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تهیه الکترود های یون گزین جهت اندازه گیری یونهای منگنز و هیدروژن

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Dedicated to :

The member of my dear father who was the best and the kindest for me.

My kind mother who is the shining star of my life.

My kind, dear husband, my best friend, who helped and supported me in this way .

The just beautiful flower of my life, my little son, Amir Hossein.

ACKNOWLEDMENTS

ABSTRACT

In part I a new PVC membrane electrode that is highly selective to Mn (II), was prepared by using 2, 2'-Bis(Salicylaldimino) azobenzene (BSAAB) as a suitable neutral carrier. The sensor exhibits a Nernstian response for manganese ions over a wide concentration range (1.1 $\times 10^{-7}$ to 8.0×10^{-2} M) with a good slope of 30.5 ($\pm$ 0.5) mV per decade and detection limit (5.51×10^{-8} M). The proposed sensor was applied for at least 2 months without any measurable divergence in potential. Also, the recommended sensor revealed a fairly good discriminating ability towards Mn^{2+} ions in comparison to some cations and anions. The electrode was also utilized as indicator electrode in the potentiometric titration of Mn (II) with EDTA solution and in determination of Mn^{2+} ion in some drug, tape and river water samples.

In part II a hydrogen ion-selective electrode poly (vinyl chloride) (PVC) membrane electrode was developed using 2,2'-Bis(Salicylaldimino) azobenzene (BSAAB) as neutral carrier. The sensor exhibits a Nernstian response for hydrogen ions over a wide concentration range (1.0×10^{-12} to 1.0×10^{-2} M) with a good slope of 58.5 ($\pm$ 0.6) mV/pH at 20°C and detection limit 5.05×10^{-13} M. The proposed sensor was applied for at least 45 days without any measurable divergence in potential. Also, the recommended sensor revealed a fairly good discriminating ability towards H^+ ions in comparison to some cations and anions. The electrode was also utilized as indicator electrode in the potentiometric titration of hydrochloric acid with NaOH solution.

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PART ONE

GENERAL INTRODUCTIUON

1.1. Potentiometric Sensors

Chemical ion selective sensors are of increasing interest within the filed of modern analytical chemistry, as can be seen both from the number of books, review papers published and from the diversity of approaches and technique applied [1-11]. To the IUPAC recommendation, an ISE is defined as follows [12]:

The essential part of a carrier-based ISE is the ion sensitive solvent polymeric membrane, physically a water-immiscible liquid of high viscosity that is commonly placed between two aqueous phases, i.e., the sample and the internal electrolyte solution (Figure 1.1). It contains various constituents, commonly an ionophore (ion carrier) and a lipophilic salt as ion exchanger. The sensor responds to the activity of the target ion and usually covers an extraordinarily large sensitivity range, from about 1 to 10^{-6} M. Its selectivity is related to the equilibrium constant of the exchange reaction of target and interfering ions between the organic and aqueous phases. It strongly depends on the ratio of complex formation constants of these ions with the ionophore in the membrane phase (Figure 1.2). Ionophores are in their uncomplexed (or unassociated) form either charged or electrically neutral. The first neutral ionophores used in ISE membranes were antibiotics.[13, 14] They were followed by a large number of natural and synthetic, mainly uncharged carriers for cations and a series of charged and uncharged ones for anions.

1.2. Classification of Electrodes

The theory of membrane processes including those that occur in ISEs has been reviewed by Buck who attempted to bring out the links between electrode kinetics and membrane processes. Starting with qualitative and quantitative electrostatic features of interfaces between a solid and a liquid electrolyte and between two liquid electrolytes, he dealt with various
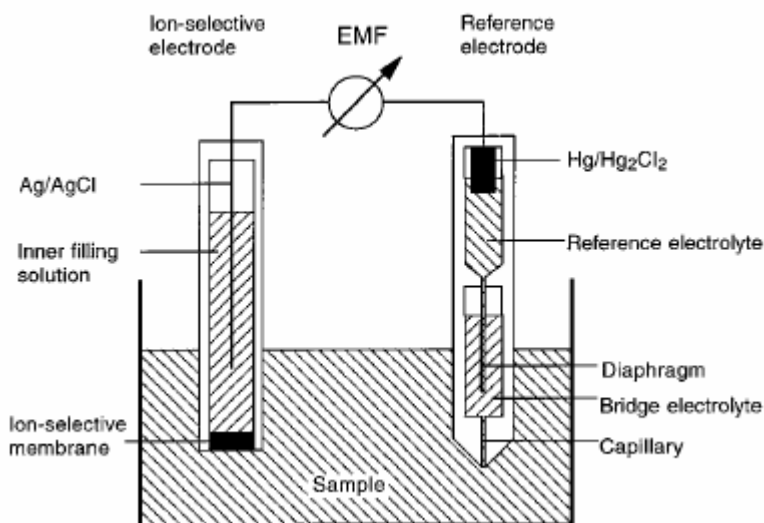
Fig. 1.1. Schematic diagram of a membrane electrode measuring circuit and cell assembly.

methods of describing membrane transport, and with ion-exchanging sites (site free membranes, fixed and mobile site membranes) in different membranes including thin bilayer lipid membranes and thick membranes, he then discussed the time dependent behavior of membranes and, finally ISEs system in a steady state and systems under current flow were

discussed. Depending on the type of membrane employed, ISEs can be classified into several groups:

(1). Electrodes with solid membranes[13-21] (solid-state), membranes formed of solid low solubility salts that can be based on single crystals, solidified melts or polycrystalline pellets . Where possible, the internal electrolyte is replaced by a metal contact (all solid –state). In addition to the homogeneous materials that are used especially in commercial electrodes, membrane can also consist of heterogeneous mixture of precipitates incorporated into polymer matrix.

(2). Electrodes with liquid membranes consisting of liquid electroactive compounds or electroactive solid materials dissolved in suitable organic solvents-mediators that are immobile with water. Electrodes with liquid membranes also include those with plasticized polymer membranes, the low-volatility plasticizer also contains a suitable electroactive substance. The electroactive substance in liquid membranes can be either an ion-exchanger or an ionophore.

(3). Glass electrodes with membranes consisting of various multicomponent glasses. These electrodes are sometime included in the same class of electrodes as those with solid homogeneous membranes. The separate classification is a result of tradition and the manner of utilization.

(4). Electrodes with suitable auxiliary membrane, with a potentiometric detection unit based on conventional glass electrodes of the types mentioned above. These include gas electrodes and electrodes with biocatalitic membranes.

Simon Stefance [13,22,23] in 1966 introduced the first neutral-carrier –based ISE and demonstrated that these antibiotics include in vitro selectivity similar to this observed in vivo.

1.3. Theory of response of ion selective electrodes

The basic theory of the response of solvent polymeric membrane electrodes was developed many decades ago.[24-27] The theory of ISE response is well-established, especially owing to the pioneering work of Eisenman's group[28] and others.[29] Formally, the membrane potential can be
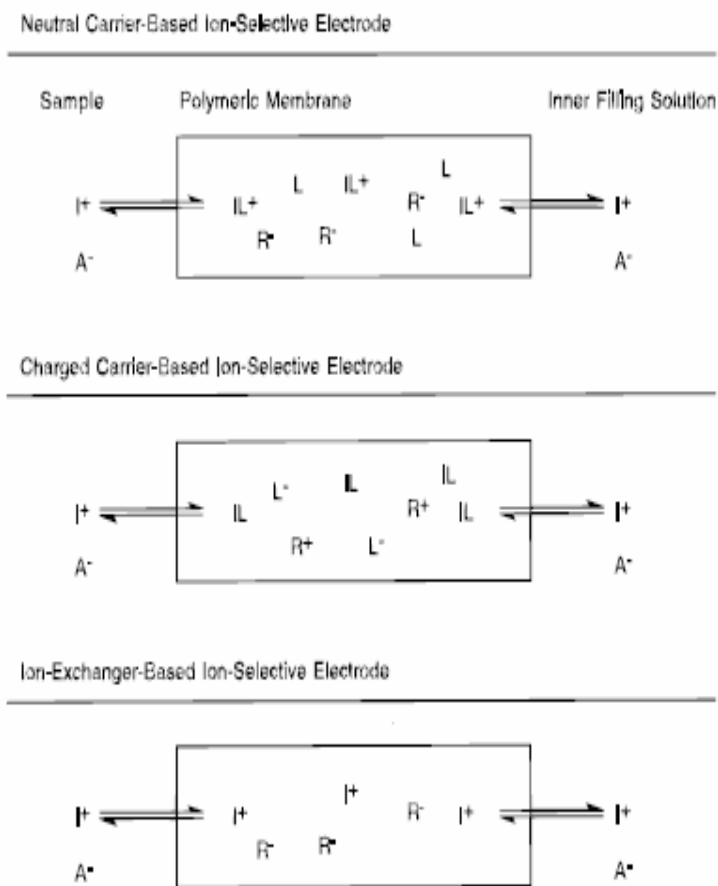
Fig. 1.2. Schematic view of the equilibria between sample, ion-selective membrane, and inner filling solution for the special case of equal sample and inner electrolytes: top, electrically neutral carrier (L) and anionic sites (R$^-$); center, charged carrier (L$^-$) and cationic sites (R$^+$); and bottom: cation exchanger (R$^-$).

described as the sum of the two phase boundary potentials and the diffusion potential within the membrane,[24,25] the latter being negligible in electrodes of practical relevance.[30,31] The selectivity dependence on ion exchange and complex formation properties is also well-

understood, but only recently a proper description of the ISE response to solutions containing ions of different valences was given.[32] The extended semiempirical Nicolskii-Eisenman equation, which had been generally used, is not appropriate in such cases. Ion-selective electrode membranes are typically investigated under zero-current conditions in a galvanic cell such as the following:

$$Hg \mid Hg_2Cl_2 \mid KCl(sat.); \; 3 \; M \; KCl \mid sample \; solution \parallel liquid \; membrane \parallel internal \; filling \; solution \mid AgCl \mid Ag.$$
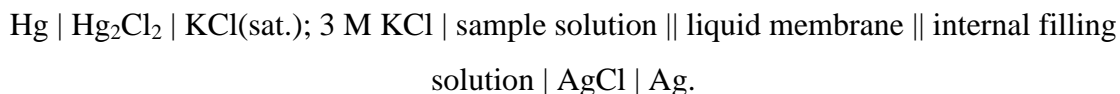
The electromotive force (emf) across this cell is the sum of all individual potential contributions. Many of these are sample-independent, and the measured emf can usually be described as where E_M is the membrane potential, and E_J is the liquid junction potential at the sample/bridge electrolyte interface, which can either be kept reasonably small and constant under well-defined conditions or be estimated according to the Henderson formalism.[33] It is important to note that it is this liquid junction potential that prohibits the true assessment of single ion activities with ion-selective electrodes; the role of the reference electrode on the overall emf measurement should, therefore, not be overlooked.[34] On the other hand, galvanic cells without liquid junctions (i.e., containing two ion-selective electrodes) respond to ratios or products of ion activities, again prohibiting single ion activity measurements. In this work, however, we will only focus on the membrane potential E_M of one electrode which is ideally a function of the sample ion activity.

1.4. Selectivity

The selectivity is clearly one of the most important characteristics of a sensor, as it often determines whether a reliable measurement in the target sample is possible. A theoretically

through selectivity description allows researchers to identify the key parameters for optimizing the performance of potentiometric sensors, e.g., by adjusting weighing parameters (i.e., absolute membrane concentrations) or choosing different plasticizers or matrices[35,36]. Virtually all selectivity considerations were based in the past on the semi empirical Nicolskii-Eisenman equation[37]. Different methods are for measuring of selectivity coefficient for an ISE. The principles of some of these methods were shown in this section as follows:

1.4.1. Mixed Solution Method (MSM)

In the mixed solution method, the selectivity coefficient, K_{MSM}, was evaluated graphically from potential measurements on solutions containing a fixed concentration of primary ion (i) ($\approx 1\times10^{-4}$ M) and varying amounts of interfering ions (M^{n+}) according to the equation (1.1):

$$K_{i,x}^{Pot} \times a_x^{\frac{2}{n}} = a_i \left\{ \exp\left[(E_2 - E_1)(\frac{F}{RT}) \right] \right\} - a_i \qquad (1.1)$$

Where E_1 and E_2 are the potentials of the primary ions alone and primary ions with interfering ions(a_x), a_i and a_x are the activities of primary and interfering ions, respectively, and n is the charge of the interfering ion. The potentiometric selectivity coefficients can be evaluated from the slope of the graph of $a_i \left\{ \exp\left[(E_2 - E_1)(\frac{F}{RT}) \right] \right\} - a_i$ versus $a_x^{\frac{2}{n}}$.

1.4.2. Match Potential Methods (MPM)

In practice, a specified amount of primary ions (a_i) is added to a reference solution (containing a_i^r) and the membrane potential is measured. In a separate experiment, interfering

ions are successively added to an identical reference solution until the membrane potential matches the one obtained before with the primary ion. The matched potential method selectivity coefficient is then defined by the ratio of the primary ion (Δa_i) and interfering ion activity (a_x) increases in the two experiments.

$$K_{i,x}^{MPM} = \frac{\Delta a_i}{a_x} \qquad\qquad \Delta a_i = a_i - a_i^{'} \qquad (1.2)$$

Generally, the matched potential method can be used without regard to the electrode slopes being Nernstian or even linear. For these reasons, it has gained in popularity in the last few years and has even been advocated by IUPAC in a recent technical report.

1.4.3. Solvent Separation Method (SSM)

According to the SSM, the potentiometric selectivity coefficients were determined using two solutions. One solution containing primary ion and another solution containing interfering ion with similar concentration to primary solution at constant conditions, the selectivity coefficient were determined utilizing the equation(1.3):

$$\log K_{i,x}^{SSM} = \frac{(E_x - E_i)}{s} - \log a_x^{Z_i Z_x} + \log a_i \qquad (1.3)$$

Where E_i and E_x are the measured emf for the solutions of primary and interfering ions, respectively; Z_i and Z_x are the charges of primary and interfering ion. S is the calibration slope of the sensor and a_i and a_x are the activity of primary and interfering ion respectively.

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1.4.4. Fixed Interfering Method (FIM)

In this method the emf of a cell comprising an ion-selective electrode and a reference electrode is measured for solutions of constant activity of the interfering ion, a_x, and varying activity of the primary ion, a_i. The emf values obtained are plotted vs. the logarithm of the activity of the primary ion. The intersection of the extrapolated linear portions of this plot indicates the value of a_i that is to be used to calculate $K_{i,x}^{FIM}$ from the equation (1.4):

$$K_{i,x}^{FIM} = \frac{a_i}{\left(a_x\right)^{\frac{z_i}{z_x}}} \qquad (1.4)$$

Both z_i and z_x have the same sign.

1.5. Detection Limit

Every ion-selective electrode has a lower and upper detection limit where the response starts to deviate significantly from a Nernstian electrode slope. Generally, they fall into activity ranges where the electrode starts to loose sensitivity toward the primary ion. According to the IUPAC recommendation of 1976,[38] the detection limit is defined by the cross section of the two extrapolated linear calibration curves (see Figure 1.3). A definition of the detection limit of ISEs in analogy to other analytical techniques has also been proposed.[39]

It is useful if the electrode is intended to be used in an activity range of severe interference, i.e., low sensitivity. However, for general use, the IUPAC recommendation is useful since it is simple and widely accepted and experimental results from different authors can be easily compared.