



Research Article



Development of Macrocyclics based Electrochemical Sensors for Copper

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1. INTRODUCTION

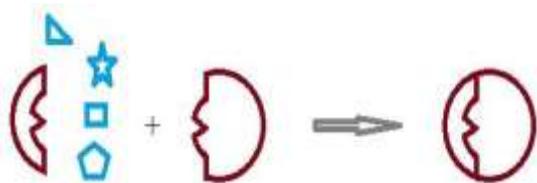
Analytical chemistry is a scientific discipline that develops and applies methods, instruments and strategies to obtain information on the composition and nature of matter in space and time. Both qualitative information and quantitative information are required in an analysis. Qualitative analysis establishes the chemical identity of the species in the sample. Quantitative analysis determines the relative amounts of these species. Analytical Chemistry has wide applications in the field of pharmaceutical, food and environmental analysis.

In Potentiometric methods the equilibrium potential difference between an indicator electrode and a reference electrode is measured. Ideally no current flows through the system at equilibrium. In general, the potential difference shows a linear relationship with the logarithm of the activity of the analyt, as in the Nernst equation.

ELECTROCHEMICAL SENSORS

An overview of development of analytical chemistry demonstrates that electrochemical sensors represent the most rapidly growing of chemical sensors. Sensors can be generally categorized into two general groups. There are physical sensors which are sensitive to physical responses such as temperature, pressure, magnetic field etc.

Then there are chemical sensors which rely on a particular chemical reaction for their response. Chemical sensors can be defined as a small device that as a result of a chemical interaction between the analyt and the sensor device, transforms chemical or biochemical information of a qualitative or quantitative type into an analytically useful signal. A schematic representation of the working of a chemical sensor is shown below.



There are two parts to a chemical sensor. Firstly, there is the region where the selective chemistry takes place and then there is the transducer. The chemical reaction produces a signal such as a color change, the emission of fluorescent light, a change in the electrical potential at a surface, a flow of electrons etc. The transducer responds to this signal and translates the magnitude of the signal into a measure of the amount of the analyst.

POTENTIOMETRIC SENSORS

Potentiometric sensors are the simplest type of electrochemical sensors with extraordinary analytical capabilities. It is a very attractive option for numerous analyses owing to the low cost and ease of use of the instruments employed. Potentiometry also has other interesting properties, such as short response times, high selectivity, and very low detection limits. Therefore, potentiometric devices could be readily miniaturized without, in theory, losing their determination capabilities.

The common glass electrodes for pH measurements were the first developed potentiometric sensors. The membrane in a glass electrode is a sodium silicate glass made by fusing a mixture of Al_2O_3 , Na_2O and SiO_2 . Increasing the amount of Al_2O_3 in the glass leads to an increasing response to other monovalent cat ions such as Na^+ , K^+ and Li^+ . The selectivity of glass electrodes to alkali metal ions was studied by voltammetric/amperometric sensors.

2. DEVELOPMENT OF POTENTIAL

The potential of ion selective membrane electrode is not generated by the electrode reaction of exchanging electron but arises from the diffusion of mobile ionophore-ion complexes in the sensing membrane and the selective ion exchange between the ions in the complexes and the sample solution, and between

the ions in complexes and the internal reference solution. The latter interaction will produce two interface potentials on both sides (the inner and outer sides) of the sensing membrane and the former one will generate the diffusion potential across the membrane. The membrane potential is the algebraic sum of the three potentials. The Nernst equation relates the membrane potential to the activities of ions in sample phase (s) and in the electrode phase (β)

$$E = E_0 + \frac{RT}{z_i F} \ln \frac{a_s}{a_i} \beta$$

E_0 = the standard potential of the sensor

a_i = the activity of the ions

z_i = the charge of the ion

2.1. Aspects of potentiometric sensors Ionophore

The critical step in the development of a chemical sensor is the rational choice and preparation of the electro active material. Most of the important properties of a sensor, such as sensitivity and selectivity, strongly depend on the characteristics of this sensing material. This electro active species enable the sensor to respond selectively to a particular analyst, thus avoiding interferences from other substances.

2.2. A brief review on potentiometric sensors based on macrocyclics

As part of the present investigations, potentiometric sensors have been developed for the Pb^{2+} , Mn^{2+} , Ni^{2+} , Cu^{2+} and salicylate based on macrocyclic ionophores. A brief review on the potentiometric sensors based on macrocyclic compounds as ionophores for the mentioned ions is presented below.

3. COPPER

A copper (II) selective membrane electrode was reported by Shamsipur et al based on a 23-member macro cyclic diamide. The electrode exhibited a Nernstian response over the concentration range of

3.2×10^{-5} - 1.0×10^{-1} M and the potential response remains almost unchanged over the pH range 3.5 - 6.0. Copper (II) selective sensors have been fabricated from PVC matrix membranes containing porphyrin as neutral carriers. The sensor showed a linear response over the concentration range 4.4×10^{-6} - 1×10^{-1} M.

The working pH range of the sensor is between 2.8 and 7.9 and it has a fast response time of 8 s. They developed a PVC membrane electrode (PME) and a coated graphite electrode (CGE) with a Nernst behavior over a wide concentration range 1.0×10^{-7} - 1.0×10^{-1} M for PME and 1.0×10^{-8} - 1.0×10^{-1} M. The potentiometric responses are independent of pH in the range 2.7 - 6.2.

3.1. Potentiometric selectivity

The most important characteristic of a membrane sensor is its response for the primary ion in the presence of other ions. So the design and development of the sensor and the evaluation of degree of interference from other ions would be of great importance. The extent of interference of other ions or species on the response of the developed sensors Ta4 and Pc3 were studied by the Fixed Interference Method (FIM). The selectivity coefficients were determined at 1.0×10^{-2} M concentration of interfering ions and the concentration of Cu^{2+} ions was varied and calculated by using equation. The result rate that the sensors has shown very good selectivity for Cu^{2+} ions in presence of Cd^{2+} , Co^{2+} , Mn^{2+} , Mg^{2+} , Zn^{2+} , Sn^{2+} , Hg^{2+} , Pb^{2+} , Ni^{2+} , Ca^{2+} , Ba^{2+} , Na^+ , K^+ and Ag^+ but only moderate selectivity in presence of Fe^{2+} ions.

3.2. Analytical applications

The developed sensors worked well Ta4 and Pc3 under laboratory conditions. They were successfully applied as an indicator electrode in the potentiometric titration of copper (II) nitrate solution with EDTA at pH 5.0. The titration curves for the sensors Ta4 and Pc3 are shown in Figures. The conventional sigmoid shaped plot is not obtained.

But the end point corresponds to 1:1 stoichiometry of Cu-EDTA complex. The applicability of the sensors Ta4 and Pc3 was further investigated in the determination of copper (II) in waste water samples collected from electroplating unit.

3.2. Synthesis of the Ionophore

Ionophore is the electro active component of a sensor. In the development of sensors 5, 10, 15, 20-tetrakis (3-methoxy-4-hydroxyphenyl) porphyrin (TMHPP) was used as the ionophore. Freshly distilled pyrrole, 3-methoxy-4-hydroxy benzaldehyde and boiling propionic acid was refluxed for 30 minutes and allowed to cool. The precipitated purple crystals were washed with methanol and purified by column chromatography. The detailed procedure for the synthesis of the ionophore and its characterization are discussed.

3.3. Potential measurement and calibration

A Metrohm ion meter was used for potential measurements. All EMF measurements were carried out at 25 ± 1 °C. A saturated calomel electrode was used in conjunction with the developed sensor. The cell assembly for potentiometric measurements may be represented as follows. For PVC membrane sensor: External reference electrode | test solution | PVC membrane based on TMHPP | internal filling solution ($0.1\text{M } \text{Cu}^{2+}$) | internal reference electrode for carbon paste sensor: Reference electrode | test solution | carbon paste electrode based on TMHPP.

A 1.0×10^{-1} M $\text{Cu}(\text{NO}_3)_2$ solution was prepared in a 100mL standard flask. The dilution series were prepared by serial dilution of the stock solution. Performance of the developed sensors were investigated by measuring the EMF of the cell in Cu^{2+} solutions prepared in the concentration range 1.0×10^{-8} - 1.0×10^{-1} M. The solutions were stirred and the stable potential reading was taken. The calibration graph was obtained by plotting EMF versus pCu^{2+} . The calibration graph was used for subsequent determination of unknown concentrations.

4. CONCLUSION

A polymeric membrane sensor Ta4 and a carbon paste sensor Pc3 was developed based on TMHPP. The prepared sensors exhibited long life time, good stability, sensitivity and selectivity. The sensors can be used most conveniently, economically and without any sample pre-treatment. The PVC membrane sensor Ta4 has better response characteristic than the carbon paste sensor Pc3. The life time of the sensor Ta4 is much better than the sensor Pc3. But its surface can be renewed by cutting a little of the paste, polishing it on a smooth surface and reconditioning it by dipping it in 1.0×10^{-1} M copper (II) nitrate solution. It can be seen that the developed sensors are superior in terms of working concentration range, PH range and slope. The sensor Ta4 is superior in terms of life time.

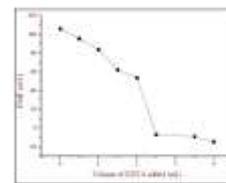


Figure 8.12 – Potentiometric titration curve of 25.0 mL of 1.0×10^{-2} M sodium acetate with 1.0×10^{-1} M HCl using the carbon paste sensor Pc3. Work as before.

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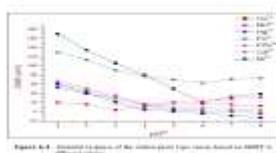


Figure 8.1 – Dependence of the potentiometric response of the PVC membrane sensor Ta4 on the pH of the solution.

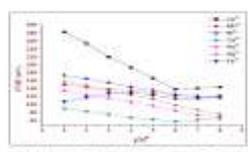


Figure 8.2 – Dependence of the potentiometric response of the PVC membrane sensor Ta4 on the concentration of the analyte.

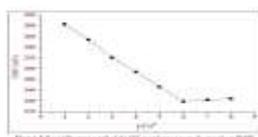


Figure 8.3 – Dependence of the potentiometric response of the PVC membrane sensor Ta4 on the concentration of the analyte.

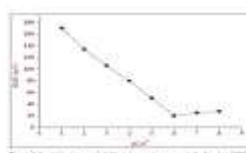


Figure 8.4 – Dependence of the potentiometric response of the PVC membrane sensor Ta4 on the concentration of the analyte.