"Potentiometric discrimination of anionic guest by receptors incorporated in a PVC membrane – A supramolecular host-guest interaction"

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Ion selective electrodes (ISEs) or potentiometric sensors is a device which responds to a particular analyte in a selective way through a chemical reaction and can be used for the qualitative and quantitative determination of the analyte. There are two parts to an ISE – a region where selective chemistry takes place and the transducer which responds to this signal and translates the magnitude of the signal to a potential which is measured by a pH meter or a voltmeter. The analyte ion can pass through the boundary between the organic phase of themembrane and between the internal and the sample solution, an electrochemical equilibrium will be set up, and different potentials are developed in the two aqueous phases. The ionophore can exchange only one certain target ion, the potential difference between thephases will reflect the activities of the target ion in the two solution and the membrane phases. The ISEs have a large number of benefits in terms of selectivity, sensitivity and lower detection limits and thus, potentiometry has come out to be one of the most popular electroanalytical methods.

In the recent years, there has been dramatic progress in the field of host-guest chemistry especially in the molecular recognition at the liquid-liquid interface. The fundamental understanding of the underlying mechanism has been the impetus for designing chemical sensors in particular, the liquid membrane ion selective electrodes (ISEs). Among the first developed ISEs are the glass electrodes which are still being used for pH measurements. And from then on, research in the development of potentiometric sensors has picked up momentum with major breakthrough coming in the determination of cations and to a lesser extent in the determination of anions, drugs and neutral molecules.

Anions are ubiquitous in biology. Anions are involved in regulating osmotic pressure, activating signal transduction pathways, maintaining cell volume and in the production of electrical signals. The transport of anions through cell phospholipid bilayers is known to be mediated by a variety of channels and anion transport proteins and about fourteen anion transport systems have been identified. Thus, the selective recognition of anions plays an importantrole in biology, medicine,

catalysis and in the environment. The mechanism for the generation of a potentiometric signal for the ionic species depends on the charge separation at the organic-aqueous interface which is the result of a selective transfer of analyte ions from the aqueous to the organic phase.

The main objective of the project was to develop two PVC plasticized membrane based potentiometric ISEs for the determination of anions. Based on the work carried out, two ISEs have been developed for salicylate and iodide ions.

Substituted Zinc-salen complex was used as the ionophore for the construction of a PVC based membrane electrode for the detection of salicylate ions. The electrode exhibited a Nernstian slope of -59.6 ± 0.8 mV/decade for salicylate ions for over a concentration range of $1.0 \times 10^{-6} - 1.0 \times 10^{-2}$ M with a limit of detection of 4.0×10^{-7} M. The electrode showed a good selectivity for salicylate ions over a range of inorganic and organic species and could be used in the pH range of 4.5-9.5. The electrode could be used for a period of 3.5 months without much divergence in potential. The electrode was successfully used as an indicator electrode in the determination of salicylate in pharmaceutical samples.

Manganese-salen complex was used as the ionophore for the construction of a PVC based membrane electrode for the detection of iodide ions. The electrode exhibited a Nernstian slope of $-59.3\pm0.6 \text{ mV/decade}$ for Γ ions for over a concentration range of $1.0 \times 10^{-6} - 1.0 \times 10^{-2}$ M with a limit of detection of 6.3×10^{-7} M. The electrode showed a good selectivity for Γ ions over a range of inorganic and organic species and could be in the pH range of 3.0-8.0. The electrode could be used for a period of 3 months without much divergence in potential. The electrode was successfully used as an indicator electrode in the potentiometric titration of iodide ion. It was also applied for the determination of iodide in water samples as well as pharmaceutical products.