Ain Shams University
College of Women
for Arts, Science and Education
Chemistry Department

Novel Polymeric Membrane Sensors Based on Some Polydentate Nitrogen Containing Organic Ligands and their Transition Metal Complexes

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بسم الله الرحمن الرحيم

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Summary

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الملخص العربي

1.1. Sensors

A sensor is a device that detects or measures a physical property and records, indicates or otherwise responds to it. Sensors can be divided into three types, namely (a) physical sensors for measuring distance, mass, temperature, pressure, etc. (b) biochemical sensors which measure chemical substances by using a biological sensing element (which will not concern us here), (c) chemical sensors which measure chemical substances by chemical or physical responses and considered one of the main interested areas in analytical chemistry over the last few decades because of their sensitivity, selectivity, and automation feasibility. Chemical sensors are defined by IUPAC recommendation **[Hulaincki, et al., (1989)]** as miniaturized transducers that selectively and reversibly respond to chemical compounds or ions and yield electrical signals which depend on the concentration. The chemical sensors are composed of three basic components: recognizer, transducer and electronic units as shown in **(Fig. 1.1).** The most important component is the recognition unit, since the development of a sensor with high selectivity is dependent primarily on this process. The recognition makes use of specific chemical reactions such as complexation, ion association, addition and redox reactions of the analyte species **[Camman, et al., (1991)].** The chemical recognition step can be transduced by a wide variety of signals including all five forms of energies, electrical, optical, thermal, magnetic and mechanical energies. The third component is the electronic unit (a preamplifier, analogue/digital converter etc.) which is directly connected to the transducer to suppress electrical noise or external influences caused by the interference of electronics or magnetic fields. A transducer is a device that converts an observed change (physical or chemical) into a measurable single. In chemical sensors, the observed chemical change is usually an electronic signal whose magnitude is proportional to the concentration of a specific chemical or set of chemicals **[Eggins, (1996)].**

Chemical sensors can be classified according to the type of energy of transduced signal into four groups, electrochemical, optical, thermal and mass sensors. Electrochemical sensors are further classified into, potentiometric(ion selective electrodes), amperometric and voltammetric , conductometric and coulometric based sensors.

1.1.1. Electrochemical sensors

An electrochemical sensor is a small device that can be used for direct measurement of the analyte in the sample matrix. Ideally, such a device is capable of responding continuously and reversibly and does not perturb the sample. Electrochemical sensors consist of a transduction element covered with a chemical or biological recognition layer . this layer interacts with the target analyte and the chemical changes resulting form this interaction are translated by the transduction element into electrical signals. The development of chemical sensors is currently one of the most active areas of analytical research . Electrochemical sensors represent an important subclass of chemical sensors in which an electrode is used as the transduction element **[Wang,(2000)].**

1.1.1.1. Voltammetric and amperometric sensors.

An increasing or / decreasing potential is applied to the cell until oxidation or/ reduction of the substance to be analyzed occurs and there is a sharp rise or / fall in the current to give a peak current. The height of the peak current is directly proportional to the concentration of the electroactive material. If the appropriate oxidation or/reduction potential is known , one may step the potential directly to that value and observe the current. This mode is known as amperometric. In many cases the concentration of a substance can be determined by measuring its steady-state limiting diffusion current. This method can be used when the concentration of the examined substance is not very low , and other substances able to react in the working potential range are not present in the solution .

1.1.1.2. Conductometric sensors.

Most reactions involve a change in the composition of the solution. This will normally result in a change in the electrical conductivity of the solution, which can be measured electrically.

1.1.1.3. Coulometric sensors

Coulometry can be regarded as an analog of titration where the substance being examined is quantitatively converted to a reaction product not by the addition of titrant, but by a certain amount of electric charge Q. Coulometry , measures the amount of charge Q consumed for the complete conversion (oxidation or reduction) of the substance being examined **[Bagotsky.(2006)].**

1.1.1.4. Potentiometric sensors

These involve the measurement of the EMF (potential) of a cell at zero current. The emf is proportional to the logarithm of the concentration of the substance being determined. The largest group among potentiometric sensors is represented by ion-selective electrodes (ISEs), the oldest and most widely used among them being a pH-sensitive glass electrode. One can find a large variety of commercially available ISEs that may be helpful in direct determination of ion concentration in liquid sample of different nature. Measurements with ISEs are performed versus stable and well-defined reference electrode contacting the sample solution through a liquid junction. In ISEs the signal is generated by charge separation at the interface between ion-selective membrane and the solution due to selective partitioning of ionic species between these two phases. Ion selective electrodes (ISE's) are membrane electrodes that respond selectively to ions in the presense of others by measuring the potential of the specific ions in solution.The potential difference depends, mainly upon the activity of the specific ion in solution, therefore, allowing the user to make an analytical measurement of that specific ion **[Camman,(1979);Buck,(1978);(1981)]** . Several ISE's have been developed for a variety of different ions . Ion-selective electrodes (ISE) are well-established analytical instruments used in many laboratories dealing with the environmental, agricultural and medicinal fields **[Singh et al , (1999)].**

1.2. Ion selective electrodes

1.2.1. Principle of potentiometric membrane sensors

Since the 1930s, potentiometric membrane sensors have found great practical applicability in different fields. The response mechanism of these sensors is based on the measurement of a potential under a zero current regime or under a low electrical current flow in a galvanic cell see (**Fig.1.2**). Potentiometric membrane sensors, which have been designed based on molecular recognition, contain a molecule that selectively recognizes another target species through various molecular interactions. As it is widely known, potentiometric electrodes possess as advantages the direct, simple, rapid, inexpensive and selective detection of ionic activities. The selectivity of these sensors stems from the highly selective interactions between the membrane material and the target species [**Ganjali, et al., (2006**)]. Ion-selective electrodes have found wide spread uses especially for the direct determination of ionic species in whole and diluted blood, serum, urine, tissue, and intracellular samples **[Meyerhoff, (1993)]**. When ion-selective electrode is placed in a solution containing the primary ions to which the membrane is selective (due to the interaction of analyte ion with the ion-selective membrane) a charge separation at the boundary of the membrane/sample interface is developed. This potential is measured against standard external reference electrode. The electromotive force (EMF) of this galvanic cell is a sum of number of local potential differences, arising at the boundaries **[Bakker, et al., (1997)].**

$$\mathbf{EMF = E_0 + E_M + E_J} \qquad \mathbf{(1.1)}$$

Where $\mathbf{E_0}$ is the external reference electrode potential,

$\mathbf{E_J}$ is the liquid junction potential,

$\mathbf{E_M}$ is the membrane potential,

The reference electrode potential is constant at a fixed temperature. The liquid junction potential ($\mathbf{E_J}$) is diminished to zero by using an electrolyte in which the mobilites of the cation and the anion have nearly equal values. Therefore, the measured EMF of the cell can be correlated only to the membrane potential developed at the membrane sample interface, which in turn reflects the activity of the analyte ion (a_i) according to Nernst equation [**Nernst, (1889)**]:

$$EMF = E^o + \frac{2.303R\ T}{Z_i F}\log a_i \qquad (1.2)$$

Where:

a_i is the activity (mol L^{-1}) of the primary ion of charge $Z_{i;}$

E^o: is the standard cell potential;