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

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APPRECIATION

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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.

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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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

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

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

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).

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.

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

$$E = \text{Constant} - RT/z\,F \ln a \quad (1.1)$$

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.

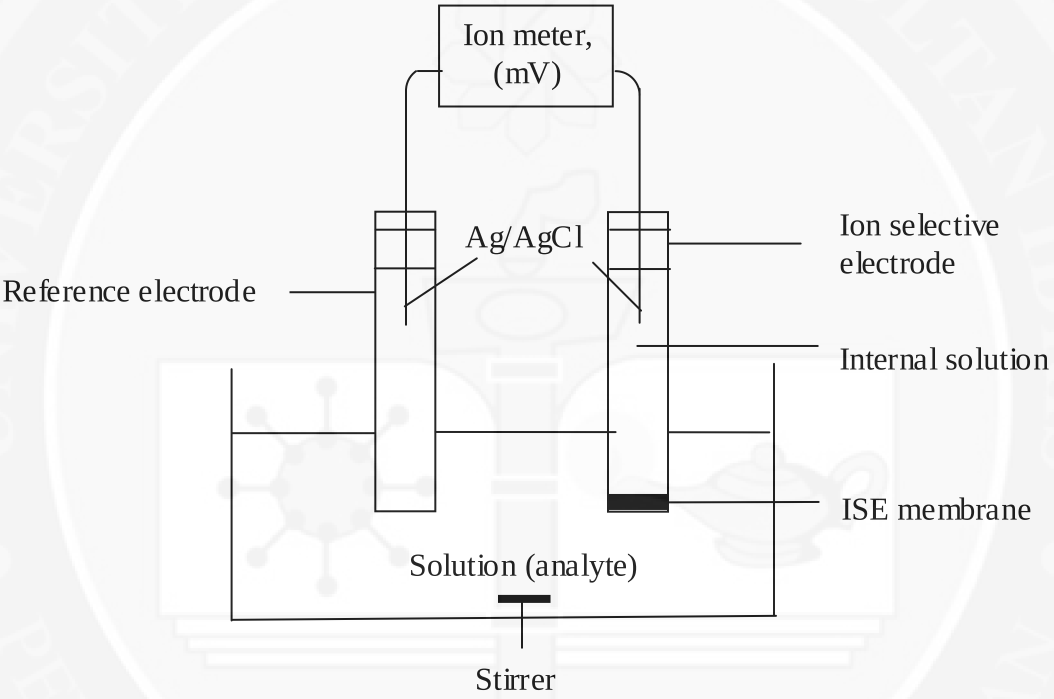

*Figure 1.1.*A classical electrochemical cell of ion-selective electrode, ISE

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.

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 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.

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.