Diffusion Polarization at Lipid Bilayer Membranes

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Summary. Expressions are derived for the decrease of the conductivity of lipid bilayer membranes caused by diffusion polarization in the aqueous solutions near the membrane. It is assumed that after a sudden change in the voltage or current, the reestablishment of the stationary state within the membrane is fast as compared to the change of ion concentration in the solutions. The time course of the diffusion polarization, then, can be calculated for experiments where either the voltage or the current are controlled. Criteria are given to distinguish diffusion polarization from other relaxation processes, and several limiting cases of experimental interest are discussed.

1. Introduction

Diffusion polarization is a well-known phenomenon in electrode kinetics (for a detailed reference see Vetter, 1961). It is observed when the ion transport in the solutions to or from the electrode is limited by diffusion. As a consequence, an ion exhaustion or enrichment layer will form near the electrode, and the electrical resistance of the electrode/solution system will increase with time. The same effects have to be expected in the ion transport through membranes. The diffusion polarization in the solutions affects the membrane conductivity and it is necessary to take it into account in order to determine membrane parameters.

In this paper we derive expressions for these effects. We restrict ourselves to lipid bilayer membranes where, in recent experiments with highly fat soluble ions, very pronounced diffusion polarization has been detected (Le Blanc, 1969; Liberman, Topoly, and Silberstein, 1970) and a mathematical description of the magnitude and time course has become desirable. The surface of the electrodes can always be made large as compared to the area of the lipid bilayer membrane. Therefore, the current density at the electrodes will be much smaller than that at the membrane and we have to deal with diffusion polarization at the membrane alone. The assumptions made in the calculations are stated and discussed in chapter 2. The most severe one implies that the concentration changes in the solutions caused by diffusion polarization are slow as compared to relaxation processes within the membrane. The validity of this approximation will be proved by estimating the different relaxation times involved in the ion transport through lipid bilayer membranes. It can be shown that in many cases, diffusion in the solutions is the slowest process so that the current decay for long times is then caused by diffusion polarization in the solutions alone.

The solution of the diffusion equation in the aqueous phases depends on the boundary conditions at the membrane/solution interfaces. These conditions differ whether in the experiment the voltage or current across the membrane is
controlled. Therefore, we will discuss in the chapters 3 and 4 the potentiostatic and galvanostatic cases separately. In both cases expressions for the time dependence of the diffusion polarization can be derived. When the ion partition coefficient at the membrane/solution interfaces is increased indefinitely, all results reduce to the formulas known from electrode kinetics.

2. General Description of the Model

A membrane of thickness \( d \) is interposed between two aqueous phases of identical composition and we want to calculate the time dependence of voltage and current due to diffusion polarization effects in the aqueous phases. In order to simplify the mathematical treatment, we introduce the following assumptions:

I. Only one ion species of valence \( z \) is soluble in the membrane.

II. In the solutions, the total ion concentration is sufficiently high so that the electrical potential is constant in these phases.

III. The reestablishment of the stationary state within the membrane is fast compared with the change of concentration in the aqueous phases caused by diffusion polarization.

IV. The electric field strength in the membrane is constant.

V. There is no convection in the solutions, i.e. the thickness of the diffusion layers is infinite.

Assumption I is valid for experiments in which the charge carrier is a highly lipid-soluble ion, such as the tetraphenylborate anion (Liberman and Topaly, 1969). Assumption II states that the ions in the aqueous phases are transported by diffusion alone. It is not a severe restriction, because at high ion concentrations in the solutions the drop of the electrical potential in the aqueous phases can be neglected. Assumption III implies that the diffusion time \( \tau_s \) in the solutions is large compared to the diffusion time \( \tau_m \) within the membrane and the relaxation time \( \tau_b \) for the ion transport across the barriers at the membrane/solution interfaces. For a thickness \( \delta = 0.1 \text{ mm} \) of the unstirred diffusion layer in the solutions (Vetter, 1961, § 60) and a diffusion coefficient \( D = 10^{-6} \text{ cm}^2/\text{sec} \) in the aqueous phases, it is \( \tau_s = \delta^2/2D = 50 \text{ sec} \). Within the membrane, the diffusion time \( \tau_m = (d/2)^2/2D_m \) is much smaller because the thickness of lipid bilayer membranes is \( d = 70 \text{ Å} \) and the value of the diffusion coefficient in the membrane will lie in the range \( D_m = 10^{-6} - 10^{-12} \text{ cm}^2/\text{sec} \). The magnitude of the relaxation time \( \tau_b \) for the ion transport across the membrane/solution interfaces has been estimated in the appendix A. For activation energies less than 15 kcal/Mol (0.65 eV), we concluded \( \tau_b \leq 10 \text{ msec} \). Therefore, the inequality \( \tau_s \gg \tau_m, \tau_b \) holds for all realistic values of diffusion coefficients and activation energies. This means that for times \( t \gg \tau_m, \tau_b \), diffusion polarization in the solutions is the only effect which can cause a further increase in the resistance of the membrane/solution system. As the concentration changes in the membrane are fast as compared to those in the solutions, the membrane always is in a quasistationary state and we can use the relation

\[
\frac{\partial C}{\partial t} = \frac{\partial J}{\partial x} = 0 ; \quad -\frac{d}{2} < x < \frac{d}{2}
\]  

(1)

\((x: \text{coordinate normal to the membrane surfaces})\) for the current density \( J \) and the ion concentration \( C \) within the membrane at any time \( t \).