Comprehensive Treatise of Electrochemistry

10 Bioelectrochemistry

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Volume 10
Bioelectrochemistry

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Preface to Comprehensive Treatise of Electrochemistry

Electrochemistry is one of the oldest defined areas in physical science, and there was a time, less than 50 years ago, when one saw "Institute of Electrochemistry and Physical Chemistry" in the chemistry buildings of European universities. But after early brilliant developments in electrode processes at the beginning of the twentieth century and in solution chemistry during the 1930s, electrochemistry fell into a period of decline which lasted for several decades. Electrochemical systems were too complex for the theoretical concepts of the quantum theory. They were too little understood at a phenomenological level to allow the ubiquity in application in so many fields to be comprehended.

However, a new growth began faintly in the late 1940s, and clearly in the 1950s. This growth was exemplified by the formation in 1949 of what is now called The International Society for Electrochemistry. The usefulness of electrochemistry as a basis for understanding conservation was the focal point in the founding of this Society. Another very important event was the choice by NASA in 1958 of fuel cells to provide the auxiliary power for space vehicles.

With the new era of diminishing usefulness of the fossil fuels upon us, the role of electrochemical technology is widened (energy storage, conversion, enhanced attention to conservation, direct use of electricity from nuclear–solar plants, finding materials which interface well with hydrogen). This strong new interest is not only in the technological applications of electrochemistry. Quantum chemists have taken an interest in redox processes. Organic chemists are interested in situations where the energy of electrons is as easily controlled as it is at electrodes. Some biological processes are now seen in electrodic terms, with electron transfer to and from materials which would earlier have been considered to be insulators.

It is now time for a comprehensive treatise to look at the whole field of electrochemistry.

The present treatise was conceived in 1974, and the earliest invitations to authors for contributions were made in 1975. The completion of the early volumes has been delayed by various factors.

There has been no attempt to make each article emphasize the most recent situation at the expense of an overall statement of the modern view. This treatise is not a collection of articles from *Recent Advances in Electrochemistry* or *Modern Aspects of Electrochemistry*. It is an attempt at making a mature statement about the present position in the vast area of what is best looked at as a new interdisciplinary field.

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Preface to Volume 10

The Comprehensive Treatise of Electrochemistry is a presentation of the various frontiers of electrochemical knowledge; however, there is no doubt that of all the areas of electrochemistry, the electrochemical application to biology is the one in which the frontier seems to be the longest and most exciting.

The seminal contribution to this area was the suggestion by Albert Szent-Gyorgyi in 1949 that electronic conductivity could occur in proteins. Prior to this time the idea that in biological ("non-conducting") substances electrons could travel, transfer, and even form pd's at interfaces would have been inconceivable. The linking of the high efficiency of biological energy conversion with a fuel cell concept of biological cells, and the experimental establishment of electronic conductivity in proteins in 1969 have opened areas of great significance in terms of molecular biology. Indeed, at present (1985) some of these considerations seem to reach out toward aspects of the cancer problem.

There is much else in bioelectrochemistry apart from these modern developments; in particular, there is the vast area associated with the names of Hodgkin and Huxley and the subject of electrophysiology, seen as an application of the Nernst-Planck equation.

The application of electrical concepts to biological phenomena is surely one of the more exciting in all science and the tenth volume of the Comprehensive Treatise of Electrochemistry is the most detailed description yet made of that field.

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The Origin of Electrical Potential in Biological Systems

S. OHKI

Electrical potential of biological systems orginates from various sources such as the existence of free ions in the biological systems, ionized molecular groups or electrical polarization of biomolecules, and various forms of assembly of biomolecules possessing such ionized molecular groups or electrically polarized or polarizable molecular groups. Another source of electrical potential may come from the occurrence of electron-transfer reactions in certain biochemical reaction systems. In certain biological systems, chemoelectrical, mechanoelectrical, and thermoelectrical coupling processes may produce a special type of electrical potential. Nonpolar molecules may exert electrical forces on each other by way of instantaneously fluctuating electrical polarization within the molecules.

Here, we would like to review systematically the electrical potentials which originate from, first, individual molecular events, then, molecular assemblies as biointerfaces, followed by discussion of the potential differences across biological membranes, and lastly, interaction forces acting between two cells.

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1. Electrical Potential of Biomolecules

1.1. Electrostatic Potential

1.1.1. Electrostatic Potential Due to Electric Charges

Let us consider an electrical potential at a point in a space where electric charges are distributed as point charges in a uniform dielectric medium. The electrical potential at a point in the space is expressed by:

$$\psi = \sum_{j=1} \frac{q_j}{\varepsilon r_j} \quad \text{(C.G.S. unit)} \tag{1}$$

where q_j is the jth point charge, r_j the distance between the jth point charge and the point being considered, and ε the dielectric constant of the medium.

In an aqueous solution containing positive and negative ions, however, the electroneutrality condition must prevail and the average of the total charge over any large region of such an electrolyte solution is zero:

$$\rho = \sum_j q_j = \sum_j eZ_j n_j = 0 \tag{2}$$

where e is the electronic unit charge, and Z_j and n_j are the valency and the number density of the jth ionic species, respectively. Therefore, the average electric potential over any large region of such an electrolyte solution is constant.

In a local region, however, taken around a particular ion as center, there is an unequal distribution of the surrounding ions, owing to electrostatic forces. A simple electrostatic example is the situation where the space charge, ρ, is distributed with spherical symmetry about a center, so that ρ is a function of r (distance from the center ion) only.

Now, consider a region where a spherical ion of radius b and charge Ze is at its center, and this charge Ze is considered to be distributed uniformly over the surface of the ion. The electrical potential function of the central ion can be designated ψ. It may be expressed as:

$$\psi = \psi_K + \psi_i \tag{3}$$

where ψ_K is the potential due directly to the central ion K under consideration and ψ_i is the potential due to the ion atmosphere.[1] Then, the concentration of the jth species near the central ion is given by the Boltzmann distribution equation:

$$n_j = n_j^0 e^{-Z_j e\psi/kT} \tag{4}$$

and the total charge per unit volume will be:

$$\rho = \sum_{j=1} n_j Z_j e = e \sum_{j=1} Z_j n_j^0 e^{-Z_j e\psi/kT} \tag{5}$$

where n_j^0 is the number density of the jth species at an infinite distance from the central ion K.

Now, the Poisson equation relates the potential function ψ to the charge density:

$$\nabla^2\psi = -\frac{4\pi}{\varepsilon}\rho \tag{6}$$

where the symbol ∇^2 is equivalent to the Laplacian operator, Δ.

From Eqs. (5) and (6), we obtain:

$$\nabla^2\psi = -\frac{4\pi e}{\varepsilon}\sum_{j=1} Z_j n_j^0\, e^{-Z_j e\psi/kT} \tag{7}$$

This equation is known as the Poisson–Boltzmann equation. By solving this equation, we may know the potential distribution and the ion distribution around the ion concerned. The Debye–Hückel solution is based on the approximation of the exponential in Eq..(7) by taking the leading terms (the first two terms) in the series expansion and applying the electroneutrality condition for bulk ionic solution ($\sum_{j=1} Z_j n_j^0 = 0$):

$$\nabla^2\psi = \varkappa^2\psi \tag{8}$$

where $\varkappa^2 = (4\pi e^2/\varepsilon kT)\sum_{j=1} Z_j^2 n_j^0$. Thus, the Debye–Hückel equation [Eq. (8)] is a good approximation for the Poisson–Boltzmann equation [Eq. (7)] when $e\psi/kT \ll 1$. Since the surface potentials of many biological membranes have magnitudes comparable to $kT/e = 25.6$ mV (25°C), the Debye–Hückel approximation may not necessarily be a good expression for the analysis of the surface electrical phenomena in such systems. The quantity $\varkappa$ is called the Debye constant and its inverse, $1/\varkappa$, corresponds to the effective thickness of the ionic atmosphere around the ion concerned.

In order to determine ψ_i, the potential at the surface of an ion due to the presence of the surrounding ion atmosphere, we consider the following model of the system. We treat the ions as conducting spheres, and assume that the distance of closest approach of any two ions is a (see Figure 1). For distance
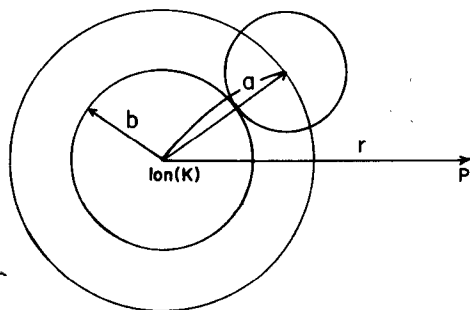

Figure 1. The central ion K of radius b and the collision diameter a which represents the distance of closest approach between the centers of two ions.

greater than *a*, we assume that the forces between ions are purely electrostatic. On the average the neighboring ions will be distributed around the central ion K with spherical symmetry. It is assumed that the charge of each surrounding ion, as if it were a point charge, is located at the center of each ion. Then, in the region between $r = b$ and $r = a$, there is no charge. In the region of $r > a$, we treat the medium as continuous; a space charge at any point is expressed as that in its corresponding volume element of the body having a continuous space charge determined by the concentrations of the various ions, and the dielectric constant ε in the region $r > a$ is constant.

In the region between $r = b$ and $r = a$, since there is no charge, ψ must be a solution of Laplace's equation:

$$\nabla^2 \psi = 0 \qquad (9)$$

After solution of the equation with the aid of Gauss's law, ψ is expressed by:

$$\psi = \frac{Ze}{\varepsilon r} + A \qquad (b < r < a) \qquad (10)$$

where A is a constant.

In the region $(r > a)$ where Poisson's equation holds [Eq. (7)], the Debye–Hückel approximation [Eq. (8)] yields:

$$\psi = \frac{B e^{-\kappa r}}{r} \qquad (r > a) \qquad (11)$$

Since the electric intensity, $\partial\psi/\partial r$, and the potential ψ are continuous functions of *r* throughout the region $(r > b)$, at the surface $r = a$ we can equate the values of ψ and $\partial\psi/\partial r$ given by Eqs. (10) and (11).

$$\frac{Ze}{\varepsilon a} + A = \frac{B e^{-\kappa a}}{a}$$
$$B = \frac{Ze \, e^{\kappa a}}{\varepsilon(1 + \kappa a)} \qquad (12)$$

In the outer region $(r > a)$, the electrical potential is

$$\psi = \frac{Ze}{\varepsilon r} \left[\frac{e^{-\kappa(r-a)}}{1 + a\kappa} \right] \qquad (r > a) \qquad (13)$$

In the above expression, $[e^{-\kappa(r-a)}/(1 + a\kappa)]$ corresponds to the contribution of the ion atmosphere to the potential. This can be compared with the expression $\psi = Ze/\varepsilon r$ which holds in the absence of the ion atmosphere. The actual potential is always less than the latter.

In the inner region $b < r < a$, the electrical potential is given by:

$$\psi = \frac{Ze}{\varepsilon r} - \frac{Ze}{\varepsilon} \left(\frac{\kappa}{1 + \kappa a} \right) \qquad (b < r < a) \qquad (14)$$