

MECHANISTIC ASPECTS OF ION-SELECTIVE MEMBRANE ELECTRODES. A SUBJECTIVE VIEW

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ABSTRACT

Progress in the field of ion-selective membrane electrodes is viewed in terms of a dynamic interplay between advances in mechanistic understanding and the development of practical electrodes. Techniques used for the elucidation of glass, liquid, and crystal membrane electrode operation are discussed and possible mechanisms are considered.

Scientific progress is limited not only by the rate of generation of new ideas but also by the state of development of appropriate experimental tools and techniques. Measurement, one of the great themes of both fundamental and applied science, represents an integrating force among divergent scientific specialities and serves as common ground for problem oriented and discipline oriented scientists.

This is especially true of the ion electrode area which now spans subfields in the biological, chemical, and physical sciences and counts among its active participants a diverse array of experimental and theoretical scientists. Although progress to date must be highly gratifying to those who in earlier years braved the scepticism of workers in the more established areas, it must also be acknowledged that much of the present state of the art is still based on empirical data and that a critical look at the mechanisms of charge transport in membranes, the mechanism of ion selectivity, and the *coupling* mechanisms between transport and selectivity-determining processes still yields new questions for every detail which can be satisfactorily settled.

Although no comprehensive coverage of mechanistic points is intended here and the emphasis is undoubtedly very subjective, most workers in the field would probably agree on several major themes which have become apparent as a general framework for the further development of mechanistic models and the continuing effort to relate mechanistic hypotheses to physical reality:

(i) The inescapable parallels and obvious interplay between ion selective membrane electrodes and biological membranes. Indeed, the parallels of transport processes, ion exchange properties, and electrical phenomena are so striking that one should take a unified view of both membrane categories and hope, ultimately, for a comprehensive theory of membrane potentials and selectivity.

(ii) The classification of membranes by physical configuration, nature of

site, or other variables. Classification into 'fixed' and 'mobile' site or 'charged' and 'neutral' carrier seems particularly appropriate and yields useful relationships which facilitate reasoning by analogy. Alternatively, classification by nature of the membrane material gives a sensible organizational scheme, e.g.

<i>Physical classification</i>	<i>Site classification</i>
Glass electrodes	} Fixed
Precipitate membranes	
Crystal membranes	
Single crystal; polycrystalline; mixed crystal	
Liquid membranes	} Mobile
Charged carriers	
Neutral carriers	
Immobilized bulk membranes	
Enzyme electrodes	

(iii) Recognition of the three-dimensional nature of membrane electrodes in cross section and the importance of interfacial processes both *inside* the membrane and at the interfaces between the membrane and the solution phase or phases.

(iv) Development of approximate relationships between ion selectivities and physicochemical parameters, e.g.

$$K_{\text{sel}} \simeq K_{\text{ex}} \left(\frac{\mu_1}{\mu_2} \right) \text{ for glass electrodes}^1$$

$$K_{\text{sel}} \sim \frac{K_{\text{f}, 1}}{K_{\text{f}, 2}} \quad \text{for some neutral carriers}^{2, 3}$$

$$K_{\text{sel}} \simeq \frac{S_{\text{ji}}}{S_{\text{jk}}} \quad \text{for precipitate or crystal membranes}^4$$

$$K_{\text{sel}} \sim \frac{\mu_{j+}^* k_{j+}}{\mu_{i+}^* k_{i+}} \quad \text{for some liquid exchangers}^2$$

Such relationships not only focus our attention on the major selectivity-determining factors but also aid in the selection of membrane materials for practical purposes.

(v) The analogies of ion selective membrane electrode processes to classical chemical topics such as ion exchange, extraction, geometries and electrostatics of sites, etc. which facilitate organization of empirical data and provide useful experimental tests of mechanistic alternatives.

In our own laboratory, more than four years of effort has been invested toward mechanistic studies, mainly through the dedicated work of Drs M. J. D. Brand, E. Eyal, and K. Srinivasan. It is convenient to consider this work in terms of the type of membrane involved.

LIQUID MEMBRANES

While liquid membrane electrodes have been known for many years, it was

probably the introduction of the calcium-selective electrode by Ross⁵ which stimulated the intensive development resulting in commercial availability of electrodes for a large number of cations and anions⁶.

A general theory of liquid membrane electrodes based on ion exchange properties has been given by Eisenman^{2, 7, 8} and by Sandblom⁹. Potentiometric response to a given counter-ion depends not only on the activity of the ion in the solution and in the membrane but also on the equilibrium constant of the ion exchange process and on the mobility of the ion in the membrane. Ionic migration has been assumed to be the only process responsible for the passage of electricity through the membrane. This is equivalent to treating the membrane as a pure resistance^{8, 9} for which the measured conductivity is independent of the frequency of the applied a.c. signal. Measurements of the conductivity of solid ion exchange membranes have indicated only small variations with frequency^{10, 11}.

The mechanism of ion transport through membranes and across the membrane-solution interface is not well understood; kinetic data on the processes involved are not all available although it is thought that the ion exchange reaction is not rate determining¹². It is apparent that such information is not available from steady state potential measurements and a different experimental approach is required. One possible approach involves the study of the power spectrum of noise generated by passage of a relatively high density current through a solid ion exchange membrane¹³. *Table 1* summarizes some of the recent experimental and theoretical methods which have been used to study liquid membrane electrodes from the mechanistic point of view.

The impedance—or its reciprocal, the admittance—of an electrochemical cell provides an index of the sum of all processes by which electricity flows through the cell between the electrodes. Processes which contribute to the impedance may be capacitative or Faradaic—i.e., those processes related to charge transfer reactions at the metal electrode-solution interfaces. Faradaic processes may be rate limited by mass transport of ionic species in solution. The rather large impedances shown by cells containing a liquid ion-exchange membrane electrode are due to transport through the cell being membrane limited. Measurements of cell impedance are therefore equivalent to measurements of the impedance of the membrane and solutions in contact with it. This conclusion is not necessarily valid for any membrane as it has been demonstrated¹⁶ that some membrane impedances, e.g. that of the chloride electrode, may actually be quite low. The use of standard ion selective liquid membrane electrodes for such mechanistic studies is experimentally attractive because the impedances fall well into the range of most commercial impedance bridges, although the measured impedances will also reflect the influence of charge transfer and other processes taking place at the reference elements.

The shape of the complex impedance plane plots indicates that the membrane cell is electrically equivalent to an R.C. network which reduces to a pure resistance at both high and low frequencies. The cell capacitance shows a continuous decrease with increasing frequency until at the highest frequencies used a value is obtained which is comparable to the stray capacitance of any electrical circuit. The limiting high frequency resistance, which may be interpreted as a frequency independent resistance, represents

Table 1. Selected mechanistic studies of liquid membrane electrodes

Technique used	System	Reference
Current-voltage curves	K ⁺ ; antibiotic containing membranes	14, 15
Impedance measurements	Ca ²⁺ , Cu ²⁺ , Cl ⁻ ; liquid membranes	16
Conductance measurements	Ca ²⁺ , Li ⁺ ; liquid membranes	17, 18
Conductance measurements	K ⁺ ; antibiotic containing bilayers	19
Conductance measurements	H ⁺ , Na ⁺ ; liquid membranes	9
Conductance measurements	Li ⁺ , Na ⁺ , K ⁺ , Cs ⁺ , Rb ⁺ ; neutral carrier containing bilayer membranes	20
Transport number determination	Na ⁺ , K ⁺ ; antibiotic containing membranes	21, 22
Double layer measurements	Theoretical analysis	23
¹⁴ C, ⁴² K tracers	Valinomycin membranes	21
⁸⁶ Rb, ²² Na, ⁴² K, ¹³⁷ Cs tracers	Antibiotic containing membranes	24
Fluorescent dye probes	NH ₄ ⁺ , K ⁺ , Cs ⁺ , Na ⁺ , Rb ⁺ -antibiotic complexes	25
I.R. spectroscopy	K ⁺ , Na ⁺ , Li ⁺ , Rb ⁺ , Cs ⁺ -antibiotic carriers	26
Freezing experiments	Valinomycin containing membranes	27
Magnetic resonance	Na ⁺ , K ⁺ , Cs ⁺ -antibiotic complexes	28, 29
Magnetic resonance	Biological membranes	30, 31
Concentration jump	Liquid exchanger membranes	32
Flash photosynthesis	Thykaloid membrane	33
Noise spectra	Ion exchange membranes	13
Theoretical study	Fixed neutral site membranes	34
Theoretical study	Carrier transport in bilayers	35
Theoretical study	Nerve impulse conduction	36
Theoretical study	Liquid ion exchangers	37

the sum of the resistances due to solutions, reference electrodes, etc. in series with a complex impedance. The equivalent circuits obtained may be interpreted as representing transport of ions through the liquid membrane and across the membrane-solution interface by electromigration and by another process for which there is no simple physical analogy. It is also apparent that counter-ions to which the electrode shows no potentiometric response can and do enter into ion exchange reactions at the membrane-solution interface. There is evidence that the structure of the double layer at the membrane-solution interface is rather different from that observed at metal-solution interfaces. With the impedance measurement techniques available, the qualitative description of the electrode processes involved in the operation of liquid membrane electrodes cannot yet be made quantitative. Accurate measurements of a high impedance over a wide frequency band width are extremely difficult to carry out, but it seems likely that refinement and improvement of the technique can lead to a possible means for quantitative evaluation of fundamental electrode parameters.

Neutral carrier liquid membrane electrodes with selective response to monovalent cations have gained considerable acceptance in recent years because of their high selectivity coefficients. Neutral carriers include polyethers³⁸, polyesters³⁹, and certain antibiotics.

Typically, valinomycin is dissolved⁴⁰ in an appropriate solvent such as hexane, octanol, or phenyl ether, and placed in a liquid membrane electrode assembly giving rise to an electrode with selectivity ratios of the order of 5000:1 for potassium over sodium; such a selectivity ratio is considerably higher than that of about 30:1 for cation sensitive glasses. Thus, an understanding of the electrode mechanism is important not only for making better electrodes but for improving understanding of ion transport in biological membranes.

In the latter connection, it must be recognized that the electrode consists of a solution of valinomycin in an organic solvent that is immiscible with water, interposed between two aqueous solutions containing the ions to be measured—just as the membrane of a living cell or of mitochondria separates the internal from the external solution of physiological character. In both cases valinomycin has been shown to greatly enhance the permeability of the membrane to potassium ions^{41, 42}. Indeed, the selectivity of the valinomycin electrode is comparable to that of biological membranes and it can be shown that some compounds with large antimicrobial activity are those for which complex formation constants with cations are high⁴³.

Various theories have been proposed to explain the role of valinomycin in ion transport through membranes. These mechanisms involve some complex formation between valinomycin and potassium ion (See *Table 1*). According to one model, the valinomycin molecule acts only at the phase interface to enable the ions to pass into the membrane wherein they move as free ions. A second model explains the enhanced permeability on the basis of channel formation involving the passage of ions through a channel of ordered valinomycin molecules which span the thickness of the membrane. We favour a third mechanism which involves initial complex formation between the valinomycin and the cation followed by the transport of the ion through the membrane in the cavity of the valinomycin ligand, which acts as a 'carrier' or transport catalyst. This model is also supported by the work of Ciani, Eisenman and Szabo¹⁷ on the actins. By measuring the potentiometric selectivities of the valinomycin electrode and the formation constants of the valinomycin-cation complexes, it was possible to show that the selectivity coefficient is approximately equal to the formation constant quotient for various pairs of alkali metal ions; in thick electrode membranes similar results were also obtained when cyclic polyethers were used as carriers⁴⁴. Furthermore, it was shown²⁷ that ion selectivity is lost when the membranes are 'frozen' even though some residual conductivity persists; this is taken to support the carrier model because it is felt that freezing the membrane greatly reduces the mobility of the bulky carrier molecule and largely negates its transport catalyzing action in electrode membranes.

GLASS MEMBRANES

Glass electrodes are of analytical importance for the potentiometric determination of hydrogen ions and other monovalent cations and the properties of such electrodes have been extensively characterized¹. Commercially available glass electrodes fall into three main categories; pH electrodes showing greatest selectivity for H⁺, sodium electrodes which may

be several thousandfold more selective for sodium than potassium, and general cation electrodes which have roughly comparable selectivities for common alkali metal ions. The mechanism of response of such electrodes is thought to depend upon ion exchange reactions at the membrane interfaces together with mobility of the cations in a lattice of fixed anion sites within the membrane. Such membrane systems do not reach a state of true thermodynamic equilibrium in practice and ions migrate under the influence of the gradient of their electrochemical potentials. Thus, the time invariant behaviour of glass membranes has been obtained by integration of the Nernst-Planck equations^{4,5} for each mobile species present at zero current and at fixed currents^{4,6}. Extension of this treatment to include the time variable properties by which the membrane steady state is established has not been given except under certain simplifying conditions. A numerical solution to the related problem of the time dependence of ion permeation into spherical ion exchange beads has been obtained^{4,7,4,8} and efforts have been made to explain the time dependent behaviour of real glass electrodes^{4,9-5,1}. Some of the recent mechanistic studies of glass electrodes in the transient state and the steady state are collected in *Table 2*.

Table 2. Selected mechanistic studies of glass membrane electrodes

Technique	System	Reference
³ H, ²⁴ Na, ⁸² Br tracers	Silicate glasses	52
⁴² K, ²⁴ Na tracers	Hydrated glasses	1
Flame photometry and spectrophotometry	Surface films on glasses	53
I.R. spectroscopy	NH ₄ ⁺ -glass interaction	54
Current-voltage curves	Silicate glasses	55
Impedance measurements	Commercial glass electrodes	56, 57, 58
Coulometry	Na ⁺ , K ⁺ , Ag ⁺ in glasses	52, 55, 59
Conductance measurements	Silicate glasses	60
Transport number determinations	Glass membranes	61
Double layer measurements	Cations on glasses	62
Concentration jump studies	Na ⁺ , K ⁺ , Ca ²⁺ , Sr ²⁺ on glass electrodes	63
Diffusion studies	Microporous membranes	64

The response time of glass electrodes is of considerable practical importance. While a relatively slow response time may be tolerable for laboratory potentiometric measurements in solutions at equilibrium, for automatic titrations and continuous analysis a fast response is desirable. Also, if the electrode is to be employed successfully in measuring reaction kinetics, the response time must be fast in comparison with the reaction rate. We have measured the response times of several glass electrodes using a rapid-mixing flowing stream to obtain a step change in ion activity^{6,3}. Typically the electrode potential reached a limiting value following a change in principal counter-ion activity in a time of the order of 10 to 100 milliseconds.

Both the steady state and dynamic properties of a glass membrane electrode should be predictable from a detailed knowledge of the mechanism of

electrode response. It is useful to consider each property of the electrode as its electrical analogue and to represent the entire membrane electrode as an equivalent electrical circuit. Buck⁵⁷ has proposed an equivalent circuit for a glass membrane with a hydrolyzed surface film. In this model the surface film is represented as a finite transmission line and the glass membrane as a parallel array of resistance, double layer capacitance, and Warburg diffusional impedance. Measurements of the impedance of glass membranes⁵⁸ supported this model. The finite transmission line representing a finite diffusion across the surface film reduced to a pure resistance at high and low frequencies. After subtraction of the high frequency series resistance, the impedance at high frequencies showed equal real and imaginary components, resembling a Warburg impedance with a 45° phase angle⁶⁵.

In our own studies⁵⁶ we found the locus of the complex impedance of general cation electrodes to be a distorted arc of a circle having a centre below the real axis, similar to that reported for liquid ion exchange membranes¹⁶. Impedance loci for the pH and sodium electrodes also showed this behaviour at high frequencies, but at lower frequencies there appeared a second distorted circular arc which was most pronounced for the pH glass. This low frequency series impedance corresponds to the presence of a nonionic hydrolyzed surface film on the glass, which was not present to an appreciable extent on the monovalent cation glass.

The transient response time of a membrane electrode may be defined as the time required for the cell potential to reach a constant value following a step change in activity of the principal counter-ion on one side of the membrane, assuming a complete absence of any potential change associated with the reference electrode. It has been shown⁴⁶ that a constant cell potential is reached as soon as a steady state is established at the membrane-solution interface. Therefore, the response time of the electrode will be determined by the kinetics of the ion exchange reaction at the interface and by transport processes occurring within the membrane.

Impedance measurements have shown that the equivalent circuit of a glass membrane in the absence of a surface film is a resistance in parallel with a nonlinear space charge capacitance. The theory of charge transfer reactions at metallic electrodes interprets such a resistance as the polarization resistance from which the exchange current can be calculated and, hence, the kinetic parameters⁶⁶.

For an ion exchange reaction at a membrane permeable to the exchanging ions, this resistance, in fact, represents the sum of two resistances in series, one related to the kinetics of the ion exchange reaction and the second representing the mobility of the counter-ions in the membrane. Where the glass membrane is coated by a surface-hydrolyzed film, the equivalent circuit has, in addition, a series Warburg diffusional impedance shunted by a resistance. It is surprising, perhaps, that under an applied electric field the counter-ions show any diffusion at all as they are the major charge carrier present in solution. The large resistance in parallel with the Warburg impedance is interpreted as representing the effect of electromigration through 'pores' in the surface film.

The results of current step measurements of potential-time curves are compatible with the equivalent circuit model obtained by impedance

measurements. In the absence of a hydrolyzed surface film, a parallel R.C. charging curve is obtained which deviates from an exponential growth curve due to dispersion of the double layer capacitance. Electrodes having surface films also show this response at short times, while over a period of seconds concentration polarization within the film is observed. For electrodes without surface films, the time required for the potential to change from the zero current to the constant current steady state will also be equal to the response time of the electrode—i.e. less than 20 milliseconds. The potential-time curve on application of a current step will be different from the potential-time curve obtained by an activity step because in the former, charging of the nonlinear double layer capacitance is involved. In the presence of a surface film it would seem that the response time should be limited by diffusion of ions through the film and it is widely held that old glass electrodes are sluggish in response. Attempts at the direct measurement of electrode response times do not support this view. The mechanism of ion transport across the film cannot be said to be well understood. Clearly, the film is porous and it may be that under vigorous stirring conditions mass transport is not diffusion limited.

For a complete understanding of the time dependence of electrode potentials it is essential that measurements be made of both the kinetics of the ion exchange processes at the membrane interface and of the mobilities of ions within the membrane. It is apparent that distinction between these two cannot be made by steady state measurements. The use of pulse perturbations could lead to measurements of kinetic data of the ion exchange processes, if a more exact description of the membrane double layer capacity can be obtained.

CRYSTAL MEMBRANE ELECTRODES

Among the more significant advances in potentiometry in recent years has been the development of ion electrodes using inorganic crystalline materials in membranes. An outstanding example is the fluoride selective electrode, developed by Frant and Ross⁶⁷, based on lanthanum fluoride as membrane material. Recently, many other electrodes responsive to various anions and cations have been introduced; generally speaking the composition of the membranes has become increasingly complex with the introduction of matrix components, binders, etc. The properties of solid membrane electrodes are analytically attractive. Their sensitivity is limited in pure dilute solutions primarily by the low solubility product of the membrane salt. Selectivities can be extremely favourable; thus hydroxide ions represent the only significant interference for the fluoride electrode. The electrodes are compatible with organic solvents and are mechanically robust.

The mechanisms of response of solid state electrodes are not as well understood as those of glass or liquid membrane electrodes. It is appealing to apply the ion exchange theory⁷ of electrode operation directly to the solid state membrane case. Thus, Buck⁶⁸ has presented such a theory assuming rapid, reversible ion exchange at the membrane interfaces and mobile defects within the membrane crystal. While it is at least highly probable that these are necessary conditions for the operation of a solid state ion selective

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membrane electrode, experimental evidence supporting this view is not available for many solids now in use as membrane materials. Pungor⁶⁹ used radiochemical methods to investigate the exchange of iodide ions at silver iodide crystals dispersed in a silicone rubber matrix and reported that the exchange rate is fast. The ion exchange reaction depends upon ion adsorption at the membrane surface, a process which may be the primary step in the ion exchange mechanism. Some other studies of these electrode systems are summarized in *Table 3*.

Table 3. Some mechanistic studies of crystal membrane electrodes

Technique	System	Reference
Current-voltage curves	BaSO ₄ membranes	70
Impedance measurements	Commercial crystal electrodes	71
Coulometry	LaF ₃ membrane	72
Coulometry	Ag ₂ S membrane	73
Conductance measurements	BaSO ₄ membranes	74
Concentration jump	Precipitate membranes	75
Tracer methods	Precipitate membranes	76
Conductivity studies	LaF ₃ membranes	77
Theoretical study	Cyanide membrane	78
Theoretical study	Solid state membranes	68

The possibilities of interference in the potentiometric response by a mechanism of mixed crystal formation and by simple adsorption without mixed crystal formation have been recognized by Buck⁶⁸ and by Ross and Frant⁷⁹. An attempt has also been made to correlate the selectivity coefficients for interfering ions with the solubility products of their corresponding silver or sulphide salts for a mixed sulphide electrode⁸⁰. Although the results were somewhat scattered, it was apparent that a relationship existed, at least in the simpler cases. Deviations were attributed to uncertainty in solubility product data and to the operation of other mechanistic effects. A critical study of selectivities for solid state electrodes, comparable to those carried out on anion selective liquid membrane electrodes⁸¹, would be of value to an understanding of solid state membrane response and a tabulation has recently been made⁶.

The requirement that the membrane must be electrically conducting can be met in theory by ion transport, by electronic conduction, or by a mixture of both. Experimental studies of conductivities in solids have most frequently been made at high temperatures⁸²⁻⁸⁵ near the crystal melting point where intrinsic conductivities can be observed. At lower temperatures, the extrinsic conductivity region corresponds to the motion of crystal defects introduced by impurities. The extrinsic conductivity may be very much greater than that which would be observed for a pure crystal at the same temperature⁸⁶. In silver halide crystals, the intrinsic conductivity is due to mobility of both silver ions⁸⁷⁻⁸⁹ and electrons⁹⁰. Silver sulphide also exhibits mixed conductivity; in the low temperature form, ionic conduction by migration of Ag⁺ may be a considerable fraction of the total, whereas above 177°C electronic conduction predominates^{91, 92}. The conductivity of lanthanum fluoride over

the temperature range 27–727°C is 10^{-7} ohm $^{-1}$ cm $^{-1}$ at the lowest temperature; the main contribution to the conductivity was thought to be migration of the fluoride anion⁷⁷.

The electrical properties of crystalline solids depend to a large extent upon the manner in which the solid was formed and on the amount and nature of the impurities present. It is not surprising, therefore, that differences are observed between electrodes with the same membrane material when these are obtained from different manufacturers. In some cases, e.g. silver chloride membranes, good agreement has been found for values of the equivalent circuit components, but generally this is not so. It has been possible to classify crystalline membrane electrodes based on their behaviour as electrical circuit elements. The following categories have been found: (1) LaF₃, (2) AgCl, (3) AgBr, AgI, Ag₂S, PbS/Ag₂S, CdS/Ag₂S, (4) CuS/Ag₂S. Commercial halide electrodes actually contain silver sulphide, but the electrical properties are largely determined by the silver halide.

The equivalent circuit of lanthanum fluoride membranes is unique in that it contains two frequency variable impedances in series, the second of which is attributed to a surface film on the electrode. This film is probably lanthanum hydroxide since it is known that hydroxide is a major interference in the operation of the electrode. It should be noted, however, that this film is rather different from those observed on glass membranes. Ion transport across a hydrolyzed glass film under an applied electric field is thought to occur by a diffusional process through the film and by electromigration through pores in the film. The film on lanthanum fluoride membranes exhibits a space charge capacitance and the ion transport is by electromigration of fluoride ions, the same as that in the bulk of the membrane.

The equivalent circuit of silver chloride membranes is identical to that of LaF₃ membranes but without the film impedance. For both types of membranes the resistance is interpreted as representing ion transport across the membrane cell and its presence implies exchange of fluoride ions at the lanthanum fluoride–solution interface and of chloride ions at the silver chloride–solution interface.

Electrodes in the third category have equivalent circuits where this resistance is absent. In this case there is no net ion transport across the membrane cell and, under an applied electric field, charges build up on either side of the membrane–solution interfaces⁹³ producing a capacitive effect. Reasons for ion-blocking at the interfaces include the absence of an ion-exchange reaction (ionic conduction within the membrane) or the absence of a charge transfer reaction (electronic conduction in the membrane). These effects, together with the possibility of significant charge carrier recombination in the membrane, increase the complexity of a quantitative treatment. The frequency dependence of the impedance does not correspond to either of the simple limiting cases described by Johnson⁹³. It must be concluded that coupling between the membrane and solutions is capacitive for this type of electrode. Thus, when a constant current is passed through the cell, a continuous change in cell potential would be observed. Under potentiometric conditions, the current drawn by most electrometer circuits ($\sim 10^{-12}$ A) produces a potential drift which is very much smaller than the minimum potential change usually considered significant in ion electrode

measurements. Very little can be said about the fourth category, e.g. the cupric ion electrode, except that the capacitative effects appear to be very large. Further study of this electrode system is needed and should include consideration of oxidation state mixtures within apparently stoichiometric membranes.

THE TIME SCALE PROBLEM

Since primary emphasis has been given, perhaps quite properly, to understanding membrane processes at steady-state or equilibrium, the whole area of time dependent phenomena is still poorly understood. This area includes such subproblems as:

(i) The transient potential response of electrodes to rapid changes of the solution environment. Both glass and liquid membrane electrodes display potential peaks, slowing or acceleration of response in the presence of diverse ions, and transient selectivity to ions with little or no equilibrium selectivity. These observed^{75,94,95} phenomena are not necessarily inconsistent with present mechanistic views but they have not been adequately rationalized by the commonly held models.

(ii) Some electrode response times seem to be extraordinarily rapid if they are to be accounted for by traditional ion transport models. Response times corresponding to linear signal velocities of 300 miles per hour (about that of the nerve impulse in living systems) are not uncommon.

In view of the known diffusion coefficients of ions in glasses, liquids, and other media—even under the influence of concentration or potential gradients—it appears that the rate of information transport (i.e. the measured signal) sometimes exceeds likely ion transport rates in thick membranes if one assumes conventional transport models. Similarly, for neutral carriers (e.g. valinomycin) in liquid membranes the carrier loading and unloading kinetics also seem to be much too fast for any one carrier to transport an ion from one interface of the electrode membrane to the other. Indeed, the observed response times of valinomycin electrodes (some of which are up to 2 mm thick) would require the carrier to be a remarkably effective transport catalyst—much more so than might be intuitively expected from our knowledge of the bulk and configuration of the valinomycin molecule. Could it be that there is some kind of relay organization or conductive bonding within the electrode membrane?

In crystal membrane electrodes of the mixed crystal type it is also hard to see how all the multiple equilibria taking place at the crystal-solution interface could operate quickly enough to produce the observed rapid response times. Some of the newer mixed crystal membranes are essentially equivalent to classical electrodes of the 'third' kind and, moreover, employ extremely insoluble matrices. The equilibrium concentrations of some of the participating ionic species, when calculated by classical means from solubility and complex formation data, are so low that less than one ion per sample volume appears to be enough to satisfy the stoichiometric relationships. This clearly cannot be so and shows that even the equilibrium model, to say nothing of the associated kinetic aspects, is rather inadequate to describe the actual situation.

(iii) Both glass and liquid membrane electrodes are usually designed to produce a self-cleaning action. In the case of glass electrodes this is achieved by the slow dissolution of the outer portions of the hydrated glass layer. The layer is simultaneously replenished by the hydration of dry glass deeper in the membrane so that the thickness of the hydrated layer is maintained at some roughly constant steady-state value. In liquid membrane electrodes, the physical design is arranged so as to encourage a slow flow of the membrane liquid out of the electrode by adjusting the relative liquid levels or pressurizing the electrode. This prevents the entry of sample into the electrode and minimizes contamination.

Both cases allow a rate of flow of membrane material quite comparable to the uptake of ions from samples having very low concentration levels. Since it is exactly the very outer layers of the membranes, where the 'action' is thought to occur, that are being lost, it is a little hard to see how rapid response times are being obtained and why equilibrium response is not much more concentration dependent. Yet the facts clearly show that both glass and liquid membrane electrodes function very well under these circumstances; it must be some facet of our model that is at fault.

THE PROBLEM OF COUPLING MECHANISMS

It is easy enough to see how ionic processes in solution can be coupled to ion transport steps inside a liquid membrane electrode even though the details of these various steps are not yet fully known. One can also visualize, albeit less clearly, how ion transport is coupled to ion selectivity in such systems. When the liquid membrane phase is used to coat a platinum wire⁹⁶, perhaps with the aid of some binding material, we are at a loss, however, to explain how such an electrode could still be reversible and selective. How do the ionic processes in the liquid coating give rise to potential changes in the electronically conducting wire? What could be the coupling mechanism—does it involve holes in the coating, oxide films on the wire, impurities with redox properties? We do not know, but cannot ignore the fact that such improbable devices do function as ion-selective electrodes and, moreover, seem to retain much of the bulk selectivity properties of the coatings used.

A similar paradox arises in connection with glass electrodes. When the inner solution and reference element of a glass electrode bulb is replaced by liquid mercury or, even, the inner glass surface is vacuum coated with a platinum film, the resulting system still functions as a glass membrane electrode with practically no changes in sensitivity, selectivity, or dynamic properties. Are there redox processes occurring at the metal-glass interface to couple the cation transport in the glass membrane with electronic conduction in the metal? Further study is needed.

It is well known that the hydrated surface film on glass electrodes facilitates ion exchange of the solution-electrode interface and, also, ion movement in the glass. At some plane in the three dimensional structure of the glass electrode, however, there is another interface between the hydrated layer and the dry glass. What causes the high surface resistance⁹⁷?

Consider a pH glass electrode consisting of silicon oxide, sodium oxide, and calcium oxide. From coulometric experiments⁵² it is known that

charge transport in the dry glass portion of such an electrode is entirely by conduction of the metal cation of lowest charge, e.g. the sodium ion. The hydrated glass layer, on the other hand, has ion exchange and mobility properties which greatly favour the hydrogen (or hydronium) ion over the sodium ion—this is why we have a good pH electrode. Yet, when tracer experiments⁵² using tritium are carried out on such an electrode, it becomes quite clear that the hydrogen ion is not transported across the membrane even at elevated temperatures and high applied voltages. What then is happening at the inner hydrated layer–dry glass interface? Is electroneutrality maintained? Is there a build-up of space charge? Just how are the several processes in the hydrated and dry glass layers coupled so as to maintain selectivity for hydrogen over sodium? In good pH electrodes the selectivity ratio favours hydrogen over sodium by a factor of 10^{11} or more; yet the inner and thickest portion of the glass membrane is entirely loaded with sodium.

RECONCILIATION OF MECHANISMS WITH FACT

In the ion electrode field, as in other areas of science, experimental observations must represent reality, provided, of course, that proper precautions have been taken and adequate confirmation is available. Mechanisms must be seen as hypotheses subject to adjustment and continuing refinement. Comprehensive critical reviews, as those of Buck⁹⁸, Läger⁹⁹, and Koryta¹⁰⁰, are most effective in focusing attention on the major contemporary issues.

Why, then, study mechanisms at all? Entirely aside from the personal pleasures to be derived from such studies, mechanisms and pre-mechanisms have the important function of guiding and organizing thought, of pointing up fruitful areas of practical research missed by purely empirical studies, and, most important, of rationalizing and systematizing diverse observations into a coherent point of view. The rapid development of ion electrodes has seen a constant interplay of empirical investigation and mechanistic refinement with one or the other leading at different points in time. It can safely be said, however, that this research field will not achieve a truly scientific basis until a further reconciliation of mechanistic models and experimental observations has taken place.

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