthiophene), poly(aniline), poly(fluorine), poly(3-alkylthiophene), polytetrathiafulvalene, polynapthalene, poly(*p*-phenylenevinylene), poly(3,4-ethylenedioxythiophene), poly(*p*-phenylene), polyazulene, poly(*p*-phenylene sulfide), polycarbazole and polydiaminonaphthalene. Figure 1.2 shows some of conducting polymers which can be used as ion as electron transducers in the construction of ISEs.

Conducting polymers have been used in the construction of ISEs according to general approaches, which have led to the development of solid contact ISEs (SCISEs), a single-piece ISEs (SPISEs) and conducting polymer based ISEs (CPISEs) (Figure 1.3). In SCISEs, the conducting polymer is electropolymerized on the surface of the electronic conductor and then, coated with the ion-selective membrane. The selective membrane determines the selectivity, and the conducting polymer only acts as an ion–to–electron transducer of the sensor.

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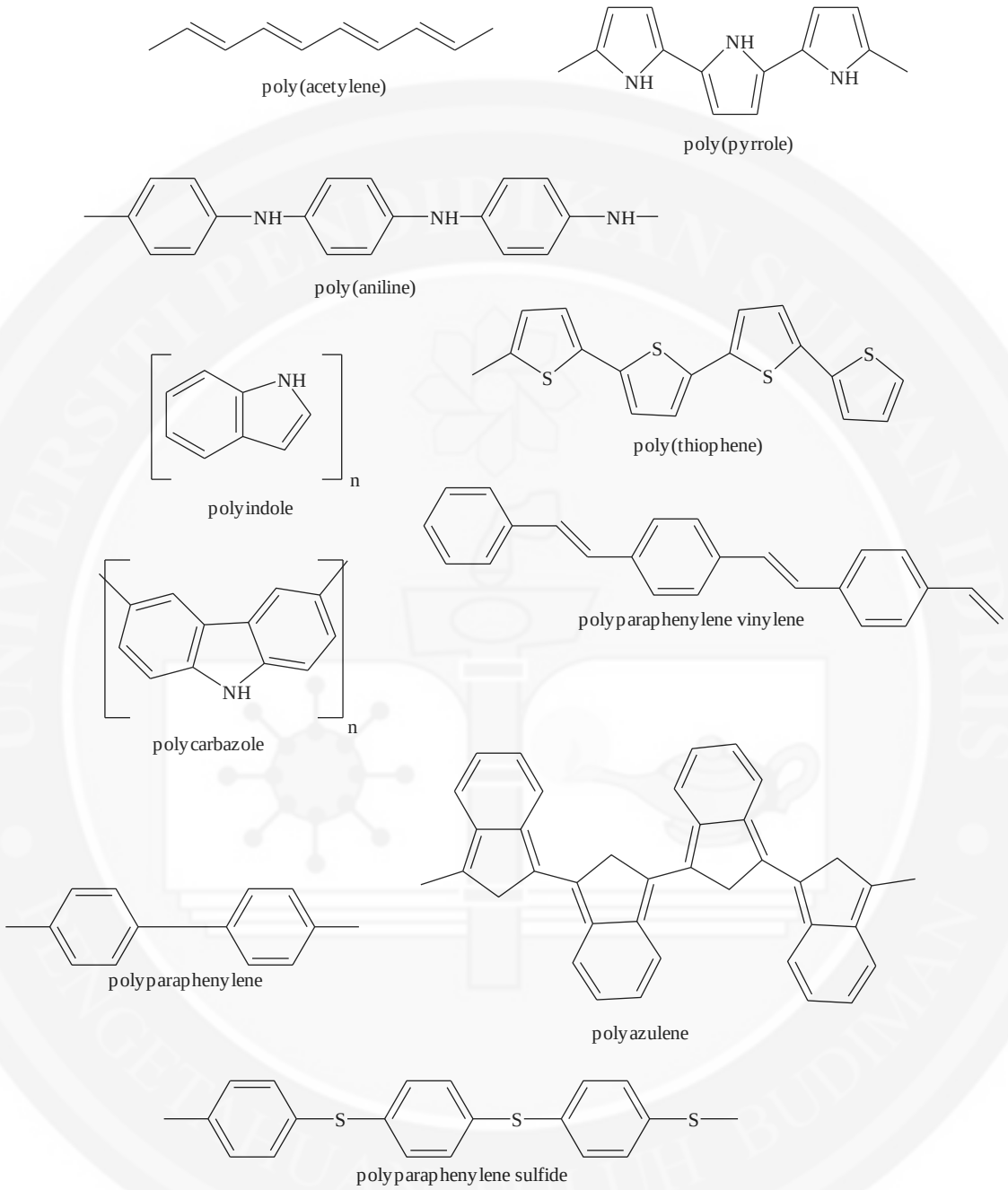


Figure 1.2. Common used conducting polymers as ion to electron transducers in construction of all solid state potentiometric sensors

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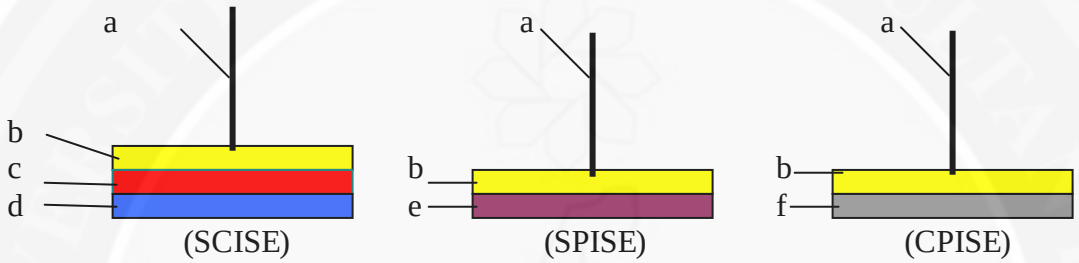


Figure 1.3. Different types of conducting polymeric based ISE; (a) conductor, (b) electronic conductor with a high work function (the work function is the minimum energy needed to remove an electron from a solid to a point close to the solid on the macroscopic scale outside the solid surface), (c) conducting polymer, (d) ion selective membrane, (e) ion selective membrane containing conducting polymer, (f) conducting polymer doped with ionophores

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This way, both the ion-exchange and redox characteristics of the conducting polymers are successfully combined with the selectivity of the ionophore based ion selective membranes. In SPISEs, the selective membrane contains conducting polymer due to the solubility and the consequent dispersability of conjugated polymers in organic solvent.

In CPISEs, the conducting polymer layer is doped with a suitable ionophore which enhances the ion selectivity of the conducting polymer while its redox response has to be suppressed. Thus, the redox sensitivity limits the use of CPISEs in direct measurements.Normally, non-conducting polymer ISEs membrane components consist of polymeric matrix, especially PVC, ionophore, solvent mediator (plasticizer), ionic additives and solvent. The ISE characteristics are considerably influenced by the nature and the amount of each component. Extensive research of non-conducting polymer PVC based ISEs are done in the period of 1999-2007 where more than 100 ISEs just employing Schiff bases as ionophore were reported (Faridhod, Ganjali, Dinarvand, Norouzi, & Riahi, 2008).

PVC has been utilized as a polymer matrix for more than 30 years (Ganjali, Norouzi, & Rezapour, 2006), despite the fact that there are many drawbacks related with its usage. Plasticizer migration is one of them. Diminished sensor lifetimes, unstable responses and sample perturbation are caused by the plasticizer exudation from the sensing membranes. Furthermore, the decreased plasticizer content can reduce the ionophore solubility and the ion exchangerwithin the membrane, leading to a considerable sensitivity and selectivity reduction. A disadvantage of the plasticized-PVC observed in the ISFETs is its poor adhesion to the gate oxide surfaces, which

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results in a shortened lifetime of the sensing device (Ganjali, Norouzi, & Rezapour, 2006).

Recently, polymers have been utilized as homogeneous or heterogeneous membrane matrices. For the preparation of a sensing membrane, a typical composition is as follows: 30–33% (w/w) PVC as the polymeric matrix, 60–66% (w/w) plasticizer for the matrix homogenization and 1% (w/w) ionophore (Kuruoglu, Canel, Memon, Yilmaz, & Kilic, 2003).

Regarding the first polymeric ISE membranes, the fabrication involved valinomycin as the neutral ion carrier in silicone rubber or PVC without the addition of lipophilic ionic sites. In such polymeric membranes, the polymer provides the required physical properties (e.g. elasticity and mechanical stability). It should be stressed that these ISE exhibited a Nernstian response, owing to the possible ionic impurity presence in the used PVC as well as in the presence of the other membrane components. Moreover, membranes with no ionic sites did not respond to the target ion concentration, as they incorporate almost completely pure membrane ingredients.

Besides from PVC, other polymers can also be employed in membrane fabrications are the acrylates and the methacrylates, the methacrylated siloxane resins, the epoxyacrylates, polystyrene and the acrylates of urethane oligomers. The suitability of the polymer to be employed in a sensing membrane is defined by the glass transition temperature (Tg) of the polymer. Tg is the temperature at which an amorphous solid, such as glass or a polymer, becomes brittle on cooling, or soft on heating. The Tg value should be below the room temperature. As a consequence, the

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designed membranes are fluid enough under ambient conditions, they allow the diffusion of the membrane components, they exhibit reasonable ionic conductivities and they illustrate the proper mechanical properties to be handled for routine processes. If the polymers are characterized with high Tg values (e.g. the Tg value of the high molecular weight PVC is 80 °C), the use of plasticizers will be necessary. On the contrary, if the polymers are characterized by low Tg values, such as soft polyurethanes with a low content of crystalline units, silicone rubber, poly(vinylidene chloride) and polysiloxanes, the use of plasticizers is not obligatory. In this way, the risk of the plasticizer leaching is avoided. Nevertheless, when no plasticizer is incorporated in the membrane, the ion selectivity modification by varying the plasticizer is no longer an alternative.

The ionophore or the ion carrier is the most vital component in a polymeric membrane sensor in terms of selectivity and sensitivity. The ionophore or the membrane active recognition element can be an ion exchange or a neutral carrier compound. The ionophore has molecules sized dimensions and cavities or semi cavity to surround the ion interest. The binding between the ionophore and ion of interest is the molecular level phenomenon, sensed by ISE. Hence, the selectivity of ISE towards the other ions is recon to drive from which the ISE is constructed. Gupta, Sigh, Al Khayat and Gupta, (2007) reported from the literature review, the ionophores with donating sulfur, nitrogen atom in their structure, sufficient insolubility in water, low molecular weight were expected to act as suitable ion carriers.

Plasticizer or solvent mediator is an additive, which increase the plasticity or fluidity of the material to which they are added. Normally, the composition of the

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plasticizer is 60-66% (w/w). Such a composition exhibits optimal physical properties, ensuring relatively high mobilities for their constituents. The plasticizer has to be physically compatible with the polymeric matrix (i.e. properties), so as to give a homogeneous organic phase. Additionally, it may affect the selectivity behavior of the electrode. In contrast, the selectivities of the carrier based ISEs are significantly influenced by the plasticizer. For example, a plasticizer change from the polar *o*-nitrophenyl octyl ether (*o*-NPOE) to the non-polar dibutyl phthalate (DBP) reduced the M^{2+} selectivity of the ISE with the ionophore 2,3,8,9-tetraazacyclododeca-1,3,7,9-tetraene.

This influence can be attributed to the plasticizer polarity, which can be estimated from the interaction of the charged species with a continuum of the given dielectric constant (Ganjali, Norouzi, & Rezapour, 2006). Nonetheless, the plasticizer selection is performed in line with its compatibility with the ionophore as well as the final ISE application. The names/abbreviations of the most common plasticizers employed in the ISE fabrication are as follows: benzyl acetate (BA) (Ganjali, Moghaddamb, Norouzi, Shirvani-Arani, Daneshgar, Adib at el., 2006), bis(1-butylpentyl) adipate (BBPA) (Xu & Katsu, 2001), bis(2-ethylhexyl) adipate (BEHA) (Saad, Zin, Jab, Rahman, Saleh, & Mahsufi, 2005), dioctyl phthalate (DOP), bis(2-ethylhexyl) phthalate (BEHP) (Ganjali, Kiani-Anbouhi, Shamsipur, Poursaberi, Salavati-Niasari, Talebpour, & Emami, 2004), bis(2-ethylhexyl) sebacate (BEHS) (Segui, Lizondo-Sabater, Benito, Martinez-Manez, Pardo, Sancenon et al., 2007), bis(*n*-octyl) sebacate and dibutyl sebacate (DBS) (Segui, Lizondo-Sabater, Martinez-Manez, Sancenon, Soto, Garcia Breijo et al., 2003), dibenzyl ether (DBE) (Siswata, Hisamoto, Tohma, Yamamoto, & Suzuki, 1994), dibutyl phthalate (DBP) (Shamsipur,

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Hosseini, Alizadeh, Talebpour, Mousavi, Ganjali et al., 2003), didecyl phthalate (DDP) (Akl, Ghoneim, El-Aziz, & Mohammed, 2006), 2-nitrophenyl phenyl ether (2-NPPE) (Peper, Gonczy, & Runde, 2005), 2-nitrophenyl octyl ether (2-NPOE) (Ganjali, Emami, Salavati-Niasari, & Yousefi, 2003) and tri-*n*-butyl phosphate (TBP) (Gupta, Jain, Ishtaiwi, Lang, & Maheshwari, 2007).

The permselectivity of the ISE membranes is a prerequisite to attain a theoretical response. The permselectivity ensures that no significant amount of the counter ions may enter the membrane phase. To achieve this so-called Donnan exclusion with the electrically neutral carriers, the counter ions (ionic sites) confined to the membrane must be present. Despite the fact that the neutral-carrier based ISE membranes could function properly, even when they contain only a very small amount of ionic sites, the addition of a lipophilic ion salt is advantageous for various other reasons. The anionic interference decrease, observed in the presence of lipophilic anions (e.g. thiocyanate) is the basic reason for the addition of a tetraphenyl borate salt to the membrane of a cation-selective electrode. Simultaneously, the electrical resistance of the membrane is diminished, which is especially important in microelectrodes. The ionic additives are ion exchangers, which themselves induce a selective response if no or only an insufficient amount of ionophore is present. It becomes obvious that their concentration must be carefully adjusted.

The most important salts used as lipophilic additives are potassium tetrakis(*p*-chlorophenyl) borate (KTPClPB) (Ganjali, Akbar, Norouzi, Moghimi, & Sepehrifard, 2005; Faridbod, Ganjalli, Larijani, Norouzi, Riahi, & Mirnaghi, 2007; Saad, Ariffin, & Saleh, 1998), sodium tetrakis-[3,5-bis(1,1,1,3,3,3-hexafluoro-2-

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methoxy-2-propyl)phenyl] borate (NaHFPB) (Katsu, Ido, & Kataoka, 2002), sodium tetraphenyl borate (NaTPB) (Ganjali, Emami, Rezapour, Shamsipur, Maddah, Salavati-Niasari et al., 2003), tetrakis(4-fluorophenyl)borate (Masadome, Imato, & Asano, 1999), tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) (Peper, Gonczy, & Runde, 2005) as cationic additive and hexadecylpyridinium bromide (HDPB) (Ganjali, Mizani, & Salavati-Niasari, 2003), hexadecyltrimethylammonium bromide (HTAB) (Ganjali, Mizani, & Salavati-Niasari, 2003), trioctylmethylammonium chloride (TOMACl) (Cabrere, Maldonado, & Rios, 2001) as anionic additive.

1.5 Membrane Potential

In potentiometry charged species or ions are generally encountered. Solution containing ions conduct electricity and are termed electrolytes and these may be subdivided into true electrolytes and potential electrolytes. True electrolytes are ionic compound, such as a sodium chloride, which on dissolving in water undergo a transformation to $Na^{+}_{(aq)}$ and $Cl^{-}_{(aq)}$. The solid state of sodium chloride consists of positively charged sodium ions and negatively charged chloride ions arranged into a regular pattern or crystal. Each sodium ion is surrounded by six chloride ions and vice versa. Potential electrolytes, on the other hand, are covalent molecules which react with water to form ions. An example of such an electrolyte is gaseous hydrogen chloride which (equation 1.2) reacts with water to form hydroxonium and chloride ion where (g), (l) and (aq) refer to gas, liquid and aqueous states respectively.

$$HCl_{(g)} + H_2O_{(l)} \longrightarrow H_3O^{+}_{(aq)} + Cl^{-}_{(aq)} \quad \text{..... (1.2)}$$

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It should be noted, however, that the behaviour of aqueous is dependent of the source and the $Cl^-_{(aq)}$ from NaCl is identical to that from HCl.

Membrane is a layer that separates two solutions, differs in chemical composition from both of them, forms a sharp boundary towards both solutions and exhibits different permeability for individual components of the solution. The utility of membrane electrodes depends upon the determination of membrane potentials. Such potentials cannot be measured directly, but can be deduced from the electromotive force (emf) of complete electrochemical cells. Thus, the membrane potential in cell may be regarded as the electric potential difference between the two bulk solution 1 and 2, and includes both the diffusion potential within the membrane and the phase boundary potential as equation 1.3 below.

$$\underbrace{\text{Electrode A|Solution1}}_{\text{Electrode potential}}\underbrace{\text{||Membrane|}}_{\text{Membrane Potential}}\underbrace{\text{Solution2|Electrode B}}_{\text{Electrode potential}} \quad \text{.....(1.3)}$$

On the other hand the absolute electronic charge on solid electrodes in electrolytes cannot accurately be known, but the changes in charge can be measured. Adding oxidant species (Ox) removes electrons and drives the potential difference of a platinum electrode positive relative to the solution. Adding reductant species (Red) injects electrons into the noble metal and drives the potential difference negative. Compared with the total electron content of metals, the extent of this charge injection is small. After 60 years of research, it was recognized that half–cell reactions need to

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be written as equilibria, and the Nernst term is indicate by a positive sign in front of ln[Ox]/[Red].

The functional potential of any selective ion sensitive membrane depends on a number of factors including the potential activity, selectivity in the presence of various interferences, operative pH range, response time, temperature and lifetime. On the other hand, the membrane electrode also should not react chemically with any species present. It should be inert, should have a Nernstian response to the activity of that species and the surface of the electrode should remain unchanged, even when a small currents passing through the cell.

With few exceptions, the electrodes follow Nernstian potential activity pattern within the working range as given by relation

$$E_{cell} = E^0 + \frac{2.303RT}{zF} \log\ a_{cation} \quad \text{..... (1.4)}$$

for cationic responsive electrodes (equation 1.4) and

$$E_{cell} = E^0 - \frac{2.303RT}{zF} \log\ a_{anion} \quad \text{..... (1.5)}$$

for anionic responsive electrodes (equation 1.5) where, E_{cell} is the measured electromotive force (emf), E^0 is the standard electrode potential, a is the activity of ion and z is the charge of the ion. R, T and F represent the gas constant value, temperature (in Kelvin) and Faraday respectively.

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The function termed activity (a), which can be defined as the thermodynamic or effective concentration. The ion in atmosphere, therefore, effectively reduces the concentration by a factor termed the activity coefficient (γ). If the concentration is represented by $\boldsymbol{c}$ (equation 1.6) then

$$a = \gamma c \quad \text{..... (1.6)}$$

If the activity coefficient is unity, then $a = c$ and the solution behaves ideally. If concentration assessment is to depend on the convenient linear relationship between response and log activity, then the knowledge of the activity/concentration relationship has to be assessed from a carefully plotted direct response (E) versus concentration (c). The calibration curve is often known as the working curve. Theoretically, the slope a monovalent (either cation or anion) species such as glutamate and hydrogen (H^+) should be Nernstian at 59.1 mV per decade concentration change at 25 ^oC. The slopes can be calculated from the Nernst equation (equation 1.7) as follows:

$$E_{cell} = E^0 \pm \frac{2.303RT}{zF} \log a_i \quad \text{..... (1.7)}$$

the Nernstian slope of the calibration line by S, i.e. $S = 2.303RT/zF$.For the H^+ and glutamate ions (monovalent), at 25 ^oC (298 K), the Nernstian slope can be calculated as following :

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$$S = 2.303RT/zF$$

$$= 2.303 \times 8.314 \times 298 \ / \ 96487$$

$$= 0.0591 \text{ V or } 59.1 \text{ mV}$$

So the theoretical Nernstian slope for a monovalent ion is 59.1 mV per decade.

1.6 Selectivity of Membrane

Many different species which are present in the sample contribute to the output signal of a sensor. High selectivity means that the contribution from the primary ion dominates and that the contribution from the interfering ion is minimal.

Potentiometric selectivity coefficient are expressed according to the Nicolsky – Eisenman equation (equation 1.8) as:

$$E = E^o + \frac{2.303RT}{zF} \log [a_A + K_{A,B}^{pot} (a_B)^{z_A/z_B}] \text{.....(1.8)}$$

Where E is the measured potential E^0 is a constant that includes the standard potential of the electrode, the reference electrode potential and the junction potential; z_A and z_B are charge numbers of the primary ion, A, and of the interfering ion , B respectively; a_A and a_B are the activities of the primary ion, A, and the interfering ion, B respectively; and $K_{A,B}^{pot}$ is the potentiometric selectivity coefficient for the primary ion, A against the interfering ion, B. R, T and F is represent the gas constant value, temperature (in Kelvin) and Faraday respectively. If $K_{A,B}^{pot} > 1$, the ISE responds to the

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interfering ions is more than to the primary ions. In most cases, $K_{A,B}^{pot} < 1$, which means that such ISE respond to the primary ion more selectively than to the interfering ions.

The Nicolsky – Eisenman equation assumes a Nernstian response not only for the primary ion but also the interfering ion. Obviously, $K_{A,B}^{pot}$ is assumed to be constant. Several experimental methods for the determination of potentiometric selectivity coefficients are based on this equation (Baker, Pretsch, & Buhlmann, 2000; Gadzekpo & Christian, 1984; Katsu, Ido, Sagara, Tsubaki, & Fuji, 2003; Shafieee-Dastjerdi & Alizadeh, 2004; Srinivasan & Rechnitz, 1969; Ueda, Hioki, Kubo, Kodama, Takaishi, Yokosu, & Katsu, 2005).

Potentiometric selectivity coefficients can be measured with different methods that fall in two main groups, the mixed solution method and the separate solution methods. The most commonly used approach is the fixed interference method, which is a mixed solution method. This method is recommended by IUPAC in 1975 (Guilbault, Durst, Frant, Freiser, Hanseb, Light et al., 1976), but other approaches have also been frequently employed.

The various methods for evaluating selectivities, based on potential measurements either mixed solution methods or separate solution methods.

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1.6.1 Mixed Solution Methods

1.6.1.1 Fixed Interference Method

The emf of a cell comprising an ISE and a reference electrode is measured for solutions of constant activity of the interfering ion, a_B, and varying activity of primary ion, a_A. The emf values obtained are plotted versus the logarithm of the activity of the primary ion. The intersection of the extrapolated linear portions of this plot indicates the value of a_A that is to be used to calculate $K_{A,B}^{pot}$ from the equation 1.9:

$$K_{A,B}^{pot} = a_A / (a_B)^{z_A / z_B} \quad \text{.....(1.9)}$$

where both z_A and z_B have the same signs (positive or negative).

1.6.1.2 Fixed Primary Ion Method

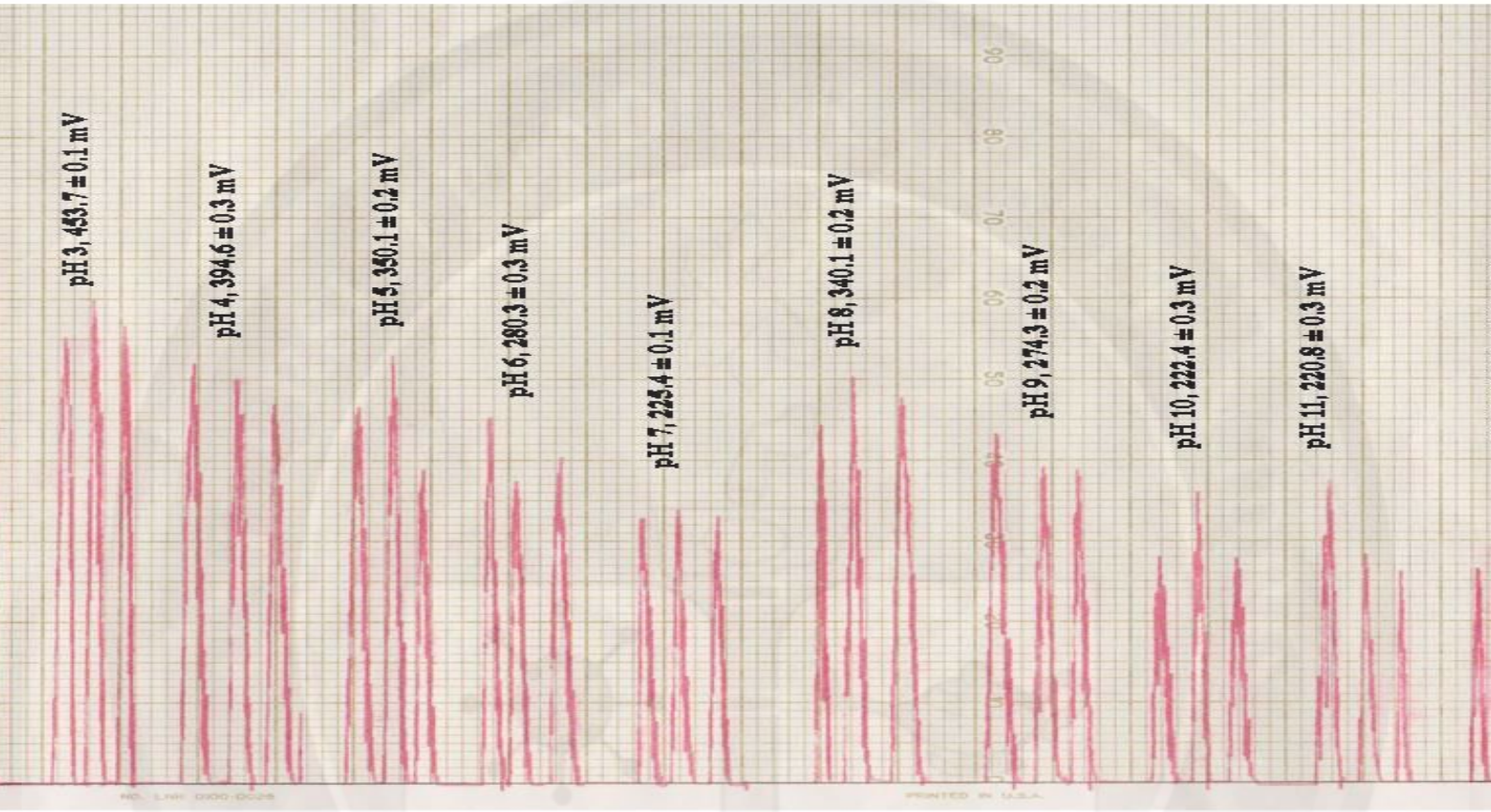
The emf of a cell comprising an ISE and a reference electrode is measured for solutions of constant activity of the primary ion, a_A, and varying activity of the interfering ion, a_B. The emf values obtained are plotted versus the logarithm of the activity of the interfering ion. The intersection of the extrapolated linear portions of this plot indicates the value of a_B that is to be used to calculate the $K_{A,B}^{pot}$ from the equation 1.9.

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1.6.1.3 Two Solution Method

This method involves measuring potentials of a pure solution of the primary ion, E_A



and a mixed solution containing the primary and interfering ions, E_{A+B}. The potentiometric selectivity coefficient is calculated by inserting the value of the difference, $\Delta E = E_{A+B} - E_{A,}$ into the equation 1.10:

$$K_{A,B}^{pot} = a_A(e^{\Delta E z_A F/(RT)} - 1)/(a_B)^{z_A/z_B} \quad \text{.....(1.10)}$$

1.6.1.4 Matched Potential Method

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This method does not depend on the Nicolsky – Eisenman equation at all. In this method, the potentiomeric selectivity coefficient is defined as the activity ratio of the primary and interfering ions that give the same potential change under identical conditions (equation 1.11). At first, a known activity (a_A') of the primary ion solution is added into the reference solution that contains a fixed activity (a_A) of primary ions, and the corresponding potential change (ΔE) is recorded. Next, a solution of an interfering ion is added to the reference solution until the same potential change (ΔE) is recorded. The change in potential produced at the constant background of the primary ion must be the same in the both cases.

$$K_{A,B}^{pot} = (a_A' - a_A)/a_B \quad \text{.....(1.11)}$$

1.6.2 Separate Solution Methods

1.6.2.1 Separate Solution Method ($a_A = a_B$)

The potential of a cell comprising an ISE and a reference electrode is measured with two separate solutions, one containing the ion A at activity a_A, the other one containing the ion B at the same activity $a_A = a_B$. If the measured values are E_A and E_B, respectively, the value of is calculated from the equation 1.12:

$$\lg K_{A,B}^{pot} = \frac{(E_B - E_A) z_A F}{RT \ln 10} + (1 - z_A / z_B) \lg a_A \quad \text{.....(1.12)}$$

which is equivalent to (equation 1.13):

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$$K_{A,B}^{pot} = a_A^{(1-z_A/z_B)}\, e^{(E_B - E_A) z_A F/(RT)} \quad \text{.....(1.13)}$$

1.6.2.2 Separate Solution Method ($E_A = E_B$)

The log *a*versus*E* relations of ISE for the primary and interfering ions are obtained independently. Then, the activities that correspond to the same electrode potential value are used to determine the $K_{A,B}^{pot}$ value.

1.7 Response Time

ISEs generally respond very quickly to the changes in concentration and steable readings are obtained within seconds of the electrode starting to respond to a change in concentration. The IUPAC definition of response time is the time taken for the potential of the cell to reach a value 1.0 mV from the final equilibrium potential. The factors influencing response time include the type of membrane, total volume of the test solution and the rate of stirring. Glass and solid state membranes tend to response faster than do liquid ion exchange membranes or gas sensing probes. Generally, small volumes and relatively fast stirring rates will decrease the response time.

1.8 Lifetime

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Based on practical experience, it is widely accepted that the slope of the response of ISEs remains fairly constant during experiment. Hence, the lifetime of the membrane electrode depend on the Nernstian slope of the membrane. The drifting of the voltage can indicate changes in the membrane composition as a consequence of ion exchange processes in the presence of high concentration of interfering ions in samples, decomposition of the ionophores and/or added charged sites in the membrane and of leaching membrane components.

The lifetime 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, Spichiger, Chaniotakis, Gehrig, Rusterholz, Morf et al., 1991). When plasticized polymeric membrane ISE are exposed to aqueous samples, the equilibrium partitioning of ions at the sample/membrane interface leads to a phase boundary potential. However, together with the sample ions, all membrane components (ionophore, plasticizer, salt additives) partition between the membrane and solution phase. For neutral carrier based membrane sensors, Oesch and Simon (1980) showed that the leaching of the ionophore from the membrane results in a loss of sensitivity and selectivity, thereby limiting the life time. The loss of selectivity is related to the change in the optimal ionophore to ionic site (fixed or mobile) ratio (Bakker, Xu, & Pretsch, 1994; Eugster, Gehrig, Morf, Spichiger, & Simon, 1991; Meier, Morf, Laubli, & Simon, 1984), but it is also accompanied by increased membrane resistance, deteriorating detection limit, increased noise and possibility of initiation of inflammatory responses in vivo (Lindner, Cosofret, Ufer, Buck, Kao, Neuman, & Anderson, 1994).

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Although a drift in the voltage is most probably related to changes in the membrane composition, by characterizing short term and long term stability of ISEs, an eventual drift in the potential of the reference electrode is generally not considered. No information is provided on the stability of the reference electrode when the performance characteristics of novel ISEs are reported. Instead of addressing the origin of the drift of ISEs membrane electrode, they are frequently calibrated to achieve the required precision and accuracy of the determinations.

1.9 Detection Limit of ISEs

In recent years, potentiometry has been extended to trace analysis and has become an alternative technique for replacing stripping voltammetry, atomic absorption spectrometry and even inductively coupled plasma/mass spectrometry (ICP/MS) (Bakker & Pretsch, 2002). Today, optimized ISEs can reach detection limits down to nmol/L and even pmol/L concentrations are reported and it has been demonstrated that potentiometric ISEs are adequate for monitoring metal ion concentration in drinking water (Bakker, Buhlmann, & Pretsch, 1999; Bakker & Pretsch, 2000; Ceresa, Bakker, Hattendorf, Gunther, & Pretsch, 2000).

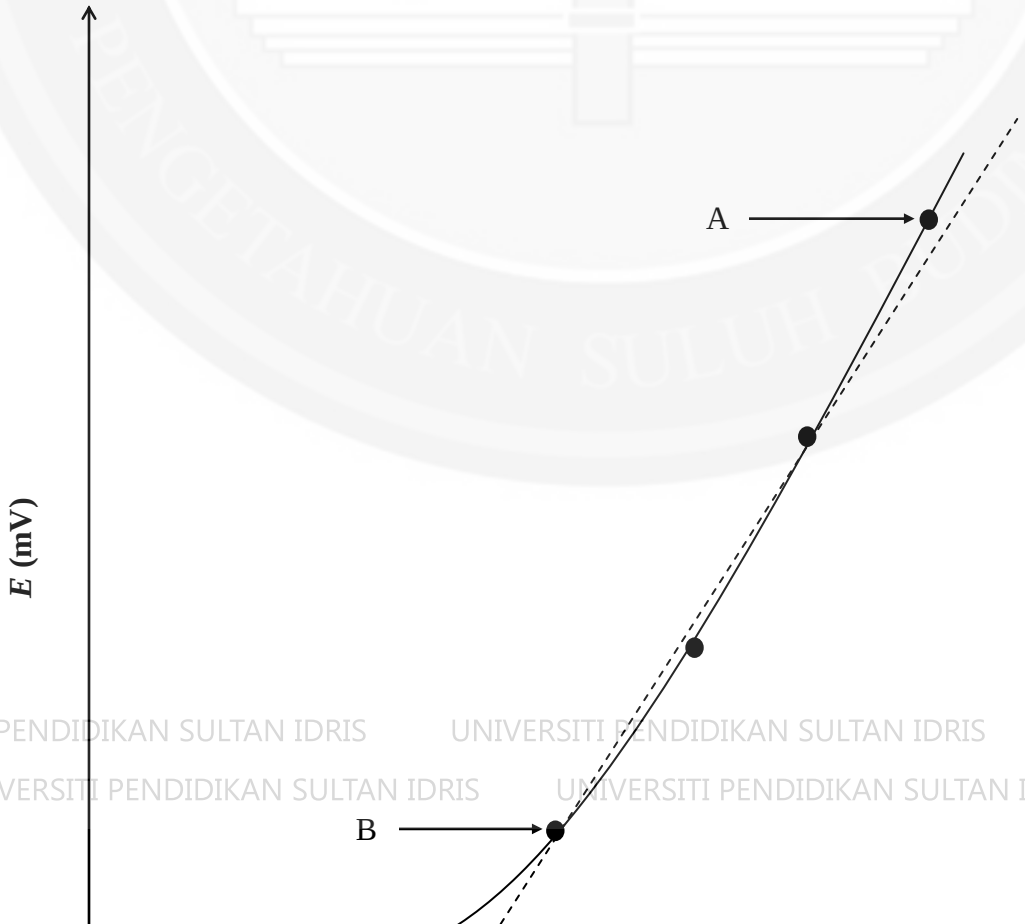
Beside the attainable detection limit, the Nernstian response range can also be used to characterize an ISE. The Nernstian range is defined as the activity range in

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which the electrode response is in accordance with Nernstian equation. Lower limit of measurement is not the same as the lower limit of detection. Figure 1.4 shows the calibration for a typical ISE.

It can be seen that the straight line calibration starts curve to at point A. This is the lower limit of Nernstian response. Whilst the calibration graph is curved below A, it can still be used for measurement. It is only when the graph becomes almost horizontal at point B that measurement of ionic concentration become possible. The IUPAC recommended that the lower of detection limit is the concentration of the ion under investigation at which the extrapolated linear portion of the calibration graph at extreme dilution of that ion intersects the extrapolated Nernstian portion of the graph (Buck & Lindner, 1994). Then, the lower of detection limit is indicated by point



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Figure 1.4. Typical activity (concentration) calibration graph for ISE

1.10 Chitosan

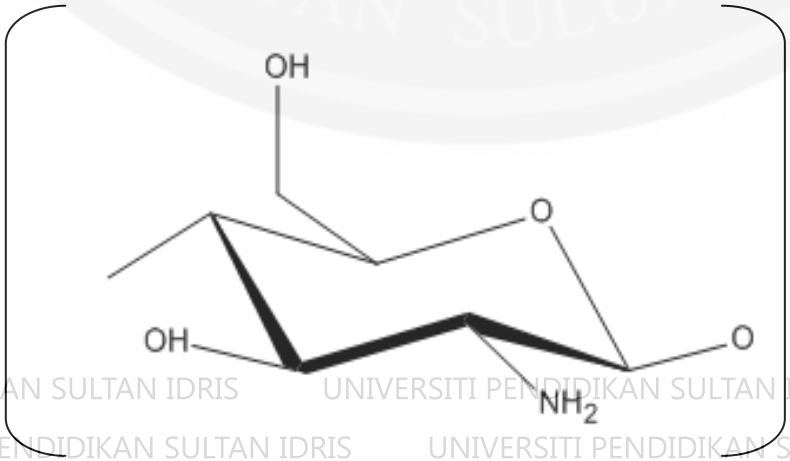
Chitosan, a poly-[1-4]-β-*D*-glucosamine, is a derivative of chitin, a naturally occurring polysaccharide found in insects, arthropods and crustaceans. A quantitative amount of chitosan is obtained by deacetylation of chitin's acetoamide groups in a strong alkaline solution. The peculiar properties of chitosan depend on the presence of reactive amino and hydroxyl functional groups that lead to a large hydrophilic surface (Figure 1.5). This explains why several groups have explored the possibility of using chitosan for developing electrochemical sensors and biosensors (Alexander, Dimitrakopoulos, & Hibbert, 1998; Cruz, Kawasaki, & Gorski, 2000; dos Santos, Riul, Malmegrim, Fonseca, Oliveira, & Mattoso, 2003; Wang, Pan, & Wang, 2005; Zhang & Gorski, 2005; Zhang, Smith, & Goraki, 2004).

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Chitosan is well known for complexing transition metal ions, through chelation at its amino group (Ngah, Ab Ghani, & Kamari, 2005; Ngah & Isa, 1998; Kantipuly, Katragadda, Chow, & Gesser, 2003; Muzzarelli, 1998). Chitosan also possesses many other useful features, including hydrophilicity, biocompatibility, biodegradability, antibacterial properties and a remarkable affinity for many proteins (Gamage & Shahidi, 2007).

Furthermore, chitosan is largely used as a non–toxic flocculent in the treatment of organic polluted wastewater and as a chelating agent for the removal of toxic (heavy and reactive) metals from industries wastewater (An, Park, & Kim, 2001).



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Figure 1.5. Molecular structure diagram of chitosan

Chitosan is also widely believed capable of removing fat, hence is it used for body slimming purposes. However, there is no scientific report on the uptake of fat, i.e. carboxylic acid as yet. On the other hand, chitosan is reported to be able to react with amino acids or proteins, humic acid and *o*-phtalic acid (Jeuniaux, Almas, Baradarajan, Blair, Decock, Deinan et al., 1986; No & Meyers, 2000).

1.11 Analytical Determination of pH

Many chemical processes and properties are pH dependent. Hence, the monitoring of pH of solution is essential in many applications. Even though glass electrode is synonymous with pH measurement, such electrode is fragile and always in need of frequent calibration before and after use. Often, it is unable to provide accurate pH

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values at the extreme end of pH scale. There are, already, various pH electrodes such as metal oxide film (Du, Hu, Huang, & Lin, 2006; Gill, Arshak, Arshak, & Korostynska, 2008; Hendrikse, Olthuis, & Bergveld, 1998; Korostynska, Arshak, Gill & Arshak, 2007; Marzouk, 2003; Ndobo-Epoy, Lesniewska & Guicquero, 2007; Park, Boo, Kim, Han, Kim, & Chung, 2005; Razmi, Heidari, & Habibi, 2008) and fluorescent pH sensors (Boswell, Szijjarto, Jurisch, Gladysz, Rabai, & Buhlmann, 2008; Gao, Tang, Dai, & Wang, 2007; Hakonen & Hulth, 2008; Liebach, Klimant, Krause, & Wolfbeis, 2001; Marshall, Blyth, Davidson, & Lowe, 2003; Martz, Carr, French, & DeGrandpre, 2003; Niu, Guan, Ronnie, Kjell, Anders, & Hjalmar, 2000; Saleh, Al-Soud, & Nau, 2008; Zaggout, Qarraman, & Zourab, 2007; Zeng, Liu, Huang, Goa, & Gui, 2005). However, due to toxicity of the metallic oxides such sensor is prohibited to be used either for biological or biomedical applications. The fluorescent pH sensors are used to measure intracellular pH, and also pH of blood. But its drawbacks are fluctuations in light source intensity of the instrument, photo-bleaching of the pH sensitive reagent, drifts in the optoelectronic setup and also background fluorescence.

A number of optical pH sensors have also been developed (Ganesh & Radhakrishnan, 2007; Goicoechea, Zamarreno, Matias, & Arregui, 2008; Kocincova, Borisov, Krause, & Wolfbeis, 2007; Noire, Bouzon, Couston, Gontier, Marty, & Pouyat, 1998; Seki, Katakura, Kai, Iga, & Watanabe, 2007; Yang & Saavedra, 1995). The fiber optic used has many advantages e.g. small size, flexibility, low propagation loss, no risk of electric shock on *in vivo* measurement and no electromagnetic interference (Grant & Glass, 1997). However, its limitations are complex removal process of cladding layer and the fragility of unclad fiber. Recently, pH electrodes

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based on polymeric membranes have attracted more researches than others (Anker, Ammann, & Simon, 1983; Cosofret, Erdosy, Raleigh, Johnson, Buck, Ash et al., 1995; Cho, Chung, Jeong, & Park, 2000; Demirel, Dogan, Canal, Memon, Yilmaz, & Kilic, 2004; Dong, Luo, Peng, & Cheng, 2008; Han, Yoo, Kim, Hong, & Chung, 2003; Lakard, Segut, Lakard, Herlem, & Gharbi, 2007; Kuruoglu, Canel, Memon, Yilmaz, & Kilic, 2003; Marxer & Schoenfisch, 2005; Oesch, Brzozka, Xu, Rusterholz, Suter, Welti et al., 1998; Panda & Chattopadhyay, 2007; Slim, Ktari, Cakara, Kanoufi, & Combellas, 2008). The electrode is rather easy to manufacture in any desired shape and size. There are rugged and reliable. In heterogeneous polymeric membrane which consists mainly a blend of an inert polymer binder, ionophore and plasticizers; polyvinyl chloride (PVC) remains the best binder (Cosofret, Erdosy, Raleigh, Johnson, Neuman, & Buck, 1996). Ionophores like calix[4]arena (Kuruoglu, Canel, Memon, Yilmaz, & Kilic, 2003), 1–octadecanoyl–4–methylpiperazine, 1–octadecanoyl–4–(2–pyridyl)–piperazine,*N*–octadecylmorpholine and octadecyl isonicotinate (Oesch, Brzozka, Xu, Rusterholz, Suter, Welti et al.,1998), *p–tert*–butylcalix[4]arene–oxacrown–4 (Demirel, Dogan, Canal, Memon, Yilmaz, & Kilic, 2004), amine (Cho, Chung, Jeong, & Park, 2000; Espadas-Torre & Meyerhoff, 1995; Han, Park, Chung, Cho, & Hong, 2001; Michalaka, Hulanicki, & Lewenstam, 1994), hexabutyl–tri–amidophosphate (Lutov & Mikhelson, 1994), azobenzenes (Yuan, Chai, & Yu, 1992) and phenoxazine derivatives (Lindner, Cosofret, Kusy, Buck, Rosatzin, Schaller et al., 1993) have been studied.

Besides these ionophores are quite environmentally friendly and is promising for monitoring pH. The presence of plasticizer in the polymeric membrane blend has increased the membrane polarity which facilitates partition of ions (Antonisse &

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Reinhoudt, 1999) and also help improve capacity of the ionophore (de los A Arada Perez, Marin, Quintana, & Yazdani-Pedram, 2003). The 2–NPOE is the best membrane plasticizer in polymeric pH sensor using macrocyclic compounds (Demirel, Dogan, Canal, Memon, Yilmaz, & Kilic, 2004). In another report (Watanabe, Toko, Sato, Kina, Takahashi, & Liyama, 1998) the dioctyl phenylphosphonate (DOPP) has been blamed of responding towards analyte.

1.12 Flow Injection Analysis (FIA)

Flow injection analysis (FIA) is based on injection of a liquid sample into a moving, nonsegmented continuous carrier stream of a suitable liquid. The injected sample from a zone, which is then transported towards a detector that continuously record the absorbance, electrode potential or other physical parameters as it continuously changing due to the passage of the sample material through the flow cell. During the past three decade, FIA becomes a wide spread methods and the advantages of potentiometric detection by flow injection system have been well recognized. These include low coast, simple instrument, rapid response, high reproducibility, high selectivity, high sensitivity, low detection limit and need very small sample for analysis (Kamari, Mousavi, & Shamsiprur, 2003).

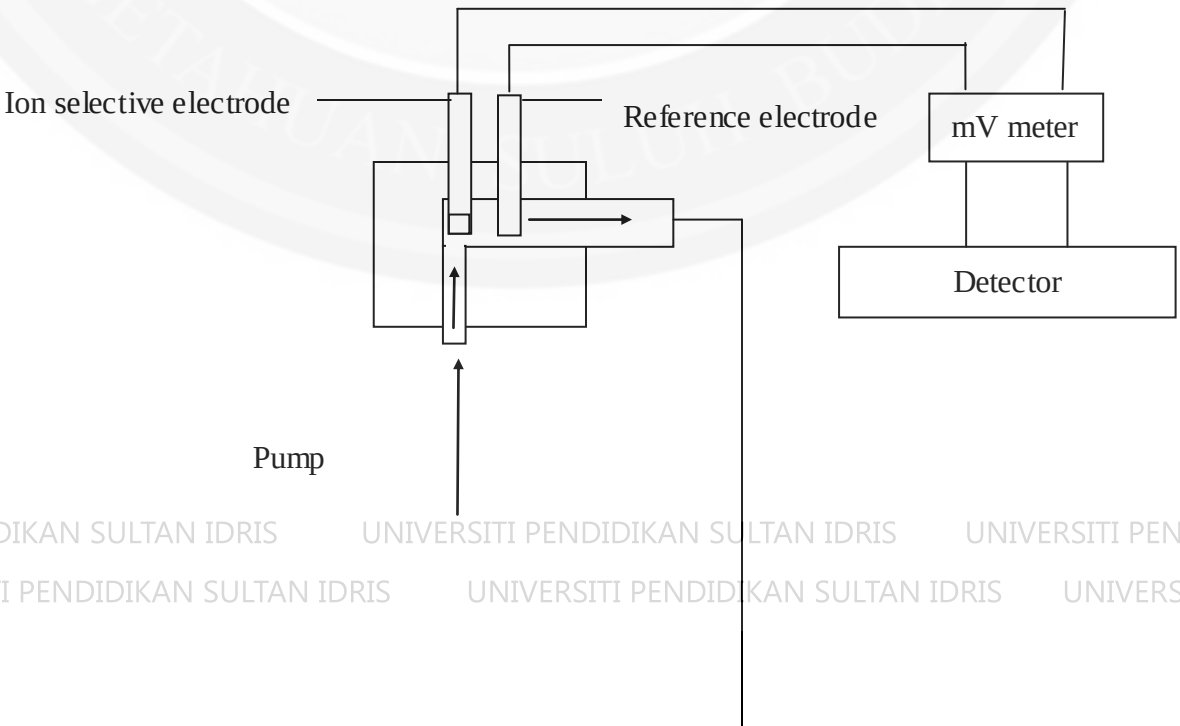
The simplest flow injection analysis consist of a pump, which is used to propel carrier stream through a narrow tube; an injection port, by means of which a well defined volume of sample solution is injected into carrier stream in a reproducible manner and a microreactor in which the sample zone disperses and react with the

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component of the carrier stream, forming a species that is sensed by a flow through detector and recorded (Figure 1.6).

Flow injection analysis is based on combination of three principles, which is sample injection, controlled dispersion of the injected sample zone and reproducible timing of its movement from the injection point to the detector. Thus, in contrast at all other methods of instrument analysis, the chemical reactions are taking place while the analyte is dispersing within the reagent, that is, while concentration gradient of the sample zone is being formed by the dispersion process. The detection for flow injection systems results in sharp current peak.



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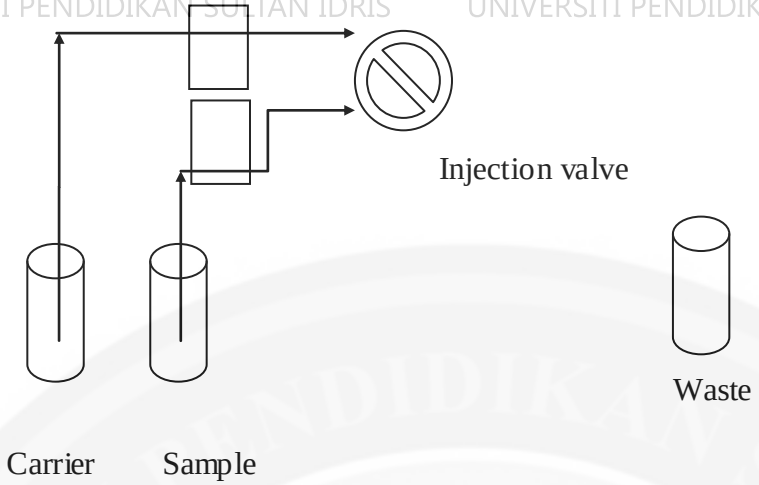


Figure 1.6. Manifold of the flow injection analysis system

The height *H*, width *W*, or area *A* is related to the concentration of the analyte. The time span between the sample injection *S* and the peak maximum which yields the analytical readout as a peak *H*, is the residence time *T* during which the chemical reaction takes place. Typically response peaks recorded during an automated flow injection operation. A well designed FIA system extremely rapid response, because *T* is in the range of 5-20 seconds. Therefore a sampling cycle is less than 30 seconds (roughly $T+ t_b$) and thus typically two samples can be analyzed per minutes. The injected sample volume may be between 1.0 to 200.0 µL (typically 25.0 µL), which in turn requires no more than 0.5 mL of reagent per sampling cycle. This make FIA is simple, automated microtechnical technique, capable of having a high sampling rate and a minimum sample and reagent consumption. Figure 1.7 shows the response peak for FIA system.

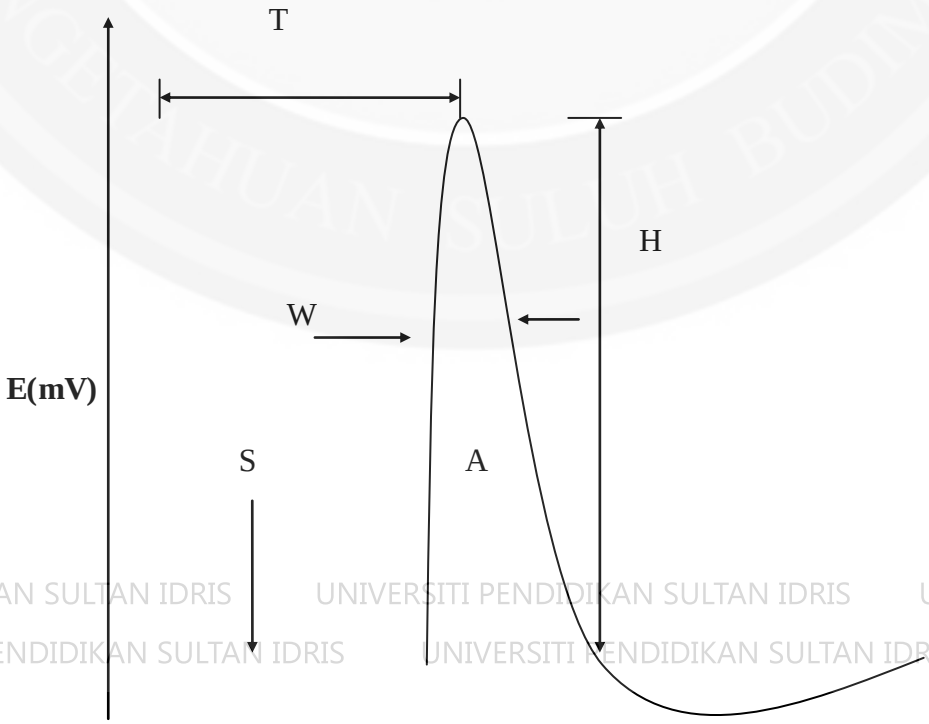
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There are several causes that effect of current peak such are superimposed on a constant background current (caused by redox reaction of the mobile phase or carrier solutions) and larger background currents, expected at high potentials, result in increase (flow rate dependent) noise level (caused by the presence of traces of air in a flowing solution due by the pulsation of the pump).

1.13 Objectives of Study

The aim of this study is to develop a pH potentiometric sensor by using chitosan as a non toxic biodegradable material, as ionophore.



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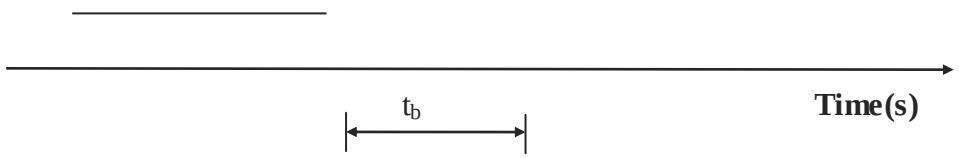


Figure 1.7. The analog recording response peaks for proposed sensor; S is the time span between the sample injection, H is peak height, W is peak width, A is peak area, T is residence time to the peak height measurement, and t_b is the peak width at the baseline

The objectives of this study were:

1. To investigate the potential of chitosan membrane towards pH solution.
2. To classified the best plasticizer.
3. To compare the proposed electrode with commercial pH glass electrode.
4. To analyze the best composition of response electrode using flow injection analysis method.

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CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The pH measurement is of importance in the field of analytical chemistry, chemical process control and environmental analysis. In the pH measurement, electrochemical devices such as a conventional glass electrode and semiconductor devices have been used. Theoretically, pH is measure of the activity of the (solvent) hydrogen ion, which is a measure of electrode potential between a hydrogen electrode and a standard electrode such the silver silver chloride electrode. So far, many approaches have been developed for constructing pH electrodes such are glass electrodes, optical pH sensors, metal oxide film sensors, fluorescent pH sensors FET (semiconductor) and polymeric membrane sensors.

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Improvement of pH measuring technique is required to provide accurate data with simple instrumentation, relatively fast response, reasonable selectivity, wide dynamic pH range and low cost.

2.2 Glass Electrode

Over the years, several attempts have been made at constructing glass electrode. A glass electrode is a type of ion selective electrode made of doped glass membrane that is sensitive to a specific ion. Glass was included in voltaic piles by Ritter as early as 1802 and during 19^{th} century several researchers studied conduction through glass. In 1932, Thompson was the first make experiments in which the possibility of surface conduction had been included, and he showed as an electrolytic conductor (Cheng & Ashraf, 1990).

Kuruoglu, Canel, Memon, Yilmaz, and Kilic (2003) reported pH glass electrodes have been widely used for pH measurement in various samples for more than 60 years. Glass electrodes have been utilized in a wide range of applications, from pure research, control of industrial processes, to analyze foods, cosmetics and comparison of indicators of the environment and environmental regulations: a microelectrode measurement of membrane electrical potential of a biological cell, analysis of soil acidity, etc. A pH glass electrode is very popular due to their high selectivity, reliability and dynamic pH range (Han, Park, Chung, Cho, & Hong, 2001).

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A pH glass electrode consist of an electrode membrane that responds to H^+, highly isolating base material to support unit, solution inside the glass electrode, internal electrode, a silver-silver chloride and a glass electrode terminal (Figure 2.1). Almost all commercial glass electrode responsive to univalent cations such as hydrogen ion, sodium ion, silver ion, ammonium ion, potassium ion, lithium ion and other ions. Only a few chalcogenide glass electrodes are sensitive to double-charged ions, like Pb^{2+}, Cd^{2+} and some others.

Inertness and wide pH range of applicability have made pH glass electrode the most frequently applied electrochemical sensor. Nonetheless, it has limitations like high resistance, brittleness, unable to provide accurate pH values at the extreme ends of pH scale, limited shape and also cannot be used in fluoride solution (Cho, Chung, Jeong, & Park, 2000; Lakard, Segut, Lakard, Harlem, & Gharbi, 2007; Liu, Peng, Liu, & Qin, 2007; Upreti, Metzger, & Buhlmann, 2004.

Baucke (1994) reported from the literature study, the measuring range of glass electrode is limited by the acid error at lower end of the pH scale and by reduced hydrogen ion selectivity, the sodium error, at the upper end of the pH scale, and in rare cases of unsuitable glass membrane composition by the irreversible sodium error. The inertness is restricted only by chemical, such as hydrofluoric acid, which attack the membrane glass strongly and perturb the equilibrium exchange current density of the potential determining equilibrium between the functional surface groups of the glass and hydrogen ion in the solution.

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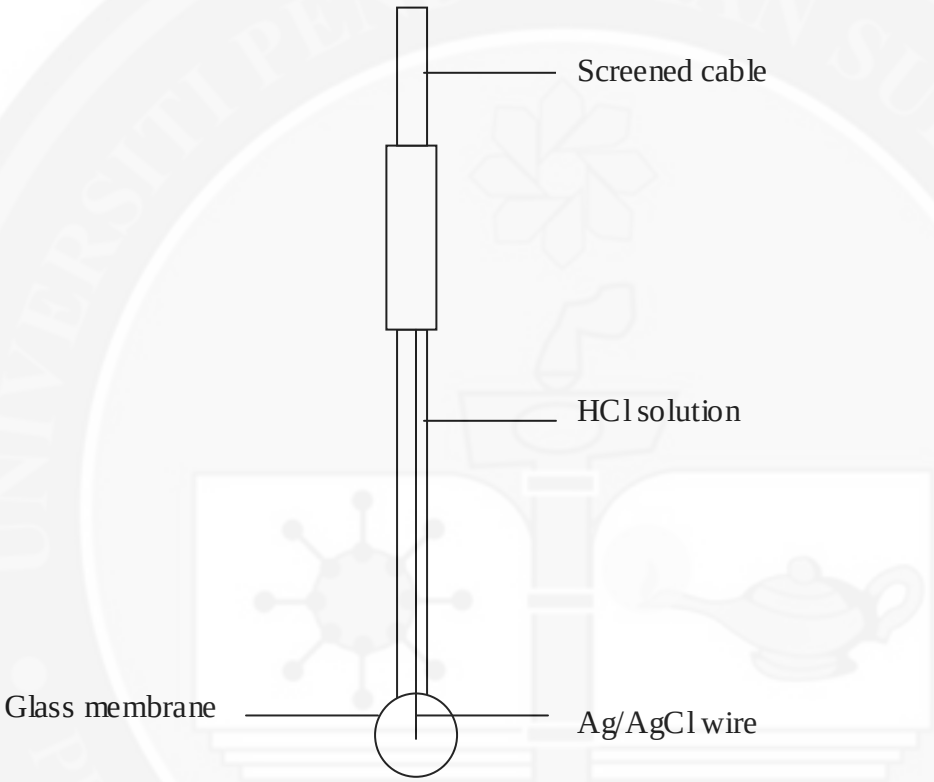


Figure 2.1. Typical glass electrode pH

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In additional, glass electrode also creates problems in the construction of microelectrodes for biological applications and in *vivo* blood pH measurement (Kuruoglu, Canel, Memon, Yilmaz, & Kilic, 2003; Liu, Peng, Liu, & Qin, 2007). Some more, it is always in need of frequent calibration before and after use. Hence, it is challenging to researchers to overcome these drawbacks. Better still if the substitute is robust, cheap, reliable and green.

2.3 Optical pH Sensor

Among many kinds of sensors, optical pH sensors have been extensively investigated and recently attained much interest due to their small size, high selectivity, capability, safety and relativly cheapness in industrial, environmental and biomedical applications (Bai, Wang, Duan, & Gao, 2004; Dong, Luo, Peng, & Cheng, 2008; Rouhani, Salimi, & Haghbeen, 2008). Optical pH sensors are based on pH induced reversible changes in optical or spectroscopic properties such as absorbance, reflectance, energy transfer, refractive index, etc (Figure 2.2). The principles of optical sensors are anchored in classical spectroscopy; only the elements of the experiment and their arrangement are different. Generally, in a spectroscopic measurement the sample is placed in a spectrophotometer, in a well-defined path of the light beam, and the emerging radiation is captured by a detector (Janata, 2009). Optical pH sensors are usually made by immobilization of pH indicator onto a solid support permeable to proton. Indicators are usually selected from dyes which are weak acids or bases. As a result, they exhibit different absorption or emission band for their dissociated and undisssociated forms in the desired range of pH.

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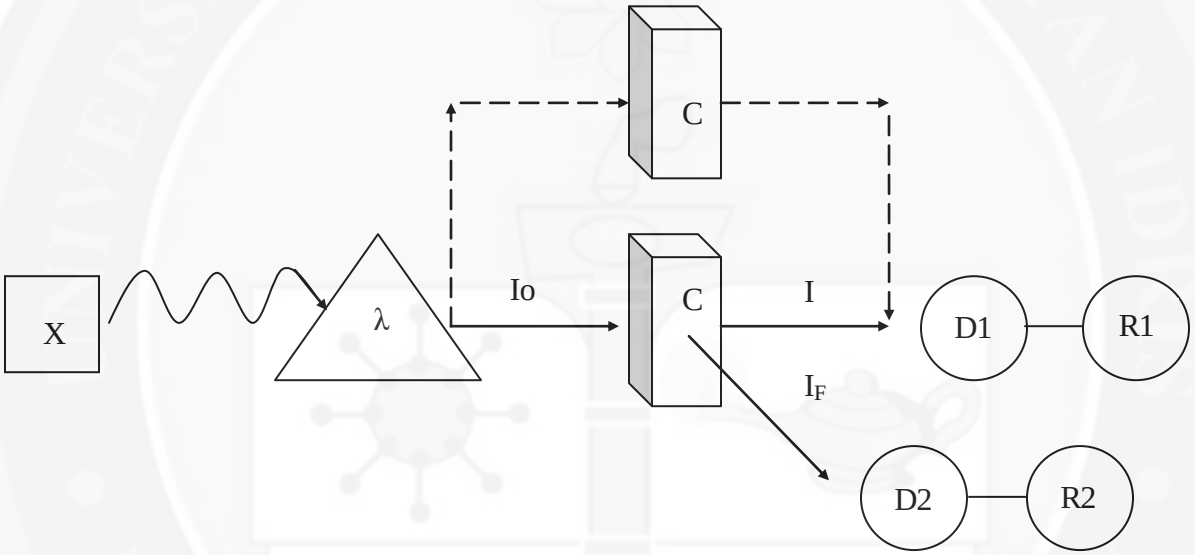


Figure 2.2. General arrangement of spectroscopic absorption/ fluorescence measurement: λ is a wavelength selector, X is a light sourse, D is a detector, R is a recorder. Intensity of initial (Io), or fluorescent (IF) light is related to the concentration of the sample C

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Most of the applied dyes show linear sensitivity in a narrow range of pH. The most commonly used pH indicators include nitrophenils, phthaleins, sulfonphethaleines and azo dyes (Rouhani, Salimi, & Haghbeen, 2008). Several reports that have been published shown that the minor structural modification of an indicator could bring about remarkable changes in the optical features of the fabrication sensor such as its p*K*a, linearity and stability.

Therefore, the different methods have been performed using the sol gel method, where the porous silica matrix is formed while entrapping the dye molecules within it. Porosity of the matrix enables penetration of the analyses and protons, and allows their easy access to the dye molecules which are permanently anchored. The sol gel technique is quite simple and produced the film tough, inert and more resistance to aggressive environments (Dong, Luo, Peng, & Cheng, 2008). Towards this method, a sensing system capable to detecting the parameter of influential to cell health like monitoring pH, oxygen, glucose and lactace.

Recently, on the other hand, a number of the optical pH sensors have studied and developed the nano size optical probe and fiber optic pH sensor. Fiber optic pH sensor are suitable for remote and real time monitoring in hazardous environment due to the many advantages such as small size, flexibility, low propagation loss, no risk of electric shock in *vivo* measurement and no electromagnetic interference (Seki, Katakura, Kai, Iga, & Watanabe, 2007). Among the various type of nanostructure considered for some applications, however, limitation of this type of sensor are complex removal process of cladding layer and the fragility of unclad fiber and also produces a change in absorption of light or the refractive index of the pH sensitive

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material with the change of pH in the solution (Arshak, Gill, Arshak, & Korostynska, 2007).

2.4 Fluorescence pH sensor

Fluorescent pH sensor has grown into a popular and also are widely used in a variety of industrial, environmental, and medical areas especially in bioanalytical chemistry and cellular biology for measuring intracellular pH and pH in blood (Zheng, Wang, Tang, Lu, & Weber, 2007). Fluorescent pH sensor has attracted much effort due to their obvious advantage at higher sensitivity and selectivity. The success of fluorescent sensor can be explained by the distinct advantages offered by fluorescent detection in terms of selectivity, sensitivity, local observation, response time, etc.

Fluorescence was first used in analytical tool to determine concentration of various species, either natural or ionic. Fluorescence sensing is a method for detection of analytes with very high sensitivity, and selectivity. The analyte was determined directly or indirectly by using fluorescent complex or fluorescence quenching method. In fluorescent sensing, fluorescent molecular sensor was a major designed especially in clinical diagnosis for measuring pH, pO_2, pCO_2, potassium ion, etc in blood by using optodes which is chemical sensors and biosensors based on optical fiber coupled with fluorescent probers (Berberan-Santos & Valeur, 1991).

According to Saleh, Al-Soud, and Nau (2008) the class of fluorescent pH sensors that undergoes photoinduced electron transfer (PET) has gained the interest of

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scientist in the early 21 century. The pH sensor of this type used a fluorescence quenching method which is consisting of flourophore linked to an amine receptor via a methylene spacer. PET causes fluorescence quenching. On the other hand, recently fluorescence sensor using fluorescence complex has been developed using metal complexes for capture and detects anions in aqueous solvents. This is because of difficulty to recognize anion in aqueous solutions, which are relevant to biological application due to their strong hydration (Ganjali, Hosseini, Aboufazeli, Faridbod, Goldooz, & Badiei, 2012).

Several florescence pH sensor dependent change in fluorescence intensity of pH sensitive fluorescent reagent, dye or synthesized pH sensitive reagent, or based on the pH dependent change in fluorescent lifetime of pH sensitive reagent. However, the inherent drawbacks of intensity based measurements included fluctuations in light source intensity of the instrument, photo bleaching of the pH sensitive reagent, and drifts in the optoelectronic setup and background fluorescence (Gao, Tang, Dai, & Wang, 2007).

2.5 Metal Oxide pH Sensor

The need for medical pH sensors causes a major problem for some of the more traditional pH measurement method especially *in vivo*. There are many different pH sensor have been commercialized in recent years that show promise in this area and one approach is sensor made of metal oxide film. This approach was chosen because it was reported metal oxides have pH sensitivity and have been exploited in pH

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sensing devises (Gill, Arshak, Arshak, & Korostynska, 2008). Different oxides have been used to developed pH sensor such as RuO_2, PtO_2, TiO_2, OsO_2, IrO_2, RhO_2, Ta_2O_5, and SnO_2 which produced from metal powders or oxidized metal (Liao & Chou, 2008). Metal oxide pH sensor have a number of advantages such are mechanically stable and can be miniaturized for the in vivo measurement, used in aggressive environment (at temperature up to 25.0°C and at pressures up to 270 bar) and also response faster to pH changes, even in non aqueous solvents (Da Silva, Lemos, Pocrifka, Marreto, Rasario, & Pereire, 2008).

The first materials used as pH sensitive dielectric was silicon dioxide (SiO_2) introduced by Bergveld in 1970 using ion selective field effect transistor (ISFET). In ISFETS technique, the devices are normally quite small usually in micrometer range (Arshak, Gill, Arshak, & Korostynska, 2007) which is suitable in pH sensing devices for biomedical purpose. Although a novel methods, Liao and Chou (2008) reported ISFETs not yet reached the precision and needed improve the sensing structure such as the poor isolation between the devices and the chemical solutions, and the sensitivity optical effects. Besides, ISFETs also suffer from degradation of response over the time and requires a modern clean room semiconductor fabrication facility for manufacturing and can prove to be quite expensive (Arshak, Gill, Arshak, & Korostynska, 2007).

Many publications have appeared in the literature referring to other approaches with other metal oxide and methods. RuO_2, SnO_2 and IrO_2 has been demonstrated with more advantages in sensor performance for various application compared to other (Huang, Cao, Deb, Chiao, & Chiao, 2011) due to their chemical

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stability and high conductivity, which inhibit the space charge accumulation solvents (Da Silva, Lemos, Pocrifka, Marreto, Rasario, & Pereire, 2008). A literature survey reveals that several techniques used RuO_2, SnO_2 and IrO_2 as a metal oxide for pH sensing including sol-gel metal oxide pH sensing film, pH array sensor and conductimetric pH sensor.

Nonetheless, from the numerous study, sensor made of metal oxide filem has a limitation due to its toxicity thus is prohibited to be used for either biomediacal or biomedical application (Arshak, Gill, Arshak, & Korostynska, 2007; Du, Hu, Huang, & Lin, 2006; Hendrikse, Olthuis, & Bergveld, 1998; Marzouk, 2003; Park, Boo, Kim, Han, Kim, & Chung, 2005).

2.6 Polymeric Membrane pH Sensors

In view of electric resistance, handling and preparation, there has been considerable interest in non-glass system. Over the years, pH sensor based on polymeric membranes has attracted more attentions than others (Anker, Ammann, & Simon, 1983; Cho, Chung, Jeong, & Park, 2000; Cosofret, Erdosy, Raleigh, Johnson, Neuman, & Buck, 1996; Demirel, Dogan, Canal, Memon, Yilmaz, & Kilic, 2004; Dong, Luo, Peng, & Cheng, 2008; Han, Yoo, Kim, Hong, & Chung, 2003; Lakard, Segut, Lakard, Herlem, & Gharbi, 2001; Kuruoglu; Canel, Memon, Yilmaz, & Kilic, 2003; Marxer & Schoefisch, 2005; Oesch, Brzozka, Xu, & Simon, 1987; Segut, Lakard, Herlem, Rauch, Jeannot, Robert et al., 2007; Panda & Chattopadhyay, 2007; Slim, Ktari, Cakara, Kanoufi, & Combellas, 2008). The attraction being that they are

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easy to manufacture in any desired shape and size, lower electric resistance, easy handling and preparation, typically, rugged and reliable. Besides, these polymeric membranes appear to be promising besides trivial problems like sluggish pH readings. This advantage is crucial importance for practical propose especially for clinical application.

Several polymeric matrices have been used in the manufacturing of ISE and polyvinyl chloride (PVC) remains one of the best choices (Cosofret, Erdosy, Raleigh, Johnson, Neuman & Buck, 1996). The ISE characteristics are considerably influenced by the nature and the amount of each component used. Extensive research of non-conducting polymer PVC based ISEs are done in the period of 1999-2007 where more than 100 ISEs just employing Schiff bases as ionophore were reported (Faridbod, Ganjali, Dinarvand, Norouzi, & Raihi, 2008). There are many factors that affect the performance of the electrode towards its ion, the most important of which are composition of the membrane, amount of ion exchanger, ratio of the plasicizer, soaking time, effect of pH and the presence of interference.

The heterogeneous polymeric membrane is commonly made of plasticized polyvinyl chloride (PVC) constitutes typically 30% (by weight) of the membrane and separates the test solution from the inner compartment, containing a solution of the target ion (into which a Ag/AgCl wire is dipped). The remaining major component of the membrane is the solvent (plasticizer), which ensures the mobility of the free and complexes ionophore, sets the dielectric constant, and provides suitable mechanical properties of the membrane. The influence of ionophore usually exhibit much improved selectivity and response to specific ions and can be an ion exchanger or a

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neutral carrier compound. Besides, it is well documented that the addition of plasticizer in the polymeric membrane blend will increase the membrane polarity to facilitate partition of ions (Antonnise & Reinhoudt, 1999) and to help improve capacity of the ionophore (de los A Arada Pirez, Martin, Quintana, & Yazdani-Pedram, 2003) have been highlighted. Nonetheless, the plasticizer selection is performed in line with its compatibility with the ionophore as well as the final ISE application. It is known that the membrane composition can affect the sensor response dramatically.

Recently, ISE in flow injection analysis (FIA) have several advantages compared to the batch measurement. They include fast sample throughput, high precision, low detection limit, small sample volume, correction of electrode drift by measurement of peak heights and ease of computer automation.

2.7 Flow Injection Analysis (FIA)

FIA is based on injection of a liquid sample into a moving, nonsegmented continuous carrier stream of a analyte liquid. During the past two decade, the advantages of potentiometric detection by flow injection system has been well recognized. The attraction include low coast, simple instrument, rapid response, high reproducibility, high selectivity, high sensitivity, low detection limit and need very small sample for analysis (Kamari, Mousavi, & Shamsiprur, 2003).

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FIA is based on combination of three principles, which is sample injection, controlled dispersion of the injected sample zone and reproducible timing of its movement from the injection point to the detector. Based on this principles, dispersion coefficient is the most important factors that should be considered on constructing a FIA system because it shown how much the original sample solution is dilute on its way towards the sample and how much time has elapsed between the sample injection and the read out.

In this method, sample was injected from a zone, which is then transported towards a detector that continuously record the absorbance, electrode potential or other physical parameter as it continuously change due to the passage of the sample material through the flow cell. The parameters of FIA such as sample volume, flow rate, reactor length and size which affect the response of an ion selective electrode on operation in FIA condition (Karim, El-Nashar, & Abadi, 2012).

A survey of literature reveals that flow injection analysis (FIA) becomes a wide spread method to evaluate the working characteristics of the constructed electrode, and make the applicability of the developed system viable for determination of different samples (Araujo, Melo, & Coelho, 2011; Beheshti & Amini, 2007; Karim, Nashar, & Abadi, 2012; Khater, Issa, & Mohammed, 2009).

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CHAPTER 3

EXPERIMENTAL

3.1 Chemicals and Reagents

All chemicals were of reagent grade and were used without purification. Chitosan PM 100 (granular), 100 mesh, was obtained from ChitoChem (M) Sdn. Bhd. (Malaysia). High-molecular weight poly(vinyl chloride) (PVC) was obtained from Fluka Chemika (Switzerland).The 2-nitrophenyloctyl ether (2-NPOE), bis(2-ethylhexyl) adipate (BEHA), tris(2-ethylhexyl) phosphate (TEHP), dibutyl phthalate (DBP) and dioctyl phthalate (DOP) were obtained from Aldrich (Germany). The tetrahydrofuran (THF) and chloride salt of all cations were obtained from MERCK (Germany). All solutions were prepared using distilled deionised water from EASYpure LF, Barnstead (USA). The stock solutions of defined pH were, freshly, prepared using analytical grade boric

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acid, acetic acid, sodium sulphate of Sigma-Aldrich and phosphoric acid of Fluka Chemika (Switzerland).

3.2 Instrumentations

The pH and emf responses of solutions were measured using Orion 720Aplus meter of Thermo Electron Corp (USA). An Orion 915600 glass electrode of Orion Research Inc. (USA) was used to determine the pH of solutions. This commercial electrode has been calibrated using standard buffer solutions of pH 4.01, 7.00 and 10.01 of Orion Research Inc. (USA). Ag/AgCl electrode of BASi, MF-2052 (USA) with a fiber junction was used as a reference electrode. The solution was stirred by a magnetic stirrer HI 200M of Hanna, Singapore. The fourier transform infrared (FTIR) spectrometer model Thermo Nicolet 6700 using ATR diamond was used to characterize the membrane. An Alltech 420 HPLC pump was used for comparison method of the electrode response in FIA. The connecting and mixing tube were made of PTFE tubing with an i.d of 0.5 mm and a proportional valve with sample loop volume of 20.0 µL. The results obtained were recorded by chart recorder of Barnstead International, (USA).

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3.3 Fourier Transform Infrared (FTIR)

Characterization of chitosan was done with fourier transform infrared (FTIR). FTIR instrument was used in determination of functional group. The KBr disc method was used by mixing the 2% (w/w) of chitosan with the potassium bromide 98% (w/w) into a mortar and was mashed so that the mixture is completely mixed. The mixture was then pressured with 10 tonnes hydraulic pressure until a disc shape obtained. FTIR KBr disc spectrum was recorded in the range 400 – 4000 cm^{-1} by using FTIR instrument Thermo-Nicolet, model 6700.

3.4 Preparation of Membrane and Electrode

Various quantities of chitosan were mixed with a fixed quantity of PVC and plasticizer (initially dissolved in 2.0 mL THF). The blend was poured into a glass ring of 35.0 mm i.d. resting on a glass plate. The mixture was left to cure overnight at room temperature as shown in Figure 3.1. After which the resulting membrane was peeled off from the glass mould. A disc of 6.0 mm diameter was cut out of the membrane. The disc was glued to the end of Pyrex® glass tube with Araldite® and left to dry for 4 days. Then, 0.1 M HCl internal filling solution was added in the tube (Figure 3.2). Electrical contact between inner solution and the signal measurement instrument was accomplished through a platinum electrode. The later has also acted as internal reference electrode. The electrode assembly was immersed in 1.0×10^{-3} M HCl for 12 hours conditioning. The polymeric membrane was rinsed with water prior to variety of tests to obtain the optimum performance.

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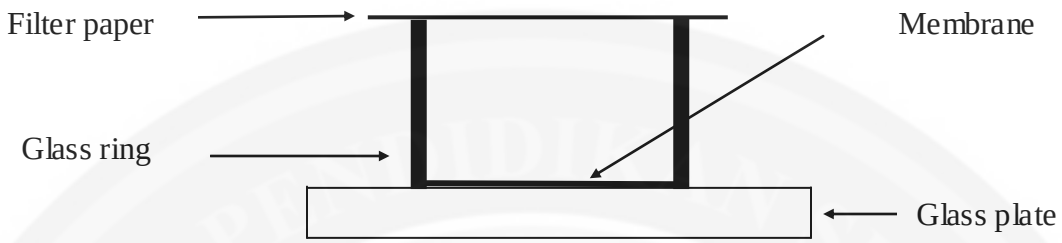


Figure 3.1. Casting of the membrane mixture

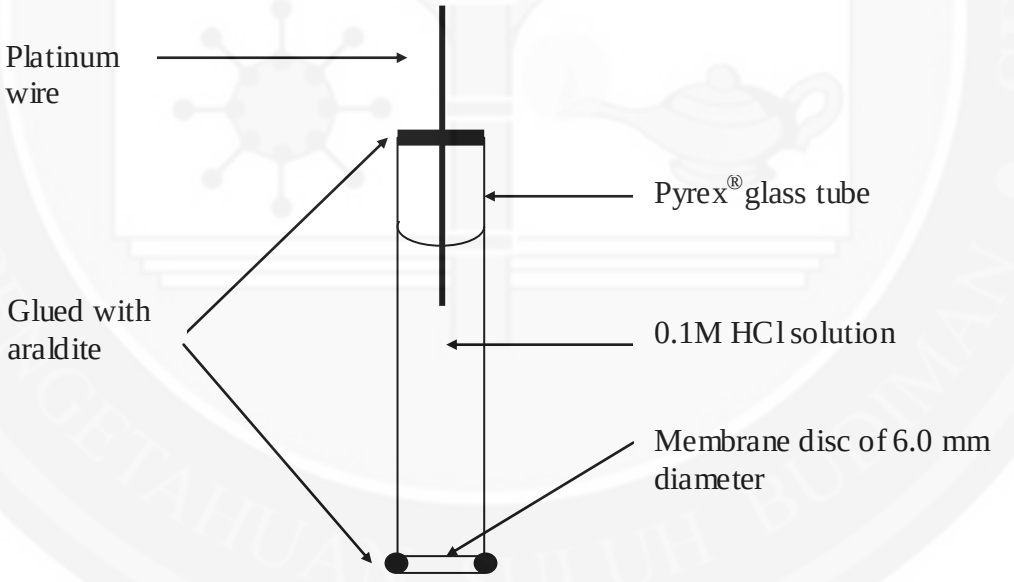


Figure 3.2. Heterogeneous chitosan membrane electrode

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The whole process was repeated in order to find the best membrane which generate stable potential and exhibited satisfactory response with regard to working concentration range and slope.

3.5 Potentiometric Measurements

A series of pH solution in the pH range 2 –12 were prepared by using Britton-Robinson buffer solution by mixing 250.0 mL of 0.04 M boric acid, acetic acid and sulfuric acid with addition 5.0 mL of 1.0 M sodium sulfate then, the pH of these solutions were adjusted with addition of 0.2 M sodium hydroxide. The heterogeneous membrane electrode was preconditioned in stirred water until the reading was stabled before measurements. The potentiometric measurements were done by dipped the heterogeneous membrane electrode (working electrode) and Ag/AgCl (reference electrode) in the solution and the solutions was continuously stirred during until a steady potential reading was then taken. All measurements of emf responses were performed at 25.0 ± 1^{o}C and carried out with the following cell scheme:

Ag, AgCl| KCl (3.0 M)|| sample solution | membrane | HCl (1.0 M)| Pt wire.

A graph of emf against pH was plotted.

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3.6 Response Time

The response time of each electrode was measured by recording the emf of the electrode as a function of time when it was dipped in the solution to be studied. The electrode was usually first dipped in a lowest pH solution (pH=2) and immediately shifted to another solution (pH=3) and will continue until solution (pH=12). The potential of the pH solution was read as zero second, that is, just after immediate dipping of the electrode in the second solution and subsequently recorded at the intervals of 5 seconds. The time during which the potential attain a constant *E* value represent the response time of the electrode. A graph of electrode potential against pH was plotted and the electrode slope determined.

3.7 Lifetime

The electrode lifetime was determined by recording the potential of the electrode in the range of pH solution 2–12 and plotting its calibration curve everyday for the determination of the slope of the membrane electrode. The electrode stability was tested over 3 months periods and during the test, the membrane electrode was daily used.

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3.8 Selectivity Coefficient, K^{pot}

In order to get the selectivity coefficient, K^{pot} for the polymeric pH membrane near to real situation, the mixed solution method was used (Isa, Dahlan, Hashim, Ahmad & Ghani, 2012; Bakeman, Isa, Ali, Ahmad, & Ghani, 2012). For potassium interfering cation, the potentials were measured in a varying of pH Britton–Robinson buffer solutions (pH 2-12) by mixing of 0.04 M boric acid, 0.04 M acetic acid and 0.04 M sulfuric acid and fixed interference of K^+ at concentration (1.0×10^{-1} M).The pH of these solutions was varied by drop wise addition of 0.2 M sodium hydroxide. The selectivity of the membrane towards H^+ in the present of potassium cation is obtained by plotted emf values versus pH (2-12). The intersection of the extrapolated linear portions of this plot indicates the value of cations. Similar procedure was performed for various cations such as Na^+, Li^+, Cu^{2+}, Co^{2+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, Fe^{3+} and Ba^{2+}.

3.9 Characterization of Membrane

The pre-requisite performance of ion-exchange membrane is its complete physic-chemical characterization, which involves the determination of all parameter that affects its electrochemical properties. These parameters were including membrane water content, porosity, thickness, swelling and characterization of adsorbent and were determined after conditioning the membrane as given below.

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3.9.1 Conditioning of Membrane

The membrane was conditioned by equilibrating it in 1.0×10^{-3} M HCl for 24 hours. The addition of 0.1 M sodium acetate was dropped wise to neutralize the acid present. The membrane characteristics were determined according to the adopting methods (Khan, 2006).

3.9.2 Water Content

The conditioned membrane was first soaked in the distilled water to elute any diffusible salts then left to dry by blotted it with Whatman filter paper to remove surface moisture and immediately weighed (W_w). The membrane was further dried in the vacuum over phosphorus pentoxide, P_2O_5 for 24 hours to obtain the constant weight (W_d). The water content (% total wet weight) was calculated based on the following equation 3.1:

$$\% \text{ total wet weight} = [(W_w - W_d) / W_w] \times 100 \quad \text{.....(3.1)}$$

The W_w is the weight of soaked/wet membrane (mg) while W_d is the weight of dried membrane (mg).

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3.9.3 Porosity

The membrane was placed in an air-circulating oven for 24 hours at 60.0 ºC and continues to further dry in a vacuum oven at 80.0 ^{o}C for 24 hours before measuring its dry weight (W_d). Then, membrane was soaked in the distilled water for 24 hours and blotted with filter paper and it was weight (W_w). The porosity (ε) was determined as the volume of water incorporated in the cavities per unit membrane volume from the water content data as in the following equation 3.2:

$$\varepsilon = (W_w - W_d) / AL\,\rho_w \quad \text{..... (3.2)}$$

The W_w is the weight of soaked membrane while Wd is the weight of dried membrane. Meanwhile, A is the area (cm^2), Lis the thickness (mm) of the membrane and ρ_w is the density of water (1 g/mL).

3.9.4 Thickness and Swelling

The thickness of the membrane was measured by taking the average thickness using digital screw gauge (micrometer 293-761-30 of Digimatic, Japan). The percentage of swelling was measured by the difference between the average thickness of the membrane which equilibrated with 1.0 M NaCl for 24 hours and the dry membrane. The percentage swelling of the membrane was calculated using the following equation 3.3:

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$$\text{Swelling} = (L_s - L_d) / L_d \times 100 \quad \text{..... (3.3)}$$

The L_s is the weight of soaked membrane while L_d is the weight of dried membrane.

3.10 Analysis of Real Samples

For real sample analysis, some fruit juice samples were obtained from local hypermarket. About 50.0 mL of the each sample was taken in a beaker and then potentiometric measurement was done by immersed the heterogeneous membrane electrode (working electrode) and Ag/AgCl electrode (reference electrode) in the sample solution and the solutions was continuously stirred during measurement and a steady potential reading was then taken.

3.11 Flow Injection Analysis Method

In this technique, the measurement potential was connected to chart recorder to record the potential signals. Before starting the measurement, it was necessary to condition the sensor in the FIA condition by passing the deionized water (carrier solution) through flow cell for 5 minutes. After this period, a constant sample volume at 20.0 µL of solution Britton–Robinson buffer with different pH in the range 2-12 were injected into a carrier solution by using peristaltic pump at a flow rate 1.5 mL per minutes through passes the cell of sample (analyte) and transient potential is recorded

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as a peak. The analyses were performing in triplicate and the average signal potential or a peak height value was measured.

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CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of Chitosan

Chitosan has been widely used for development electrochemical sensor and biosensor due to the presence of reactive amino and hydroxyl functional groups (Alexander, Dimitrakopoulos, & Hibbert, 1998; Cruz, Kawasaki, & Gorski, 2000; dos Santos, Riul, Malmegrim, Fonseca, Oliveira, & Lattoso, 2003; Wang, Pan, & Wang, 2005; Zhang & Gorski, 2005; Zhang, Smith, & Gorski, 2004). Figure 4.1 shows the infrared spectrum of chitosan membrane.

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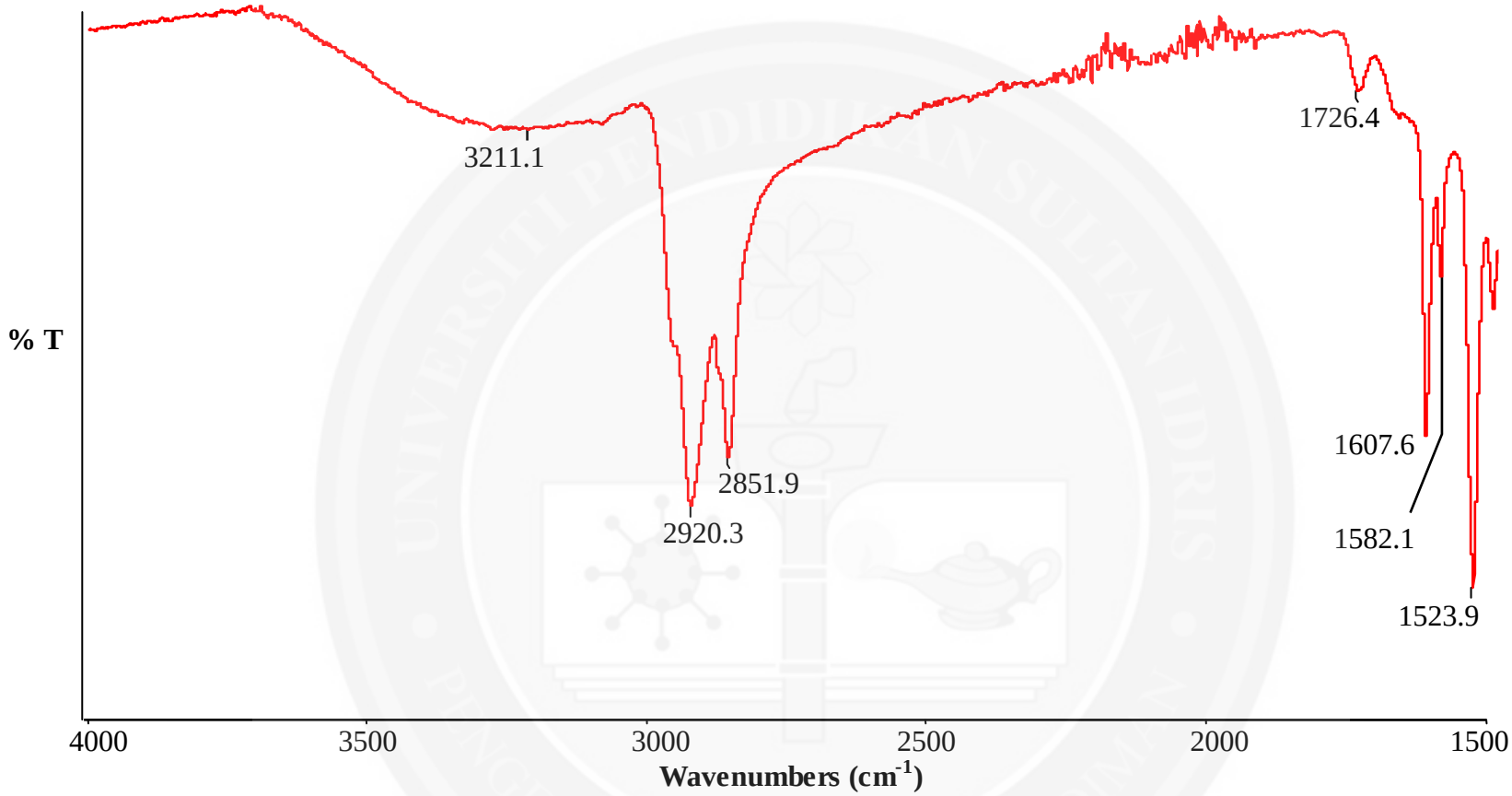


Figure 4.1. FTIR spectrum for chitosan membrane

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The characteristic adsorption peaks of amine (N-H) group at 1607.6 cm^{-1} and 1581.5 cm^{-1} were observed in the spectrum of chitosan membrane. The presence of N-H group is important for exchange mechanism in acidic condition. The existence of amine group as the electron donor makes the hydrogen ion of hydrochloric acid possible to form interaction through a lone pair of electron to one of the nitrogen atom and vice versa, which give an ionic current (Wan, Creber, Peppley, & Bui, 2003). The possible mechanism of chitosan membrane is shown in Figure 4.2.

In acid condition the formation of the later is dominant even in the presence of other cations (Chen, Tsaih, & Lin, 1996). Coordination with most cations, especially of transition metals are achieved in neutral and slightly acidic condition (Muzzarelli & Rochetti, 1974). FTIR absorption peaks at 2920.3 cm^{-1} and 28551.9 cm^{-1} were assigned to the stretching of C-H bonds, whereas peak at 3211.1 cm^{-1}, 1726.4 cm^{-1} and 1523.9 cm^{-1} corresponded to the O-H, C=O and C-C stretching vibrations.

4.2 Selection of Electrode

An ideal ISE consists of a thin membrane across which only the intended ion can be transported through. The transport of ions from high concentration to low one through a selective binding with some sites within the membrane creates a potential difference. Polymer ISE membrane consist of polymer matrix, plasticizer and active component such as ionophore and ion exchangers.

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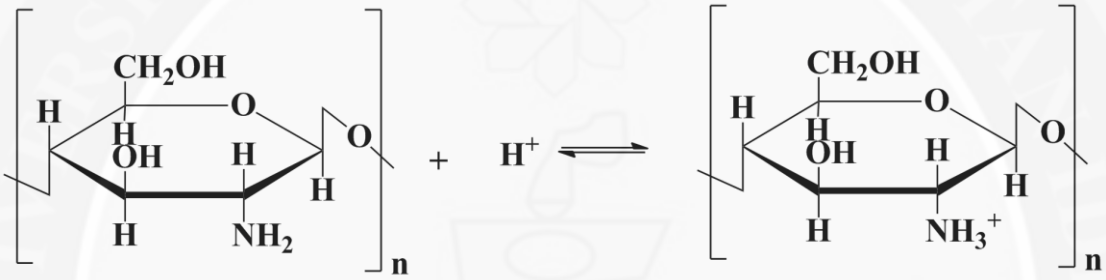


Figure 4.2. Possible mechanism at membrane solution interface

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It's well known that the sensitivity as well as selectivity and linearity of ISE not only by nature of ionophore but also significantly by membrane composition and nature of solvent mediator and lipophilic additive used (Gupta, Sigh, Al Khayat, & Gupta, 2007; Sanchez, Guttierrez, & Blanco, 1995; Tavakkoli & Shamsipur, 1996). Besides, contact time and concentration of equilibrating solution must also be optimized in order to develop a reproducible, stable and noiseless potentials membrane (Gupta, Mangla, & Agarwal, 2002; Srivastava, Gupta, & Jain, 1996; Gupta, Jain, Singh, & Khurana, 1997).

The literature described, the selectivity of the ISE is related to the equilibrium constant, of the exchange reaction of the primary and interfering ions between membrane phase and the aqueous phase. It is depends on the complex formation constant of the ions with ionophore in the membrane, and the membrane composition. Furthermore, the concentration of the internal solution affects both the transmembrane electric potential and the stability of the cell potential (Shamsipur, Hosseini, Alizadeh, Eskandari, Sharghi, Mousavi et al.,2003).

The performances of heterogeneous chitosan : PVC (w/w) membranes are normally accessed by increasing the percentage of chitosan in the membrane whilst keeping the percentage of binder PVC constant. Therefore, the effect of plasticizers i.e. 2-NPOE, DOP, BEHA, TEHP, DBP is the variable and without plasticizer as a control. Its known that for ionophore based membrane electrode, sensor performance can be optimized by choosing suitable plasticizer and ion exchangers (Liu, Peng, Liu, & Qin, 2007). The emf responses of the polymeric membranes with

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various plasticizers added towards a series of Britton–Robinson buffers solution (pH 2.0 – 12.0) with 0.1 M Na_2SO_4 are investigated.

The optimizations of these sensors are tabulated (Table 4.1). The overall result indicates that electrode no. 8 with composition ratio (w/w) of chitosan (20): PVC (30): 2-NPOE (30) performs near to Nernstian, linear range from pH 2 to 9 and limit of detection pH 9.5 (Figure 4.3). From the Nernst equation (equation 4.1):

$$E_{cell} = E^0 \pm (2.303RT/nF) \log a \quad \text{..... (4.1)}$$

The theoretical Nernstian slope, S = 2.303RT/nF, for a monovalent ion at 25.0 ^oC is 59.1 mV decade^{-1}. Theoretically, a higher dielectric constant of a plasticizer increase polarity of the membrane and favor divalent ion, which will alter the selectivity of the membrane. It is apparent that the best polymeric pH sensor with plasticizer 2–NPOE has nearly ideal slope at 56.6 ± 0.4 mV decade^{-1} as compared with the other plasticizers. The 2–NPOE as the preferred plasticizer for monovalent ions ISE has been highlighted elsewhere (Demirel, Dogan, Canal, Memon, Yilmaz, & Kilic, 2004; Gupta, Jain, & Pal, 2010).

The presence of plasticizer in the binder matrix acts as a fluidizer, allowing homogeneous dissolution and diffusion mobility of the ion-pair inside the membrane (Norouzi, Rashedi, Alipour, Faridbod, Shahtaheri, & Ganjali, 2011). The slope value of each of the added plasticizer polymeric membrane decreased in the order of 2–NPOE > DOP >BEHA > DBP> TEHP ≈ without plasticizer.

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Table 4.1

Optimised membrane composition and their potential response

Electrode no.	Mass (w/w)							Slope (mV decade^{-1})	Linear range (pH)
	Ionophore	Plasticizer					PVC		
		2-NPOE	DOP	BEHA	TEHP	DBP			
1	10	-	-	-	-	-	30	40.1 ± 0.2	2-7
2	10	30	-	-	-	-	30	54.5 ± 0.3	2-9
3	10	-	30	-	-	-	30	51.3 ± 0.2	2-8
4	10	-	-	30	-	-	30	49.8 ± 0.4	2-7
5	10	-	-	-	30	-	30	41.7 ± 0.2	2-8
6	10	-	-	-	-	30	30	42.6 ± 0.2	2-8
7	20	-	-	-	-	-	30	42.3 ± 0.3	2-7
8	20	30	-	-	-	-	30	56.6 ± 0.4	2-9
9	20	-	30	-	-	-	30	53.1 ± 0.2	2-8
10	20	-	-	30	-	-	30	51.3 ± 0.2	2-7
11	20	-	-	-	30	-	30	44.1 ± 0.3	2-8
12	20	-	-	-	-	30	30	45.4 ± 0.2	2-8
13	30	-	-	-	-	-	30	41.4 ± 0.2	2-7
14	30	30	-	-	-	-	30	52.3 ± 0.3	2-9
15	30	-	30	-	-	-	30	53.1 ± 0.4	2-8
16	30	-	-	30	-	-	30	47.5 ± 0.2	2-7
17	30	-	-	-	30	-	30	41.1 ± 0.3	2-8
18	30	-	-	-	-	30	30	44.2 ± 0.2	2-8

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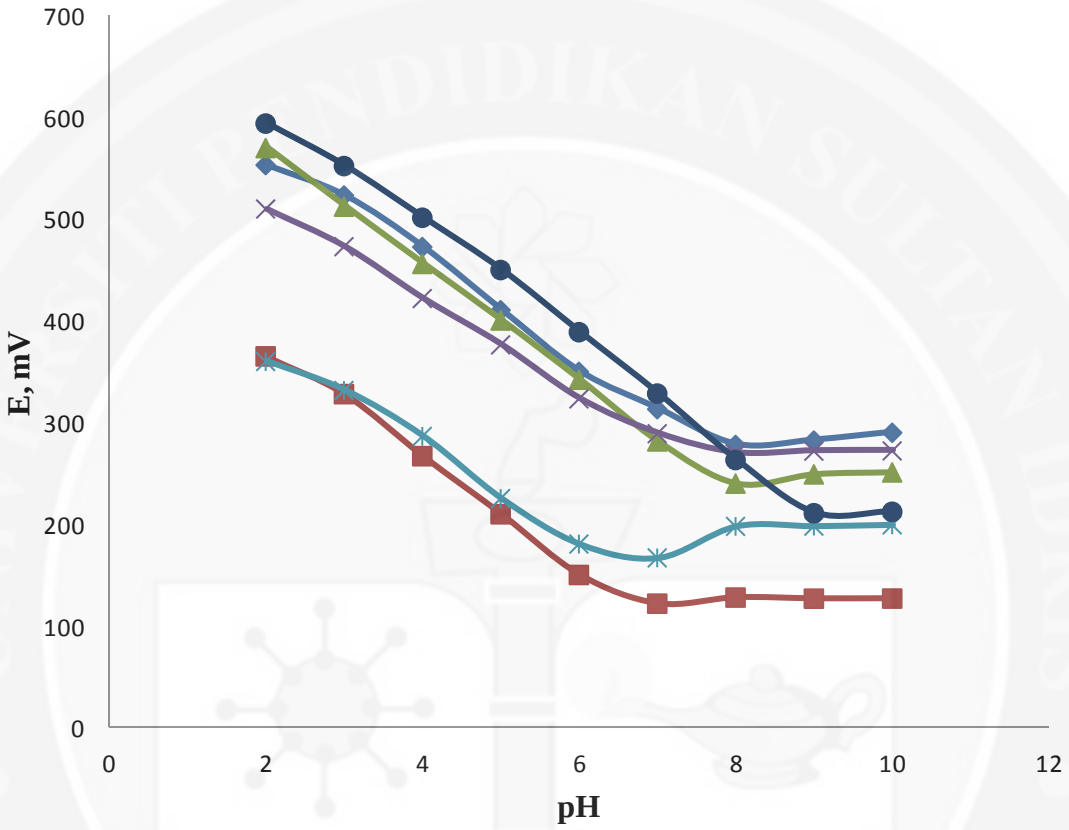


Figure 4.3. Calibration plots of chitosan membrane electrode with composition ratio of chitosan (20), PVC (30) and different plasticizer (30): (●) NPOE, no.8;(▲) DOP, no.9; (■) BEHA, no.10; (×) TEHP, no.11; (◆) DBP, no.12 and (✳) without plasticizer, no.7

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4.3 Selectivity Coefficient of the pH Electrode, K^{pot}

The selectivity coefficient, K^{pot}, of the pH sensor towards other ions is also investigated. This is the most important characteristic of any ion sensor. K^{pot} determines the extent to which a sensor can be employed in the analysis of real samples (Gupta, Jain, & Kumar, 2006).

In order to get the K^{pot} for the developed polymeric membrane as near as possible to real situation the mixed solution method is used. The concentration of interference cations e.g. potassium, sodium, lithium, calcium, barium, copper, magnesium, cobalt, zinc and iron (III) were fixed at 1.0×10^{-1} M. The pH of Britton–Robinson buffer solutions were varied by drop wise addition of sodium hydroxide. It appears that the calculated K^{pot} are less than 1 for all cations (Table 4.2) indicating that the proposed pH sensor (electrode no.8) is not sensitive to the cations tested, especially, the alkali metal ions. Thus, it can be used, conveniently, for pH measurements in media containing these cations e.g. environmental waters. The interfering effect of the cations is in the following order: $Na^{+} > Li^{+} \approx Cu^{2+} > K^{+} > Co^{2+} > Mg^{2+} \approx Ca^{2+} \approx Zn^{2+} \approx Fe^{3+} \approx Ba^{2+}$ which is, apparently, an anti-Hofmeister Series.

4.4. Response Time and Lifetime of the Electrode

The response time of an ISE is important in analytical applications and it depends slightly on the concentration change. Therefore, it is determined by recording

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Table 4.2

Selectivity coefficients of chitosan membrane electrode (no. 8) towards various interfering cations

Interference	K^{pot}
Na^{+}	2.5×10^{-11}
Li^{+}	6.3×10^{-11}
Cu^{2+}	6.3×10^{-11}
K^{+}	1.0×10^{-12}
Co^{2+}	7.9×10^{-12}
Mg^{2+}	1.0×10^{-13}
Ca^{2+}	1.0×10^{-13}
Zn^{2+}	1.0×10^{-13}
Fe^{3+}	1.0×10^{-13}
Ba^{2+}	1.0×10^{-13}

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the elapsed time to reach a stable potential value after the electrode and the reference electrode were immersed in calibration solutions from low to high H^+ concentrations. The response time of the proposed pH sensor (electrode no.8) is in the region of 20 0 ± 5 seconds. This is comparable to those reported in literature (Cho, Chung, Jeong, & Park, 2000; Seki, Katakura, Kai, Iga, & Watanabe, 2007). However, the response is slightly longer in the basic region 30.0 ± 5 seconds. This is possibly due to the exchange of anion OH^- is harder due to formation of inorganic salt. This indicates that in acidic medium Donnan equilibrium is more favourable as the proton, H^+, in the quaternary ammine is easily detachable from the tertiary amine functional group of the ionophore and is later exchanged with the proton in solution. The possible mechanism involved in the generation of the emf response is shown.

$$\underset{\text{(membrane)}}{Ø\text{—}NH_2\,H^+} + \underset{\text{(solution)}}{H^+} \leftrightarrow \underset{\text{(membrane)}}{Ø\text{—}NH_2\,H^+} + \underset{\text{(solution)}}{H^+}$$

The repeatability of pH measurements is studied by performing several runs from pH 2 to 12 and vice versa. There is no drift observed during the measurements indicating that sensitivity, reversibility and repeatability of this pH sensor are excellence. Throughout the measurement no hysteresis is observed either.

The lifetime of the electrode membrane usually determined by measuring the responses of the membrane stored in solution at different period time, therefore the lifetime of proposed electrode is determined by recording its potentials at an optimum

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pH value and by plotting calibration curves every day. The slope of calibration curve indicates no significant changes within a period of 3 months (Figure 4.4).

This shows that operational stability of the proposed pH sensor is not affected for a period of at least 3 months of continuous use. Also the membrane has no experience of ingredients leak from the organic layer which affects response after several time of usage as has been reported elsewhere (Norouzi, Rashedi, Alipour, Faridbod, Shahtaheri, & Ganjali, 2011).

4.5 Membrane Characterization

The best membrane of electrode no.8 was characterized to find out whether the characteristics such as water content, porosity, thickness and swelling influence the electrochemical performance and the results are summarized in Table 4.3. As it can be seen, the selected membrane showed the lower order of water content, swelling and porosity with less thickness. These characteristics of membrane suggest that the interstices are negligible and diffusion across the membrane would occur mainly through the exchange site (Khan & Baig, 2012). Hence, it is observe that the selected membrane shown a good performance with low order results.

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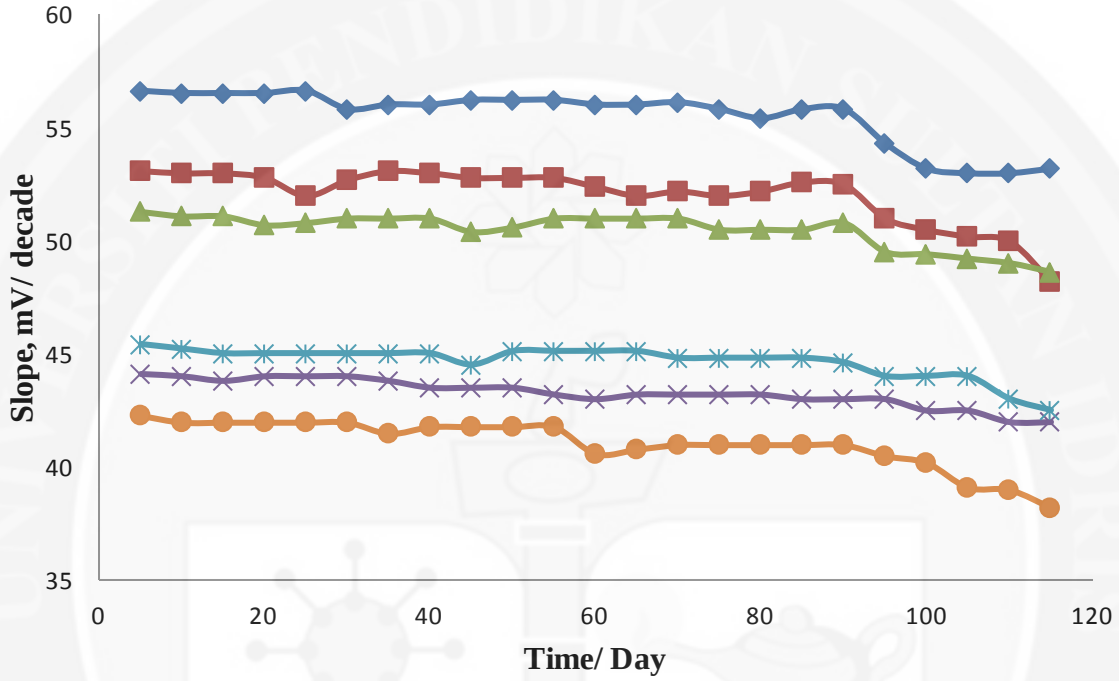


Figure 4.4. The lifetime of chitosan membrane electrode: (◆) NPOE, no.8; (■) DOP, no.9; (▲) BEHA, no.10; (×) TEHP, no.11; (✳) DBP, no.12 and (●) without plasticizer, no.7

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Table 4.3

Characterization of chitosan membrane no.8

Electrode	Membrane composition (w/w)			Water content as % of weight of wet membrane	Porosity	Thickness (mm)	Swelling as % of weight of wet membrane
	Chitosan	PVC	Plasticizer				
8	20	30	30	3.59	1.93×10^{-3}	0.04	0

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4.6 Analysis of Real Samples

The proposed pH sensor (electrode no.8) is used to determine the acidity of some fruit juice samples. Table 4.4 shows the results obtained by the proposed pH electrode and that of commercial glass electrode. It appears that both set of results are in good agreement with each other with no significant changes and correlation coefficient, R^2= 0.981. Thus, the proposed pH sensor is, definitely, viable to be used as the alternative pH electrode in place of glass electrode.

4.7 Sample Analysis with FIA

Ion sensor with high selectivity, high sensitivity, wide dynamic range and fast response are highly desirable for flow injection analysis (FIA) application. FIA becomes wide spread of methods which are characterized by its versatility, high sampling frequency and minimum sample treatment prior to injection into the system, reduce time of analysis and low consumption of reagent compared the manual procedure (Khater, Issa, & Mohammed, 2009). Other than that, this method is one approach toward simple, cheap and reliable detector (Baheshti & Amini, 2007).

The FIA method was used to evaluate the working characteristic of the proposed electrode. In FIA condition, the parameters (sample volume, flow rate, reactor length and size) that affect the response of an ion selective electrode was studied and taken into consideration on designing the flow system.

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Table 4.4

pH determination of fruit juice samples using proposed electrode (no.8) and glass electrode

Samples	Proposed pH sensor	Glass elecrode
Lemon juice	3.15 ± 0.08	3.20 ± 0.10
Grapefruit juice	3.20 ± 0.10	3.10 ± 0.09
Orange juice	3.10 ± 0.10	3.05 ± 0.09
Apple juice	3.50 ± 0.10	3.40 ± 0.10

*All the values were the mean ± SD, $n = 3$.

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Figure 4.5 shows the recorder traces for series of runs, in triplicate, under optimized condition. The result shown using a constant injection volume, the residence time of the sample is inversely proportional to the flow rate and short response time (less than 10 seconds). Thus, the proposed electrode can be applied for the determination of pH with nearly the same precision and accuracy in ion selective electrode and FIA conditions from the calibration plot obtained present in Figure 4.6. The calibration plot was linear over at pH range (2-7) with slope at 57.1 ± 0.2 mV decade^{-1}.

The transient (baseline to baseline) time of the FIA signal is 30 to 90 seconds. The electrode is highly stable and no significant change in its response characteristics was observed during 1 month of continuous use.

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Figure 4.5. Recording chart graph at FIA conditions

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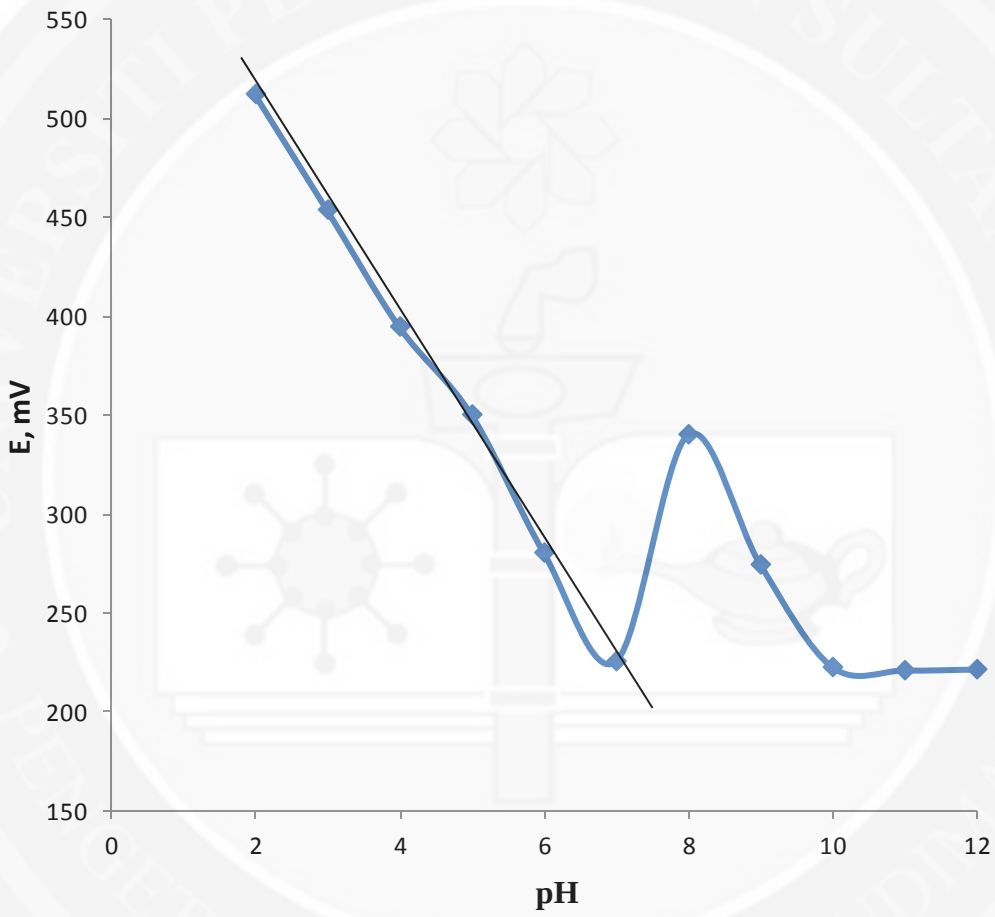


Figure 4.6. The corresponding calibration curve at FIA conditions

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CHAPTER 5

CONCLUSION

5.1 Conclusion

The ion-selective electrode's method for the determination of pH has been investigated to obtain a more rapid and simplified analytical approach. Throughout inquisition of various membranes compositions, it is shown that membrane with ratio of chitosan (20): 2-NPOE (30): PVC (30) gives the best performance in terms of reproducibility and other sensor characteristics such as good selectivity, broad working range and reasonable shelf life. It performance was comparable with reported electrodes (Table 4.1) and plasticizer 2-NPOE was the best plasticizer then others. Besides, comparison has be done and the result shown the comparable between the

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proposed electrode and commercial pH glass electrode with no significant changes and correlation coefficient, R^2= 0.981. Hence, chitosan can be used, successfully, an ionophore in polymeric membrane pH electrode

In FIA conditions, the result of the electrode response shows the proportionality from the calibration plot obtained with linearity at pH range (2-7) and slope at 57.1 ± 0.2 mV decade^{-1}. On the other hands, the use of FIA lead to shorting the time required for analysis. Thus, a chitosan as ionophore in a new PVC besed electrode can be applied for determination of pH with economic procedures, less time consuming, sensitive and easy to manufacture in any desired shape and size.

Further research also can be made in a modification of this sensor membrane electrode such as miniaturization of this electrode for use in small sample volume, space, remote kit and in vivo studies.

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APPENDIX A

1. Article published in International Journal of Electrochemical Science.

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APPENDIX B

AWARDS

1. BRONZE MEDAL for the invention of CHITOSAN BASED HETEROGENEOUS MEMBRANE SENSOR FOR pH-A PROTOTYPE at the 22nd International Invention, Innovation & Technology Exhibition ITEX 2011, Kuala Lumpur, Malaysia, 20th – 22nd May 2011.

2. BRONZE MEDAL for the invention of CHITOSAN BASED HETEROGENEOUS MEMBRANE SENSOR FOR pH-A PROTOTYPE at the 24th Malaysia Technology Expo MTE 2013, Kuala Lumpur, Malaysia, 21st – 23rd Febuary 2013.

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Chitosan Based Heterogeneous Membrane Sensor for pH – A Prototype

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A heterogeneous membrane pH sensor based on chitosan, polyvinyl chloride (PVC) and a suitable plasticizer was developed. The best overall performance was shown by a membrane with composition ratio of chitosan (ionophore) : PVC (binder) : 2-nitrophenyl octylether (2-NPOE) (plasticizer) at 20 : 30 : 30 (% w/W) respectively. The potentiometric responses was linear within pH 2 to 9, limit of detection at pH 9.5, slope 56 mV decade^{-1} at 25 ± 1 ^{o}C and response time of 20 ± 5 s. A life time of more than 3 months was obtained. The sensor established good selectivity and reproducibility towards hydrogen ion in the presence of other cations. Results were in good agreement with a commercial pH electrode for pH measurement in fruit juice samples.

Keywords: Chitosan, Heterogeneous membranes, pH sensor, Potentiometry

1. INTRODUCTION

Measurement of acidity (pH) of an aqueous solution is very important for various applications. Glass electrode is by far the best mean for this purpose. Nonetheless, it has its limitation like unable to provide accurate pH values at the extreme end of pH scale, limited shape and also cannot be used in fluoride solution [1]. Some more, it is always in need of frequent calibration before and after use. Its fragility hinders it being miniaturized for biological purposes. Hence, it is a challenge to researchers to overcome these drawbacks. Better still if the substitute is robust, cheap, reliable and green.

Numerous studies have been devoted to the development of new pH sensor based on different materials during the past two decades. Sensor made of metal oxide film [2-8] due to its toxicity is prohibited to be used for either biological or biomedical applications. However, fluorescent pH sensors [9-18] are, widely, used in bioanalytical chemistry and cellular biology for measuring intracellular pH,

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and also in medical science for monitoring pH in blood. But its drawbacks are fluctuations in light source intensity of the instrument, photo-bleaching of the pH sensitive reagent, drifts in the optoelectronic setup and also background fluorescence. Lately, a number of optical pH sensors have been studied and developed [19-24]. The fiber optic, the main item used in its fabrication, has many advantages over glass e.g. small size, flexibility, low propagation loss, no risk of electric shock on *in vivo* measurement and no electromagnetic interference [25].However, the limitations for this type of sensor are complex removal process of cladding layer and the fragility of unclad fibre.

Over the years pH sensors based on polymeric membranes have attracted more attentions than others [26-39]. The attraction being that they are easy to manufacture in any desired shape and size. Besides, these sensors are, typically, rugged and reliable. While several polymeric matrices have been used in the manufacturing of ion selective electrodes (ISE) polyvinyl chloride (PVC) remains one of the best choices [35]. The heterogeneous polymeric membrane is, mainly, a blend of PVC, ionophore, plasticizers and in some instances, a lipophilic anion. Ionophores like calyx[4]arene [28],1–octadecanoyl–4–methylpiperazine, 1-octadecanoyl–4–(2–pyridyl)–piperazine, *N*–octadecylmorpholine and octadecylisonicotinate [29], *p*–*tert*–butylcalix[4]arene–oxacrown–4 [38], amine [39-42], hexabutyl-tri-amidophosphate [43], azobenzenes [44] and phenoxazine derivatives [45] have been studied. The influence of plasticizer in the polymeric membrane blend such as to increase the membrane polarity to facilitate partition of ions [46] and to help improve capacity of the ionophore [47] have been highlighted. It is reported 2-NPOE is the best membrane plasticizer in polymeric pH sensor using macrocyclic compounds [38]. In another report [48] the diocthylphenylphosphonate(DOPP) has, however, been blamed of responding towards analyte. These polymeric membranes appear to be promising besides trivial problems like sluggish pH readings.

Chitosan, a polysaccharide, has been reported to be promising polymer not only in the biological field, but also in various industrial applications [49]. Up to date there has been no report yet on the application of chitosan as ionophore in the polymeric membrane of pH sensor. However, earlier report has indicated that chitosan membrane is sensitive towards pH changes [4]. The polymeric heterogeneous chitosan membrane electrodes have been used to measure iron (III) [50] and glutamate [51].This paper reports on the study carried out to get the alternative pH sensor by making use of chitosan, a non toxic biodegradable material, as the active material or ionophore.

2. EXPERIMENTAL

2.1. Reagents

All chemicals were of reagent grade and were used without purification. Chitosan PM 100 (granular), 100 mesh, was obtained from ChitoChem (M) Sdn. Bhd. (Malaysia). High-molecular weight poly (vinyl chloride) (PVC) was obtained from Fluka Chemika (Switzerland). The 2-nitrophenyloctylether (2-NPOE), bis(2-ethylhexyl)adipate) (BEHA), Tris(2-ethylhexyl)phosphate (TEHP), Dibutyl phthalate (DBP) and Dioctyl phthalate (DOP) were obtained from Aldrich (Germany). The tetrahydrofuran (THF) and chloride salt of all cations were obtained from MERCK

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(Germany). All solutions were prepared using distilled deionised water from EASYpure LF, Barnstead (USA). The stock solutions of defined pH were, freshly, prepared using analytical grade boric acid, acetic acid, sodium sulphate of Sigma-Aldrich and phosphoric acid of Fluka Chemika (Switzerland).

2.2. Preparation of electrode

Chitosan of various quantities was mixed with a fixed quantity of PVC (initially dissolved in 2 ml THF). The membrane was, then, blended with various plasticizers. The blend was placed in a glass ring (35 mm i.d.) resting on a glass plate. After overnight solvent evaporation, the resulting membrane was peeled off from the glass mould and a disc (6 mm i.d.) was cut out. The membrane disc was mounted to one end of Pyrex® glass tube with Araldite®. The 0.1 M HCl internal filling solution was added into the tube. Electrical contact between inner solution and the pH meter was accomplished through Ag/AgCl pseudo-reference electrode. The assembly was conditioned in 1.0×10^{-3} M HCl solution for 12 h. The polymeric membrane was rinsed with water prior to various tests to get the membrane with optimum performance.

2.3. Potential measurements

The pH and emf of solutions were measured using Orion 720A plus meter of Thermo Electron Corp. (USA). A glass pH electrode 915600 of Orion Research Inc. (USA) was used to determine the pH of solutions. This was used as standard with prior calibration using standard buffer pH 4.01, 7.00 and 10.01 of Orion Research Inc. (USA). An Ag/AgCl (3M KCl) of Bioanalytical System (USA) was used as external reference electrode. The electromotive force (emf) measurements were performed at 25 ± 1 ^{o}C. The experimental solution was stirred by a magnetic stirrer bar HI 200M of Hanna (Singapore). All measurements were carried out with the following cell scheme;

Ag, AgCl | 0.1 M HCl | membrane | sample solution | | KCl (3M) | AgCl, Ag

3. RESULTS AND DISCUSSION

3.1. The characterizations of the membrane

The sensitivity and selectivity of a given membrane depends significantly on the ingredients, including plasticizer and additives used [52-54]. Besides, contact time and concentration of equilibrating solution must also be optimized in order to develop a reproducible, stable and noiseless potentials membrane [55-57]. The performances of heterogeneous chitosan : PVC (% w/W) membranes are normally accessed by increasing the percentage of chitosan in the membrane whilst keeping the percentage of binder PVC constant. Therefore, the effect of plasticizers i.e. 2-NPOE, DOP, BEHA, TEHP, DBP is the variable and without plasticizer as a control. The emf responses of the polymeric membranes with various plasticisers added towards a series of Britton–Robinson buffers

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solution (pH 2 – 12) with 0.1 M Na_2SO_4 are investigated. The characteristics of these sensors are tabulated (Table 1). The overall result indicates that electrode no. 8 with composition ratio of chitosan (20%), PVC (30%) and 2-NPOE (30%) performs near to Nernstian, linear range from pH 2 to 9 and limit of detection pH 9.5 (Fig. 1).

Table 1. Effect of membrane compositions on the slope of membrane electrodes based on chitosan.

Electrode	Mass (w/W %)							Slope (mV decade^{-1})	Linear range (pH)
	Ionophore	Plasticizer					PVC		
		2-NPOE	DOP	BEHA	TEHP	DBP			
1	10	-	-	-	-	-	30	40.1 ± 0.2	2-7
2	10	30	-	-	-	-	30	54.5 ± 0.3	2-9
3	10	-	30	-	-	-	30	51.3 ± 0.2	2-8
4	10	-	-	30	-	-	30	49.8 ± 0.4	2-7
5	10	-	-	-	30	-	30	41.7 ± 0.2	2-8
6	10	-	-	-	-	30	30	42.6 ± 0.2	2-8
7	20	-	-	-	-	-	30	42.3 ± 0.3	2-7
8	20	30	-	-	-	-	30	56.6 ± 0.4	2-9
9	20	-	30	-	-	-	30	53.1 ± 0.2	2-8
10	20	-	-	30	-	-	30	51.3 ± 0.2	2-7
11	20	-	-	-	30	-	30	44.1 ± 0.3	2-8
12	20	-	-	-	-	30	30	45.4 ± 0.2	2-8
13	30	-	-	-	-	-	30	41.4 ± 0.2	2-7
14	30	30	-	-	-	-	30	52.3 ± 0.3	2-9
15	30	-	30	-	-	-	30	53.1 ± 0.4	2-8
16	30	-	-	30	-	-	30	47.5 ± 0.2	2-7
17	30	-	-	-	30	-	30	41.1 ± 0.3	2-8
18	30	-	-	-	-	30	30	44.2 ± 0.2	2-8

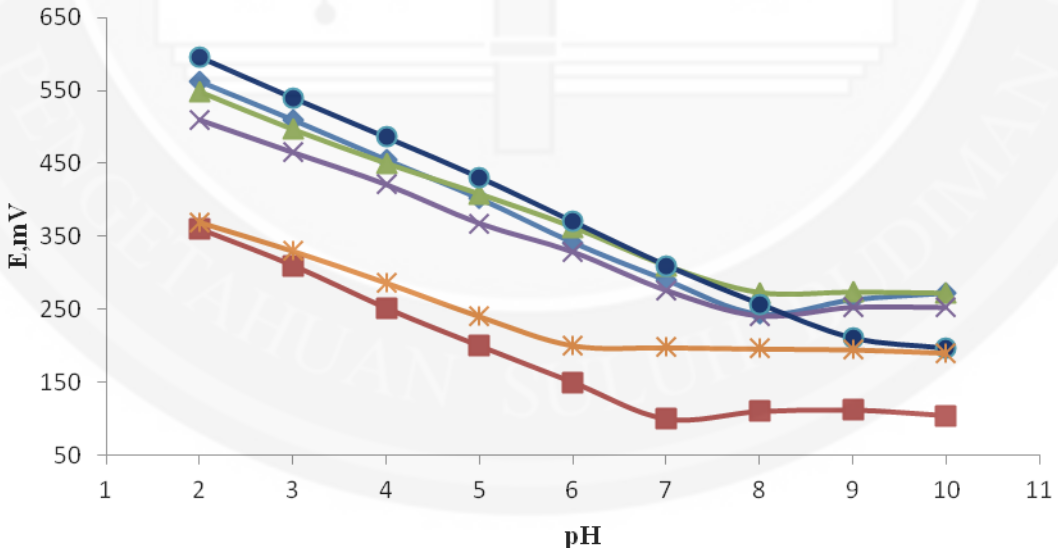


Figure 1. Calibration plots of pH sensors with membrane containing chitosan (20 %), PVC (30 %) and plasticizer (30%): (●) NPOE, (◆) DOP, (■) BEHA, (×) TEHP, (▲) DBP as plasticizer and (✳) without plasticizer.

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From the Nernst equation;

$$E_{cell} = E^0 \pm (2.303RT/nF) \log a \qquad (i)$$

The theoretical Nernstian slope, S = 2.303RT/nF, for a monovalent ion at 25 ^oC is 59.1 mV decade^{-1}. It is apparent that the best polymeric pH sensor with plasticizer 2–NPOE has nearly ideal slope at 56 mV decade^{-1} as compared with the other plasticizers. The 2–NPOE as the preferred plasticizer for monovalent ions ISE has been highlighted elsewhere [38, 58]. The presence of plasticizer in the binder matrix acts as a fluidizer, allowing homogeneous dissolution and diffusion mobility of the ion-pair inside the membrane [59]. The slope value of each of the added plasticizer polymeric membrane decreased in the order of 2–NPOE > DOP >BEHA > DBP> TEHP ≈ without plasticizer.

3.2. Response time and lifetime of the electrode

The response time of an ISE is important in analytical applications and it depends slightly on the concentration change. Therefore, it is determined by recording the elapsed time to reach a stable potential value after the electrode and the reference electrode were immersed in calibration solutions from low to high H^+ concentrations. The response time of the proposed pH sensor (linear range pH 2 - 9) is in the region of 20 ± 5 s. This is comparable to, or even shorter than, those reported in literature [39, 60]. However, the response is slightly longer in the basic region 30 ± 5 s. The exchange of anion OH^- is harder due to formation of inorganic salt. This indicates that in acidic medium Donnan equilibrium is more favourable as the proton, H^+, in the quaternary ammine is easily detachable from the tertiary amine functional group of the ionophore and is later exchanged with the proton in solution . The possible mechanism involved in the generation of the emf response is shown (eqn (ii)).

$$\underset{\text{(membrane)}}{Ø\text{—}NH_2\,H^+} + \underset{\text{(solution)}}{H^+} \leftrightarrow \underset{\text{(membrane)}}{Ø\text{—}NH_2\,H^+} + \underset{\text{(solution)}}{H^+} \qquad (ii)$$

The repeatability of pH measurements is studied by performing several runs from pH 1 to 12 and vice versa. There is no drift observed during the measurements indicating that sensitivity, reversibility and repeatability of this pH sensor are excellence. Throughout the measurement no hysteresis is observed either.

The lifetime of the electrode is determined by recording its potentials at an optimum pH value and by plotting calibration curves every day. The slope of calibration curve indicates no significant changes within a period of 3 months (Fig. 2). This shows that operational stability of the proposed pH sensor is not affected for a period of at least 3 months of continuous use. Also the membrane has no experience of ingredients leak from the organic layer which affects response after several time of usage as has been reported elsewhere [59].

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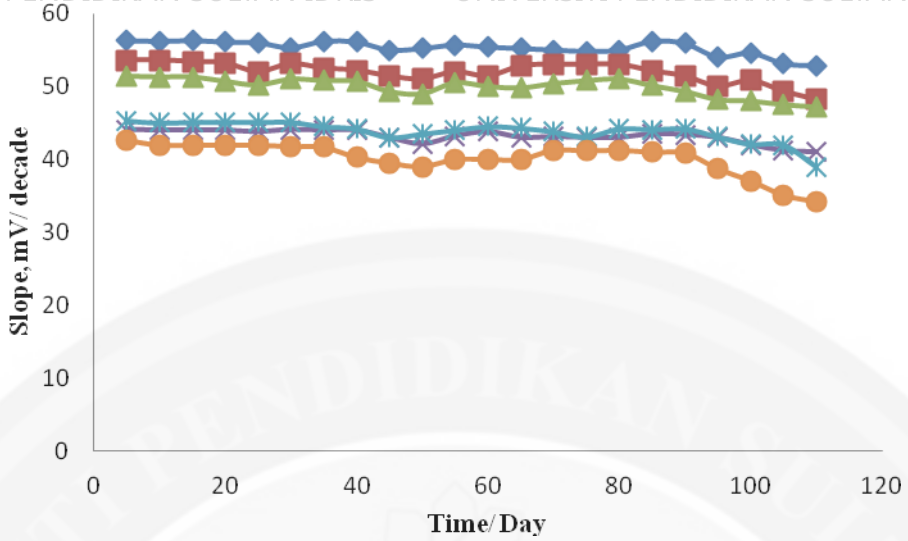


Figure 2. The lifetime of the pH electrode: (◆) NPOE, (■) DOP, (▲) BEHA, (×) TEHP, (✳) DBP as plasticizer and (●) without plasticizer.

3.3. The selectivity of the electrode

The selectivity coefficient, K^{pot}, of the pH sensor towards other ions is also investigated. This is the most important characteristic of any ion sensor. K^{pot} determines the extent to which a sensor can be employed in the analysis of real samples [61]. In order to get the K^{pot} for the developed polymeric membrane as near as possible to real situation the mixed solution method is used. The concentration of interference cations e.g. potassium, sodium, lithium, calcium, barium, copper, magnesium, cobalt, zinc and iron(III) were fixed at 10^{-1} M.

Table 2. Selectivity coefficients of chitosan membrane sensor towards various interfering ions.

Interference	K^{pot}
Na^{+}	2.5×10^{-11}
Li^{+}	6.3×10^{-11}
Cu^{2+}	6.3×10^{-11}
K^{+}	1.0×10^{-12}
Co^{2+}	7.9×10^{-12}
Mg^{2+}	1.0×10^{-13}
Ca^{2+}	1.0×10^{-13}
Zn^{2+}	1.0×10^{-13}
Fe^{3+}	1.0×10^{-13}
Ba^{2+}	1.0×10^{-13}

The pH of Britton–Robinson buffer solutions were varied by drop wise addition of potassium hydroxide. It appears that the calculated K^{pot} are less than 1 for all cations (Table 2) indicating that the

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proposed pH sensor is not sensitive to the cations tested, especially, the alkali metal ions. Thus, it can be used, conveniently, for pH measurements in media containing these cations e.g. environmental waters. The interfering effect of the cations is in the following order: $Na^+ > Li^+ \approx Cu^{2+} > K^+ > Co^{2+} > Mg^{2+} \approx Ca^{2+} \approx Zn^{2+} \approx Fe^{3+} \approx Ba^{2+}$ which is, apparently, an anti-Hofmeister Series.

3.4. The analytical applications of the electrode

The proposed pH sensor is used to determine the acidity of some fruit juice samples. Table 3 shows the results obtained by the proposed pH sensor and that of conventional glass electrode. It appears that both set of results are in good agreement with each other with correlation coefficient, R^2, 0.981. The slight difference in values is presumably due to (i) differences in kinetic of exchange equilibria achieved by the proposed and glass electrodes and (ii) complexation of ionophore (chitosan) membranes with metal ions in complex sample matrices [62]. Nonetheless, the proposed pH sensor is, definitely, viable to be used as the alternative pH electrode in place of glass electrode.

Table 3. pH determination of fruit juice samples using proposed and glass electrode.

Samples	Proposed pH sensor	Glass electrode
Peel fresh orange (Marigold)	3.15 ± 0.08	3.20 ± 0.10
Orange juice (Marigold)	3.20 ± 0.10	3.42 ± 0.09
Orange juice (Sunkist)	3.20 ± 0.10	3.05 ± 0.09
Apple juice (Marigold)	3.50 ± 0.10	3.40 ± 0.10

*All the values were the mean of triplicate measurements (n = 3).

4. CONCLUSIONS

Chitosan can be used, successfully, as an ionophore in polymeric membrane pH sensor. The plasticiser 2–NPOE has to be included to get better response. The developed sensor is not sensitive towards most available cations in environmental waters especially alkaline metal ions. At the moment it is only a prototype but since it is robust, eco-friendly and performs equally well it is expected to be able to replace glass electrodes once its assembly is perfected.

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