ION - SELECTIVE ELECTRODES IN ANALYTICAL CHEMISTRY

Edited by
Henry Freiser

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ION-SELECTIVE ELECTRODES IN ANALYTICAL CHEMISTRY

VOLUME 1

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Preface

Ion-selective electrodes continue to be one of the more exciting developments in electroanalytical chemistry in the last 10 years. This is evidenced in the large and continually growing literature in the field. It is important and necessary in such a rapidly growing area to be able to "take stock," i.e., to present a well-rounded, up-to-date review of important developments. In this volume, reviews by many of the leading practitioners and pioneers in this field contribute to what we consider to be a generous coverage of both fundamental aspects of ion-selective electrodes and their applications to analytical chemistry. Although this volume is not intended to be exhaustive, we have attempted to produce a "stand alone" text dealing with all major current developments. Indeed, since some of the theoretical approaches are not yet universally agreed on, each of the first five chapters deals with theory and principles of the nature and behavior of ion-selective electrodes from the vantage point of the authors' own experience and understanding. In view of the rapid expansion of this field, plans for future volumes are now being formulated.

Tucson, Arizona Henry Freiser

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Chapter 1

Theory and Principles of Membrane Electrodes

R. P. Buck

1. POTENTIAL GENERATING PROCESSES[1-8]

Modern ion-selective electrodes (ISEs) are based on passive membranes, regions of space that separate two phases in such a way that material transport between the outer, contacting phases is in some way modified or inhibited compared to transport that would occur when the phases are in direct contact. Material transport can include both neutral and charged complex species or simple ions and electrons (or holes). The reason that membrane transport is interesting and useful in analytical chemistry is that membrane-modified transport can lead to development of electrostatic potential differences across membranes. These so-called membrane potentials reflect the composition of the exterior phases, usually the contacting bathing solutions on either side, and can be related, in most cases, to the activities of ions in the exterior solutions. When membrane potentials can be interpreted in a definitive way in terms of ion activities, one has the beginning of an analytical technique for single measurement or continuous monitoring of solutions adjacent to a membrane.

1.1 Interfaces, Fixed Charges, Charged Sites, and Charge Carriers[2,5,7,8]

Membranes are most frequently liquids or solids. They are usually thick enough that they possess an inside region and two outer, boundary-

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defining surfaces that separate the membrane from the exterior phases. For the purpose of describing potential-generating processes, it is convenient to consider membranes as being thick enough to have an interior region of unique composition with respect to the regions outside. This concept is useful for most tangible membranes that are used as ISEs. However, when a membrane is so thin that it is only one or even a few molecules thick, the notion of an interior region is not appropriate. A dye adsorbed at the contact surface between two immiscible liquids is an example of a membrane with virtually no interior region so that the two boundary surfaces can be considered collapsed into a single boundary.

When a membrane is thick enough to provide two boundary surfaces we consider that the membrane has two interfaces as shown in Fig. 1. Each interface is a hypothetical surface, which separates the physical–chemical properties of the membrane from the outer phases, where another set of chemical and physical properties exists. Location of the interfaces is not clearcut because important properties such as charge density and potential distribution vary continuously from one phase to another. There are advantages in considering ISE membranes to be composed of homogeneous (or heterogeneous) interior regions surrounded by interfacial boundaries. This model emphasizes similarities in potential generating processes regardless of the membrane composition. It allows separation of processes occurring on one side (usually the exterior side) of an interface

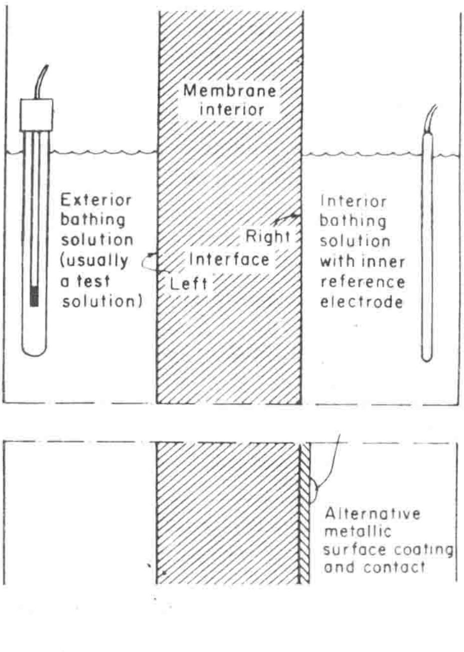

Fig. 1. Schematic essentials of membrane cells. Top: Membrane configuration in which the membrane separates two electrolyte bathing solutions. The left side, designated (′) or (0) in the text, is the exterior or test solution. The right side, designated (″) or (d), is the interior or inner reference solution. Also shown is a typical exterior reference electrode (junction type) and interior reference electrode (electrode of the second kind). Bottom: "All-solid-state" configuration in which an electronically reversible contact replaces the interior reference solution and inner reference electrode.

from processes involving transfer of material across other interfaces, and from processes of transport within the membrane bulk. Reversible and irreversible adsorption, reversible and irreversible ion and electron exchange, and irreversible transient and steady-state bulk transfer become separable processes for consideration in terms of microscopic chemical properties of the membrane material and the bathing solution compositions. Local application of basic electrostatic, equilibrium, quasi-thermodynamic steady-state, and nonequilibrium kinetic laws becomes possible and convenient. Conventional ion exchange, neutral species and salt extraction, and interfacial kinetic processes described in separation science and in electrochemical kinetics can be applied to membrane systems to provide descriptions that are recognizable in the larger context of electrochemistry. One can thereby avoid much of the "black box" approach to membrane science, which can easily creep into the theory, whereby membranes are considered to be merely geometric barriers with characteristic "permeabilities" that bear no obvious fundamental relations to molecular and local chemical properties of the membranes themselves.

The thickness of membranes as active components for ISEs is determined by two overriding factors: the potentiometric measuring circuit and the long time response leading to a steady-state potential value. The membrane impedance to current must be less than the input impedance of the measuring device and, in addition for those membranes requiring bulk transport steady state, the square of thickness divided by the mean diffusion coefficient of transported ions gives an ultimate response time, which must be less than the time allowed for measurement. Although it is frequently the case that membranes are thin in one dimension relative to the other two, this property is operational and not fundamental. Similarly, the fact that most useful membranes are cast in disk shape follows mainly from the present theories of membrane potentials, which are almost always worked out for transport in one dimension, the thinnest dimension.

Membranes for ISEs are immiscible or at least partially immiscible with respect to the bathing solutions or solid contacts. Hydrophobic organic liquids and solids and low water-solubility inorganic solids constitute the main materials of membrane construction Nevertheless, useful membranes are not electrical insulators. They are permeable to an easily measurable extent for species in their immediate environment. Porous membranes are those such as organic liquid and solid, synthetic ion exchangers, which dissolve an external solvent, usually water, and allow water from two bathing solutions with nonidentical ionic strengths (nonidentical osmotic pressures) to pass slowly from one side of the membrane to another. However, many membranes are nonporous and solvent transport is usually not an important process to contend with in deducing membrane potential responses. Useful membranes are most often solid or liquid electrolytes, because they are composed of partially or completely ionized acids, bases, or salts, or because they contain potentially ionizable species.

Most widely studied are those membranes of polyelectrolytes ("solid" synthetic ion exchangers), aqueous–immiscible organic liquid electrolytes ("liquid" ion exchangers), and solid, ion-conducting electrolytes including silver halides, silver sulfide, rare earth fluorides, and alkali silicate and alumino-silicate glasses. All of these materials contain ionic species or ionizable groups whose electrical state depends upon the membrane dielectric constant and extent of solvent penetration. A characteristic of these membranes is the presence of charged sites. If ionic groups are fixed in space in a membrane as $-SO_3^-$ and $-COO^-$ attached to a cation exchanger resin backbone, the membrane is considered to contain fixed, charged sites. Liquid ion exchangers such as salts of phosphonic acids and quaternary ammonium salts possess mobile sites that are free to move, but remain trapped in the membrane. Membranes need not contain sites of only one sign. However, it is frequently necessary to incorporate sites of one sign. Single-crystal Frenkel membranes, silver halides, sulfide, and LaF_3, for example, behave as though they contain fixed, charged sites. At room temperature impurities determine the mobile ionic species: interstitials or vacancies. A divalent anion impurity in AgX generates mobile cation interstitial silver ions and fixed sites that are the divalent anions.

In membrane electrochemistry and in the design of ISEs, the kind, location, and mobility of charged species in membranes and in the exterior phases are of primary importance. It is the distribution of charge that gives rise to the electric field and resulting membrane potentials. Among the charged species in membranes are the fixed and mobile sites already mentioned. In addition, and more important, are the ions of opposite sign to the sites (assuming only one sign type for sites). These ions, called counterions, are present to fulfill the requirement of electroneutrality, and may be initially built into a membrane or placed there by the process of ion exchange. In contrast with site ions, counterions are not restricted to the membrane phase, but can be transported under electroneutral diffusion conditions, from bathing solutions to membranes and vice versa. Membranes also contain some mobile ions from bathing solutions with the same sign as the sites. These ions are called co-ions. Together with the counter ions, mobile charged species are charge carriers.

Membrane systems including a membrane and outer phases must be overall electrically neutral. If one imagines the electrical character in passing from the bulk of one bathing solution (or metallic contact) through a membrane to the other bathing solution, this hypothetical experiment takes the observer from electroneutral bulk to another electroneutral bulk. Yet the total region contains nonelectroneutral (space charge and adsorbed charge) sections as double layers at the interfaces and within the membrane. These space-charge regions extend out into the bathing or contacting phases and inward into the membrane. The width of the space charge region is variable and depends on the activity of charge carriers and their energy (standard ionic chemical potential in each phase). The existence of space charge and potential curvature are synonymous general features of membrane systems. The membrane itself will normally possess a net charge and this charge resides at the inner side of the interfaces. The interior of the membrane will most frequently contain a region of electroneutrality in the bulk. The compensating space charge for the membrane exists in diffuse and adsorbed charges on the bathing solution or metal contact side of each interface.

1.2. Ion Exchange as a Potential-Generating Process[2]

Ion exchange is a general type of process that describes the reversible and irreversible transfer of ions from one phase to another. Ion exchange includes transfer of ions across such phase boundaries as an interface between a metal and an electrolyte, two immiscible liquids, a metal and an ionic crystal, an ionic crystal and an electrolyte solution, as well as between liquid and solid ion exchanger resin membranes and bathing solutions. The broad classification of ion exchanger includes phases with ions in common, as well as phases that initially contain different ions. Usually the ion exchange processes occur at zero current. However, even when a net flux or current is passing, the ion exchange processes, while perturbed, continue to function. Thus an AgCl wafer is an ion exchanger for Ag^+, as can be demonstrated by exposing the wafer to radioactive Ag^+ and counting the incorporated radiosilver after different lengths of exposure. Similarly, silver metal is an ion exchanger when it is exposed to radiosilver ions. The latter are rapidly incorporated into the metal and an equivalent number of nonradiosilver ions are released to the solution.

Possibly the more characteristic view of ion exchange at zero current is the equilibration of two or more ions of the same charge, or same sign of charge between two phases. However, ion exchange involving ions of more than one kind is simply a historic case observed with ion exchange resins. The phenomenon is quite general and is a property of all membrane electrode systems and classical electrodes of the first, second, and third kinds.

Ion exchange at zero net flux is characterized by the equal and opposite fluxes of ions across the phase boundary as shown in Fig. 2. The quantitative measure of the rate of ion exchange is the exchange current or exchange flux density. It is the number of moles of ions that flow in opposite directions per second per square centimeter. Rapid, reversible ion