The Electrical Conductance of Semipermeable Membranes

Dear Sir:

In the November 1965 issue of this *Journal* the formal analysis by Dr. L. J. Bruner of the equilibrium and steady state of a membrane-solution system contains two assumptions which are physically inadmissible. The following comments will be confined to the equilibrium analysis:

The first assumption appears as an assertion concerning the boundary conditions at the membrane-solution interface (*Biophysic. J.*, 1965, **5**, 879), namely, the concentration of a permeant ion is a continuous function of position despite a discontinuity in the dielectric constant. This assumption cannot be justified in view of a basic *experimental* fact: in general the concentration of an ionic species depends on the structure of the solvent phase—as a rule, the concentration increases with the dielectric constant. (In the case of a single electrolyte the asymmetry in the concentration is expressed as a ratio or "partition coefficient.") In the language of thermodynamics this behavior is reflected in the dependence of the standard state on the nature of the solvent phase. Thus while the electrochemical potential of an ionic species is a constant throughout a phase, it differs from one phase to another by a constant, the difference in the standard states. Accordingly, the total electrochemical potential is continuous, but the concentration is not continuous. The electrical state in such a system has been treated by Verwey and Niessen (*Phil. Mag.*, 1939, **28**, 435) by means of the Poisson-Boltzmann equation; see also "The Theory of the Stability of Lyophobic Colloids," (Verwey and Overbeek pp. 34 to 37 and 40 to 50, Amsterdam, Elsevier Publishing Company, 1948). This analysis has been extended to include a finite surface charge density by Verwey, (*Koninklijke Nederlandse Akademie* van *Wetenschappen* Vol. L111, No. 3, 1950, 3. (A more complete treatment must include perturbations in the concentration profiles at the interface due to the Gibbs adsorption law.)

The second inadmissible assumption pertains to the "special case" of "unipolar" conduction which is defined as the case in which "permeant ions of only one valence state are present" (*Biophysic. J.*, 1965, **5**, 887). (In the second paper the results are given for unipolar conduction of positive ions.) Since by statement (*c*) on page 868 the author considers fixed charges to be absent, the fundamental error here follows from the fact that within the membrane phase ("region II") it is utterly impossible for permeant ions of only one sign to exist. Indeed in the membrane both positive and negative permeant species must be present at equal total concentration with asymmetry in the concentrations (space charge) gradually developing near the interfact at II and at III. In fact, even throughout the solutions containing impermeant ions ("region I" and "region III") positive and negative permeant species must be present; i.e., counterions will predominate but *coions* must be present at some finite concentration.

It need hardly be emphasized that with these incorrect assumptions the predictions for the steady state of current flow must also be in error.

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