

Determination of Nitrate by Electrochemical impedance spectroscopy and potentiometric Techniques

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Abstract

Ionophore derivative anion receptor has been tested as electroactive material for the development of anion selective electrodes. The receptor was incorporated in plasticized poly (vinyl chloride) membranes of different compositions. The membrane that provided the best response and selectivity towards nitrate was selected to develop a new nitrate-selective electrode. In this work a new strategy for optimizing membrane components by electrochemical impedance spectroscopy (EIS) is used. The performance of this electrode was investigated using potentiometric and EIS techniques. The electrode exhibited a Nernstian response over the nitrate concentration range of 1.0×10^{-7} to 1.0×10^{-1} M with a slope of 59.5 mV/decade by potentiometric technique. It showed good selectivity to nitrate relative to many common anions. While using the EIS technique, the linear concentration range was 1.0×10^{-8} to 1.0×10^{-1} M and the pH range increased to 4.0-10.0. The proposed electrode was applied to the determination of nitrate in wastewaters.

Introduction

Potentiometric measurements using ion-selective electrodes (ISE) for determination of the respective metal ions is advantageous due to speed, wide dynamic ranges, and no requirement for the sample pretreatment [1]. Electrochemical impedance spectroscopy (EIS) is a powerful technique for studying the structure of the electrical double layer formed at the semiconductor electrode/electrolyte interface, the charge transfer processes in the semiconductor and electrolyte, as well as the parameters defining the limiting steps of the electrode processes [2]. Nitrates are widely used in explosives, fertilizers, drugs and many industrial products and hence their effluents may contain appreciable concentrations of nitrates and related ions [3]. Nitrate (NO_3^-) is

an important and commonly occurring nitrogen species in the environment. It is applied in both urban and rural areas as a component of fertilizer and is a major component of concern in the effluent of waste water treatment plants [3].

Experimentals

A mixture of dioctyl phthalate (DOP), Methyl trioctyl ammonium chloride (MTOAC), and the ionophore was dissolved in THF. PVC was dissolved in THF separately and was added to the mixture. The total mass of these compounds should be 0.1 g. An opening PVC tube with 3 mm in diameter and 2 cm in length was dipped into the mixture for about 10 s to form a 0.3 mm thick transparent membrane and was kept at room temperature for about 24 h. Then, the tube was filled with the nitrate ion solution and conditioned by 1.0×10^{-2} M KNO_3 solution for 2 h. Finally, the nitrate-selective electrode was prepared by incorporating the tube to a saturated calomel electrode (SCE).

Potentiometric Measurements: Potentials were measured with a digital pH-ion and an electrochemical cell consisting of two electrodes; a SCE as the reference electrode and a Ag/AgCl electrode embedded in a nitrate anion-selective membrane as the working electrode.

The performance of the electrode was investigated by measuring its potential in prepared solutions in a concentration range from 1.0×10^{-8} to 1.0 M. During these measurements, the sample solution was stirred using a magnetic stirrer. Additionally, the pH changes were measured using a pH meter and a pH electrode.

Electrochemical Impedance Measurements: EIS measurements were carried out using a potentiostat/galvanostat Autolab instrument controlled by Frequency Response Analyser (FRA) software and an electrochemical cell consisting of three electrodes: a SCE as reference electrode, a Ag/AgCl electrode embedded in the nitrate-selective membrane as the working electrode, and a platinum electrode as the counter electrode. During this analysis, a frequency range of 50000–60 Hz with 40 frequency points, the sample solution was fully static and the system was held at the open circuit potential (OCP).

Results and Conclusions: The best performing nitrate- selective membrane was composed of PVC (0.0327g), ionophore (0.0043g), additive (0.0006g), plasticizer (0.0635g).

These studies were carried out under the same experimental conditions using a 1.0×10^{-2} M solution of the corresponding anions as the internal and external solutions of the electrode, that between all the salts, KNO_3 solutions have the best Nernstian slope. The proposed membrane electrode was also examined with different concentrations of the inner reference solution from 1.0×10^{-1} M to 1.0×10^{-5} M, so the best inner solution was choosed 1.0×10^{-2} M. Selectivity coefficients for the phosphate ion were determined by fixed primary ion method (MPM).

Evaluation of EIS Studies of the Membrane with and without Ionophore: In this study, impedance measurements were carried out on the membrane with and without ionophore, and 1.0×10^{-3} M solutions of potasium nitrate as the internal and external solutions of the electrode were used, respectively. The charge transfer resistance of the membrane without ionophore (34.585 Mohm) is more than that of the membrane with ionophore (4.336 Mohm).

Keywords: *Ion selective electrode, Potentiometric, nitrate, Membrane, Plasticizer, Additive.*

References

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