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# Applications of Polyvinyl chloride membrane Electrodes Series of Organic and Inorganic Anions

**Kuldeep Singh[1] & Dr. Sanjeev Kumar Saxena[2]**
[1]Research Scholar, Shri Venkateshwara University, Gajraula, Amroha (U.P.)
[2]Research Supervisor, Shri Venkateshwara University, Gajraula, Amroha (U.P.)

**ABSTRACT-**

*Today, many industrial technologies generate an increase of the concentration of anions present in the environment or introduce anionic species, which unknown in ecosystems. The presence of these anions is crucial in medical and environmental concerns. High concentration of anions in organisms or a miss-regulation of anion transport can have harmful effects on human health and can be the origin of a number of diseases such as cancers. For example, problems with the transport of such a simple anion as chloride cause illnesses like cystic fibrosis [4] and excessive phosphate concentrations provoke disorders of the calcium distribution within human organisms.*

***Key Words:*** *Concentration, organisms, coordination.*

## INTRODUCTION-

It is generally agreed that the progenitor of ion selective electrodes (ISEs) is the glass membrane acidity electrode. Cremer is credit with making the discovery that a large potential difference exists across a thin glass membrane in contact with solutions with large difference in acidity on opposite sides of the membrane [31]. It is fascinating to note that Cremer's work was actually the culmination of many studies on the electrical properties of glasses staring as far back as 176 [32]. At that time, glasses were considered to be materials that consisted of silicon dioxide and various other oxides. The properties of the glasses were known to depend on which other oxides were added and on the stoichiometry of the resultant material. Thus, some glasses were shown to be conductors of electricity, while others were shown to be electrical insulators, Cremer, who was interested in the potential difference generated across certain biological tissues, recognized that the Warburg model of glass meant that it should be an Ideal semi permeable membrane. He performed several experiments using a flask containing an electrolyte solution immersed in a breaker, also containing an electrolyte solution. A platinum wire was in contact with each solution. He Found that when the two electrolytes in their acidities, a large potential difference could be measured across the two platinum electrodes.

Systematic, quantitative studies on this phenomenon were made by Haber and Klemensiewicz on glass-bulb electrodes [33]. In that paper, the theoretical model for the electrode response was developed by Haber, and the experimental confirmation of the model was performed by Klemensiewicz. For the theoretical model, Haber extended the work of H.W. Nernst [34] of particular relevance to the development of the mathematical from of the electrode potential of an ISE is Nernst's treatment of the potential difference across the interface between two electrolyte solutions, the well-known liquid junction potential, generated by non- Faradaic process. He showed that the steady-state potential difference across an interface between a dilute solution of HCI (concentration $c_1$) and a more concentrated solution of HCI (concentration $C_2$) has the form of Equation (i) [34].

$$E = \frac{RT}{F}\left(t_{+} - t_{-}\right)\text{In}\left(\frac{c_1}{c_2}\right) \qquad \text{...(i)}$$

Where E is the potential of the interface on the side of the more concentrated solution to the more dilute solution, t, is the transport number for the cation, t is transport number for the cations and F is Faraday's constant. (Note) that in this and other equations, the expressions for E have been written in modern form. In the original equations. R. the gas constant, is given in electoral dimension. In modern usage. R is given in energy dimensions. R, in electrical units is equal to R in energy dimensions divided by the Faraday constant F). To verify his theory, Nernst studied concentration cells of the form in Equation (ii).

$$\text{MA MX } (C_1) \text{ A MX } (C_2) \text{ A K} \qquad \text{...(ii)}$$

Where, MX is strong electrolyte and $C_1 \neq C_2$. Here, Nernst proposed that the mathematical relationship for the potential difference across the mental electrolyte interface under conditions of zero current flow is given by Equation (iii) [34] :

$$E = \frac{RT}{F}\ \text{In}\left(\frac{C}{c}\right) \qquad \text{...(iii)}$$

Where, C is the concentration of ion cores in the metal and c is the concentration of the electrolyte, According to Nernst, dissolution of the metal may occur, such that ions cross to the solution side and electrons remain in the metal, or metal ions from the electrolyte may specifically absorb on the surface. These processes are also non-Faradaic. Thus, Nernst clearly proposed that his mathematical treatment was a general one valid for all electrified interface under conditions of equilibrium or steady-state charge transport. Haber extended Nernst's treatment to the case of a concentration cell involving a solid electrolyte MX and an aqueous electrolyte MX, with the cell notation as in Equation (iv):

$$\text{MA } MX_{(s)} \text{ A } MX_{(aq)}\text{A M} \qquad \ldots\text{(iv)}$$

He showed that the potential at the interface between the aqueous and the solid electrolytes is given by Equation (v) :

$$E = \frac{-RT}{F}\,\text{In}\,(C_M) + K \qquad \ldots\text{(v)}$$

Where, $C_M$ is the concentration of the metal ion in the aqueous electrolyte solution and K is constant. Haber then proposed that a hydrated glass membrane is a type of solid water phase. By considering the cell in Equation (vi) :

$$H_{2A}\ H_2O_{(s)}\text{ A } H_2O_{(t)}\text{A } H_2 \qquad \ldots\text{(vi)}$$

He arrived at Equation (vii) for the potential difference across the glass membrane –water interface.

$$E = \frac{RT}{F}\,\text{In}\,(C_{H^+}) + K \qquad \ldots\text{(vii)}$$

Where $C_{H+}$ is the concentration of hydronium ions and K is constant. Similarly, by considering the cell in Equation (viii) :

$$O_s\text{A } H_2O_{(s)}\text{A } H_2O_{(1)}\text{A } O_2 \qquad \ldots\text{(viii)}$$

He arrived at second expression for the potential difference across the glass membrane – water interface (Equation (ix)):

$$E = \frac{RT}{F}\,\text{In}\,(C_{OH^-}) + K \qquad \ldots\text{(ix)}$$

Where $C_{OH^-}$ is the concentration of hydroxide ions and K' is a constant. It is clear that Haber recognized the glass membrane could sense either hydronium ions or hydroxide ions. He further indicated that Equation (ix) could be written in terms of $C_{H^+}$ by making use of the relationship $C_{OH}{}^{=}\ K_w\ /\ C_{H+}$ , giving Equation (x) :

$$E = \frac{-RT}{F}\,\text{In}\,(C_{H^+}) + \frac{RT}{F}\,\text{In}\,(K_w) + K' \qquad \ldots\text{(x)}$$

Haber then stated that Equation (vii) and (x) are identical, which meant that K and K' are related by Equation (xi) :

$$K = \frac{RT}{F}\,\text{In}\,(K_w) + K' \qquad \ldots\text{(xi)}$$

Haber's statement, given without proof, was widely accepted by subsequent analytical chemists. Later, in describing the microscopic behavior-giving rise to the electrode response, many analytical chemists only considered Equation (vii), which has led to some misconceptions. Haber used his results to derive an expression for the potential difference across a glass membrane electrode, which had an acidic solution on one side and an alkaline solution on the other. Thus, for the scheme in equation. (xii):

1. Alkaline water [$H_2O(s)$]  2. Acidic water ...(xii)

He wrote Equation (xiii):

$$E = \frac{RT}{F} \text{In} \left( \frac{C_{H^+,2}}{C_{H^+,1}} \right) \qquad \text{... (xiii)}$$

Where $C_{H^+,1}$ is the hydronium ion concentration in the alkaline water, $C_{H^+,2}$ is the hydronium ion concentration is the acidic water and E is the potential difference between the alkaline water ‘- $H_2O_{(s)}$ interface and the acidic water –$H_2O(s)$ interface.

The important role of anions in process involved in living organisms and in ecosystems as well as in industrial technologies creates the need of fast and selective anion detection methods allowing real-time monitoring of anion concentration changes. Design of anion receptors for such applications is a great challenge for chemists, considering anion properties such as various geometries, small electric charges vs. anion sizes, pH dependence, multiple oxidation states of the central atom in ox anions and high salvation. The May be the reason why anion coordination chemistry has emerged only recently as compared to that of cations which is well- developed.

In many anion receptors, which have been synthesized, non- covalent interactions are responsible for host- guest recognition. They include electrostatic interactions, hydrogen bonding, and hydrophobicity, coordination to a metal ion or combination of these interactions.

Despite the variety of anion receptors developed so far, the problem of achieving selective anion recognition in today an increasingly topical field in supramolecular chemistry due to the possible applications in selective ion sensors for biological and environment concerns.

## ASSUMPTIONS-

Sensor technology has a long tradition. The chemical sensors provide reliable information about their physical, chemical and biological environments. Physical sensors, such as flow-meters, thermo elements and IR-position sensors, occupy a key position in most innovate technical systems, whereas the applications of chemical sensors has been limited to some special areas, Supramolecular chemistry has a great potential for such possible applications. The quality of information provided by chemical sensors is fundamentally different from that supplied by traditional methods. In some cases, this has been the source of unexpected uncertainties in comparing methods.

Chemical sensors have allowed the identification and quantification of specific species and have had a great impact on the study of biological systems. Anion receptors are now applied as the selector element in separation membranes and in ion- selective electrodes. As one of each uses the application of macro cyclic oligopyrrole compounds are their use in molecular recognition for HPLC separation of biologically important anionic substrates can be mentioned.

## RESEARCH METHODOLOGY

1. Ion selective electrodes, calomel electrode gas electrode etc.
2. Variois Ani onic species sucj as fluorideion and perchlorate ion $ClO^-_4$ etc.
3. Journals.

The electrochemical sensors that provide the supporting infrastructure to enable the direct processes to operate under the repceired controls and continually improve.

This application ususally requires the immobilization of receptors on a polymeric matix or silica gel.

Here three methods are involve

1. Nernst equation method
2. Calomel electrode method
3. Ion selective electrodes method

In present work, five expanded porphyrins have been synthesized, according to the reported methods, by the thereafter and then used as metal ion selective PVC based membrane electodes as electroactive materials. These metalloporphyrins are highly sensitive and selective towards some specific anions. The electrodes developed have been analysed by testing some practical samples and using them as an indicator electrode. The five expanded porphyrins synthesized are as mentioned below:

| S.No. | Metalloporphyrins |
|---|---|
| 1 | Iron (II) derivative of 5,10,15,20-tetrapheny1porphyrin |
| 2 | Manganese derivative of 5,10,15,20—octamethoxyprophrin $[(CH_3)_8$ OTPPM$_n$(III) CI ] |
| 3 | Zinc (II) mono (4-aniline-ethynyI)biphenyIporphines (Zn-AEBPPs) |
| 4 | 5,10,15,20-meso-tetrakis(p-methoxybenzylpyridinium-4 yl)-porphyrin, (PdTMeOBzPyP) |
| 5 | Meso-$n^1$- Platiniometalloporphyrin {(meso-[Pt Br (Co(DDP)($PPh_3$)]}<br>(DPP = dianion of 5.15-dipheny1-porphyrin) |

## RESULTS & FINDINGS-

The free base iron (III) derivative of 5, 10, 15, 20-tetraphenylporphyrin has been used as an ion-carrier in construction of ion-selective sensors for some common anions like nitrate, thiocyanate, iodide, salicylate, acetate, etc. The potential responses of these electrodes are shown. As can be seen, the membrane senor displays selectivity for $CH_3COO^-$ ions over other anions as result of the selective interaction between the central metal ion and acetate ions. The preferential response towards $CH_3COO^-$ is believed to be associated with the coordination of acetate with the central metal of the carrier resulting in an increase in size and axial coordination. It is well understood that the sensitivity and selectivity of the ion-selective electrode depend not only on the nature of the ion-carrier used, but also significantly on the membrane composition and the properties of solvent mediators and additive used [7-12]. The potentiometric response curve of this acetate selective electrode exhibits stable potentiometric respomses for acetae anions after conditioning for 2-3 days in $1.0\times10^{-2}$ M NaCl solution. The effect of the membrane composition, nature of solvent mediator and additive on the response characteristics of the acetate sensor are given. Since the nature of the plasticizers influences the dielectric property of the membrance phase and mobility of the ionophores in the PVC matrix, its selection is one of the most important takes in designing a sensitive and selective anion selective electrode. The responses of the acetate sensor based on expanded porphyrin using three plasticizers having different polarities have different polarities have been investigate.

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