Equilibrium Potentials of Membrane Electrodes

glass electrode/pH

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ABSTRACT A simple thermodynamic theory of the equilibrium potentials of membrane electrodes is formulated and applied to the glass electrode for measurement of pH. The new formulation assumes the selective adsorption or binding of specific ions on the surface of the membrane which may or may not be permeable to the ion, and includes the conventional derivation based on reversible ion transport across membranes as a special case. To test the theory, a platinum wire was coated with a mixture of stearic acid and methyl-tri-n-octyl-ammonium stearate. When this coated electrode was immersed in aqueous phosphate solution, its potential was found to be a linear function of pH from pH 2 to 12 with a slope equal to the theoretical value of 59.0 mV per pH unit at 24°C.

Since its modest debut in the form of a glass electrode early this century (1, 2), the ion-selective membrane electrode has gradually risen to become one of the most important analytical tools in chemical as well as biomedical science and technology. Contemporary theories of ion-selective membrane electrodes often involve quantitative treatment of charge and matter transport based on an assumed molecular mechanism. Although these kinetic treatments (3–5) and equivalent circuit models (6) have been very valuable in helping us to understand the characteristics of electrode response, they lack the generality of a thermodynamic theory of electrode potentials. As the variety of useful ion-selective membrane electrodes continues to multiply, so does the number of relevant molecular mechanisms. Consequently, it becomes increasingly difficult to develop a general kinetic treatment applicable to all ion-selective membrane electrodes. On the other hand, a purely thermodynamic theory is independent of the detailed molecular mechanism and, hence, should be more widely applicable.

The customary thermodynamic treatment of membrane potential is based upon the following condition of membrane equilibrium first deduced by Gibbs (7):

$$
\mu_{i1} + Z_iFV_i = \mu_{i2} + Z_iFV_2
$$  [1]

where $$\mu_{i1}$$ and $$\mu_{i2}$$ denote the chemical potentials of ionic species $$i$$ in phases 1 and 2, respectively, which are separated by a membrane permeable to ionic species $$i$$, $$Z_i$$ its charge number, $$F$$ the faraday, and $$V_i$$ and $$V_2$$ the electric potentials at the locations under consideration in phases 1 and 2, respectively. As an example, let us consider a glass electrode for measurement of pH. Gibbs emphasized in his epoch-making paper that Eq. 1 is not valid if the membrane is not permeable to ionic species $$i$$ (8). Therefore, before applying Eq. 1 to the system, we have to convince ourselves that the passage of $$n$$ faradays of electricity from phase 1 to phase 2 is accompanied by the transfer of $$n$$ mol of hydrogen ions across the glass membrane in the same direction. Experiments designed to detect the transfer of hydrogen ions across glass membranes with tritium-labeled solutions gave negative results (9). When the inner solution of a glass electrode is removed and replaced by mercury (10) or a vacuum-coated platinum film, the resulting assembly still functions as a glass electrode with no noticeable change in sensitivity and selectivity. These observations cast doubt on the assumed applicability of Eq. 1 to glass electrodes, and a reformulation of the theory of electrode potentials seems to be in order.

THEORY

In the present treatment, we shall remove the requirement of membrane permeability, and consider the equilibrium between ions $$i$$ in liquid solution and the same ions adsorbed or bound to the membrane surface in contact with the liquid solution. The equilibrium condition analogous to Eq. 1 and applicable to the present system may be written as

$$
\mu_{i1}^* + RT \ln(C_{i1}/C_{i1}^*) + Z_iFV_i = \mu_{i2}^* + RT \ln(C_{i2}/C_{i2}^*) + Z_iFV_2
$$  [2]

where $$\mu_{i1}^*$$ represents the standard chemical potential of the ionic species $$i$$ in liquid solution at concentration $$C_{i1}^*$$ chosen for its standard state, $$C_{i1}$$ the actual concentration and $$f_i$$ the activity coefficient of ionic species $$i$$ in the liquid solution, $$R$$ the gas constant, $$T$$ the absolute temperature, and $$V_i$$ the average specific potential of the bulk of the liquid phase. $$\mu_{i1}^*, C_{i1}, f_{i1},$$ and $$V_{i1}$$ represent similar quantities at the surface of the membrane in contact with the liquid solution.

Since the unsaturated valences on a membrane surface are best satisfied by ions compatible to the membrane structure, it is reasonable to assume that selectivity of the membrane resides in its strong preference to adsorb or bind such a specific ionic species $$i$$ at the interface, i.e.,

$$
\mu_{i1}^* - \mu_{i2}^* < \mu_{j1}^* - \mu_{j2}^*
$$  [3]

where $$j$$ represents any other ionic species in the liquid solution. Let us further assume that the surface layer of a good ion-selective membrane contains such a large number of ions $$i$$ and oppositely charged sites that a relatively very small change in $$C_{i1}$$ is sufficient to produce a change of several volts in the average surface potential $$V_m$$. Inasmuch as ordinary measurements with ion-selective electrodes seldom involve a potential difference greater than 1 volt, we may safely use the approximations $$C_{i1} \approx C_{i1}^*$$ and $$f_{i1} \approx 1$$, and attribute the changes in the electrochemical potential $$\mu_{i1}^* + Z_iFV_m$$ entirely to the changes in the average electric potential $$V_m$$ at the membrane surface due to the adsorption or desorption of ions $$i$$. With these approximations, Eq. 2 may be
written in the following dimensionless form:
\[
(Z_i F/RT)(V_m - V_i) = (\mu_{i1} - \mu_{i1m})/RT \\
+ \ln(C_{i1}/C_{i0}) + \ln f_{i1}
\]

When a glass electrode that selectively adsors or binds protons is dipped into an aqueous solution of variable hydrogen ion concentration [H\(^+\)] but maintained at constant ionic strength by a given supporting electrolyte, \(f_{i1}\) is \(\approx\) constant, and hence from Eq. 4,
\[
\Delta(V_m - V_i) = \frac{RT}{F \log e} \Delta \log [H^+]
\]

For measurement of [H\(^+\)], a reference electrode with potential independent of [H\(^+\)] is dipped in the same solution, and the resulting electrochemical cell is counterbalanced with an external electromotive force E so that no steady or transient current of either resistive or capacitive nature flows through the cell when the circuit is closed, i.e., the operational null-point is reached. Changing the hydrogen ion concentration from one value to another results in a corresponding change, \(\Delta E = \Delta(V_m - V_i)\), in the counterbalancing electromotive force. Consequently, if the first of the [H\(^+\)] values is known, the second can be computed from the experimental value of \(\Delta E\) by means of Eq. 5. Therefore, under these conditions a pH-meter with such a glass electrode measures \(\text{pH} = -\log [H^+]\) as originally defined by Sorensen (11).

The validity of Eq. 5 is based upon the assumption that only hydrogen ions are adsorbed or bound at the glass surface in contact with the aqueous solution and that for electrodes of macroscopic size the number of excess (or deficit) hydrogen ions adsorbed or bound, which determines the net charge of the surface, is negligibly small as compared to the total number of hydrogen ions present at the interface. \(\dagger\) However, at very low [H\(^+\)] the electric potential at the interface may be so low that other cations may also be adsorbed or bound to it and thereby increase \(V_m - V_i\). Similarly, at very high [H\(^+\)] the electric potential at the interface may be so high that anions from the solution may also be adsorbed to it by forming ion pairs in the surface layer and thereby decrease \(V_m - V_i\). In either case, Eq. 4 is no longer valid, and the pH values determined with certain glass electrodes under these extreme conditions may show positive deviation at very high pH and negative deviation at very low pH from those predicted by Eq. 5. The magnitude of these deviations will of course depend on the properties and concentrations of the other ions in solution, as well as the nature of the glass surface. These projections are entirely consistent with the well-known experimental results (12, 13).

The customary justification for using a kinetic approach to replace the thermodynamic treatment for ion-selective membrane electrodes is that the selectivity ratio determined by means of radioactive tracers is often quite different from that observed potentiometrically. For example, a typical K\(^{+}\)-selective glass electrode shows nearly a 100-fold ion-exchange preference of K\(^+\) over Na\(^+\), although it exhibits only a 10-fold potentiometric selectivity ratio of K\(^+\) over Na\(^+\). But this apparent discrepancy may be unreal, since potentiometric measurements determine the net adsorption of the positively charged ions (excluding cation exchange) in the surface layer of the membrane, whereas tracer measurements determine the total incorporation (net absorption plus cation exchange) of the radioactive ions into the surface layer and, possibly, some inner layers of the membrane. Therefore, the latter experimental value cannot be used as a measure of the former quantity required in a thermodynamic treatment.

It is also well known that a conventional pH-meter with a glass electrode gives pH readings in D\(_2\)O solutions (pD) that are consistently 0.4 pH unit (equivalent to 24 mV at \(25^\circ\)) lower than the corresponding pH readings in ordinary aqueous solutions (14). This observation had defied explanation in terms of the conventional theory of membrane equilibrium. It is extremely unlikely that the activity coefficient of D\(_2\)O\(^+\) in D\(_2\)O is 2.5-times as large as that of H\(_2\)O\(^+\) in H\(_2\)O or that the difference in the liquid junction potentials in equivalent D\(_2\)O and H\(_2\)O solutions is as large as 24 mV. In the present theory, this phenomenon can be accounted for in terms of the hydrogen isotope-effect on the equilibrium between the binding and dissociation of protons or deuterons at the glass surface. If the glass surfaces, in contact with H\(_2\)O and D\(_2\)O solutions, respectively, are considered as acids with intrinsic dissociation constants \(K_{HA}\) and \(K_{DA}\), we obtain from Eq 4 the following relationship by introducing Glasse and Long’s experimental conditions (14), \([D_2O^+] = [H_2O^+]\) and \(fDO = fHO^+\):
\[
\frac{F \log e}{RT} \{(V_m - V_i)_{D_2O} - (V_m - V_i)_{H_2O}\} \approx \log \frac{K_{HA}}{K_{DA}}
\]

Since the changes in pH and pD are given by changes in the measured value of \(-F(\log e)/(RT)\) \(V_m - V_i\), Eq. 6 may be written as
\[
\text{pH} - \text{pD} = \text{pK}_{DA} - \text{pK}_{HA}
\]

The experimental value of 0.40 \(\approx\) pK\(_{DA}\) - pK\(_{HA}\) at \(25^\circ\) suggests that the intrinsic dissociation constant of the glass surface corresponds to that of a moderately strong acid (15).

The present treatment includes the conventional thermodynamic derivation based on reversible ion transport across membranes as a special case. Since Eq. 4 is not dependent upon what happens inside or on the other side of the membrane, it should be applicable to a wide range of ion-selective membrane electrodes that may or may not be permeable to the specific ions (16, 17). Indeed, even a reversible metal electrode may be pictured as having a thin surface layer containing an excess or deficit of conducting electrons in electron-transfer equilibrium with specific ions and molecules in solution.

To include all reversible electrodes, Eq. 2 should be replaced by the following more general equilibrium relationship:
\[
\sum \{r_{s1}(\mu_{s1} + Z_{s1}FV_1) + r_{e1}(\mu_{e1} + Z_{e1}FV_m)\}
\]
\[
= \sum p \{r_{s1}(\mu_{s1} + Z_{s1}FV_1) + r_{e1}(\mu_{e1} + Z_{e1}FV_m)\}
\]
where the \(r\)s are stoichiometric numbers and the indices \(r\) and \(p\) refer to reactant and product species, respectively. For membrane electrodes that selectively bind ionic species

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\* Later definitions of pH in terms of hydrogen (single) ion activity, or hydrogen-ion concentration multiplied by a mean activity coefficient, or as measured after correction for estimated liquid junction potential, are ambiguous.

\† Haber and Klenmewicz (2) also recognized the need of such an approximation, but unfortunately they introduced the equivalent of such an approximation through the buffering action of silicic acid.
A_1 \text{ only, } A_{11} \leftrightarrow A_{1m}, \text{ we have } \mu_{11} + Z_{1}\text{FV}_1 = \mu_{1m} + Z_{1}\text{FV}_m. \text{ Therefore, } Z_{1}\text{F}(V_m - V_1) = \mu_{11} - \mu_{1m} = \mu_{11}' \text{ which is equivalent to Eq. 4. For a Zn-electrode in Zn}^{++} \text{ solution, } Zn^{++} + 2e^- (Zn) \leftrightarrow Zn, \text{ we have } \mu_{\text{Zn}^{++}} + 2\text{FV}_1 + 2\mu_{-}\text{e}(Zn) - 2\text{FV}_m = \mu_{Zn}. \text{ Therefore, } 2\text{F}(V_m - V_1) = \mu_{\text{Zn}^{++}} + 2\mu_{-}\text{e}(Zn) - \mu_{Zn} = \mu_{Zn}^{++} + 2\mu_{-}\text{e}(Zn) - \mu_{Zn}', \text{ which is a familiar result. For a Pt-electrode in Fe(CN)_6^{-3} + Fe(CN)_6^{-4} solution, } Fe(CN)_6^{-3} + e^- (Pt) \leftrightarrow Fe(CN)_6^{-4}, \text{ we have } \mu_{Fe(CN)_6^{-3}} - 3\text{FV}_1 + \mu_{-}\text{e}(Pt) - \text{FV}_m = \mu_{Fe(CN)_6^{-4}} = 4 \text{FV}_1. \text{ Therefore, } F(V_m - V_1) = \mu_{Fe(CN)_6^{-3}} + \mu_{-}\text{e}(Pt) - \mu_{Fe(CN)_6^{-4}}, \text{ which is also a familiar result. Such a formulation is more generally applicable than that based upon charge transport across phase boundaries. The new formulation is particularly advantageous in dealing with electrodes coated with nonmetallic material. It enables us to calculate } \Delta \text{E without knowing the actual charge relay mechanisms inside the nonmetallic layers, since there is no net flow of either charge or matter in any direction in a system at equilibrium. The observed equilibrium potentials of coated wire ion-selective electrodes (18), which are difficult to explain in terms of either the conventional thermodynamic theory or the contemporary kinetic theories, become readily understandable from the present point of view.}

**MATERIALS AND METHODS**

In order to test the present simple theory of electrode potentials, a membrane electrode was made by coating a platinum wire with an equimolar mixture of stearic acid and methyl-tri-n-octyl-ammonium stearate. The coating mixture was prepared in the following way: 25 ml of 0.2 M solution of methyl-tri-n-octyl-ammonium chloride (Aliquat 338, General Mills Chemicals) in 1-decanol was shaken with several pellets of potassium hydroxide (Fisher, Certified A.C.S.) in a stoppered flask at 22°. The resulting liquid suspension was centrifuged, and the supernatant was again shaken with KOH pellets for 2 hr. This procedure was repeated until no more KCl was formed when the supernatant was shaken with KOH pellets. 1 ml of the centrifuged supernatant was subsequently mixed with 2 ml of 0.2 M stearic acid (Fisher, Reagent Grade) solution in 1-decanol. A white precipitate was formed upon mixing and was dissolved by addition of 15 ml of 1-decanol and gently warming the resulting mixture.

The membrane-coated electrode was prepared by dipping a platinum wire (30-gauge) twice in the decanol solution, followed by drying in air at room temperature. The operation was repeated four times. The tip of the coated platinum wire was further covered with a tiny ball of paraffin. The coated electrode was soaked in distilled water for 30 min, then dipped in 0.01 M phosphoric acid (Baker Analyzed) and titrated with 1 M NaOH or KOH. A Beckman pHasar I pH Meter with a calomel electrode (filled with saturated KCl solution) as the reference electrode was used. The pH of the titration mixture was determined with a conventional glass electrode (Orion pH Electrode, model 91-01-00). The temperature of the titration mixture was kept constant at 24.3 ± 0.3°.

**RESULTS AND DISCUSSION**

Inasmuch as the coated electrode contains high concentrations of both –COOH and –COO– groups on its surface, we expect the relatively small changes in these concentrations throughout the titration process to be negligible and, hence, Eq. 5 should be applicable to the present data.