Electrodes and the Henderson Liquid Junction Potential Equation

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Electrical signals in our technology are carried by electrons, but electricity in our bodies, as in electrochemical applications, is carried by charged ions, often the hard spheres sodium, potassium, calcium and chloride. The flow of charged ions is measured by converting their charge to the charge flow of electrons using (almost always) the special properties of the compound silver chloride. AgCl is a metal that allows steady current flow from electrons to silver and chloride ions in solution and vice versa. The chemical reaction AgCl (metal) to the ions Ag^+ and Cl^-. The ions carry current in the ionic solution.

Simply putting a pair of AgCl wires (that is commercially available) into a solution seems to work, and is used by unsophisticated scientists, but is to be avoided.

1) Ag^+ ions are highly toxic to biological systems and produce strange effects on ion channels.
2) The chemical reaction depends on the difference in free energy of reactants and products and so depends on the free energy of chloride ions in water. This free energy has an electrical component, an ideal chemical component (RT log_e C) and an excess component. Thus, the electrons in the wire measure the electrical component, the ideal component, and the excess component as well. What is desired is a measurement of only the electrical component. The concentration of chloride is measured other ways and the excess component is a serious nuisance since its value depends on ALL the components of the system (NOT just chloride) and proteins present and all sorts of things.
3) Thus, an arrangement is used in which the AgCl wire is kept in a constant environment namely a 3 molar KCl solution. The silver ion soon saturates this solution and potentials are found to be stable to less than 10^{-3} volts, which is fine. (The experimental scale is determined by RT/F i.e., kT/e which is 25 x 10^{-3} volt at room temperature.)
4) The KCl solution must be kept stable and brought into contact with the solution of interest. This is done usually by making a KCl bridge, which is a tube filled with a mixture of Agar (like jello) and 3M KCl. The agar greatly decreases bulk transport (but NOT to zero) and the 3M KCl is large enough that current flows of minutes or less duration do not change the concentration significantly

5) At the interface between the Agar bridge and the bulk solution, there is an electrodiffusion regime that creates a significant and variable electrical potential. This is often small (but not always!) because the diffusion coefficient for potassium and chloride are nearly the same.

6) An equation the Henderson Liquid Junction potential is used (as if it were true, which it is not!!!) to calculate this potential and correct for it in an enormous number of papers, since say 1905.

7) The equation was derived by integrating the PNP equations from a boundary condition of 3M KCl to a boundary condition of XX solution (XX is whatever we are interested in) with the electrical potential at the boundaries being an output of the integrated system of equations.

8) The PNP equations can be integrated exactly if the TOTAL concentration of all IDEAL components (excess free energies are assumed to be zero) is assumed to vary linearly with x. This is easy to verify and we (following I do not know how many others) have a paper on it as well.[2]

9) The Henderson equation is derived assuming that the INDIVIDUAL concentrations of EACH species varies linearly with x. This is inconsistent with the Poisson equation and the error in the assumption is not evaluated.

10) What should be done is to integrate the PNP equations that include a description of nonideal properties (finite size effects producing excess chemical potential).

11) The work of Compton's lab (I know of [3, 4, 9-11]) documents the common experience that over long time scales (hours) something different, most likely convection through the agar bridge, changes things a lot.

12) Thus in a SEPARATE investigation the PNP treatment should be extended to include hydrodynamic effects using for example the EnVarA treatment [5-8].

13) The goal is an adequately accurate approximate equation to replace the Henderson equation and (if that is not possible) an easily executed numerical code that can be made available widely through (perhaps and for example) the services of Peter Barry [1] see JPCalcW Home Page i.e., http://web.med.unsw.edu.au/phbsoft/default.htm

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