Breakdown of a Stationary Solution to the Nernst–Planck–Poisson Equations

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This report shows an oscillatory instability, at sufficiently high voltage, of a representative steady solution to equations describing the passage of current through an unstirred layer of electrolyte adjacent to an ideal cation exchange membrane. This instability may be the harbinger of further " turbulent-like " transitions that correspond to observed unsteadiness at high voltages.

In prototypical electrodialysis, water to be desalinated flows between two parallel membranes that ideally permit the passage, respectively, solely of anions and cations. An electric field is oriented perpendicularly to the membranes in such a way as to drive the positive and negative ions toward the appropriate ion-exchange membrane. In some circumstances this arrangement provides the basis of a practical method of desalination, and modifications have recently been suggested that may make electrodialysis more practical [see ref. (1) for example].

From considering such a prototypical arrangement some questions of electrochemical importance arise. One fundamental question stems from the observation that the voltage against current (V, C) curve tends to level off as voltage increases, and then to resume its upward climb. Until recently the levelling off was attributed to depletion of solution in layers adjacent to the membranes with the interface salt concentration virtually approaching zero, and the renewed " overlimiting " climb was ascribed to the splitting of water molecules. There is preliminary evidence [2] that the expected pH changes do not occur, and an alternative explanation has been advanced,[3] based on a breakdown in electroneutrality. The present investigation is an extension of the analysis in ref. (3).

Another challenging phenomenon is the marked unsteadiness in the current measurements at high voltages. It has been suggested that convection causes the unsteadiness,[4] but evidence against this explanation appears in experiments where unsteadiness is observed even when the liquid is confined to the small cells of a filter.[3]

In this paper we shall exhibit an oscillatory instability, at sufficiently high voltages, of a representative steady solution to basic equations of electrodialysis. In our view,

this instability makes it likely that a similar instability (albeit one that is much harder to calculate) lies at the root of the observed unsteadiness we have mentioned.

Electrodialysis is governed by equations of diffusion type, but such equations have been shown (if their nonlinearity is sufficiently strong) to generate diffusive instabilities [5, 6] or dissipative structures [7] that are analogous to more familiar spatio-temporal structures of fluid flows. Extrapolating from these findings, we suggest that there may be a transition to more and more complicated unsteady electrochemical fields as the voltage is raised that is analogous to the transition to turbulence in fluid mechanics.

An earlier investigation [3] of the "overlimiting" climb in the (V, C) curve used as a model the passage of electric current through an unstirred layer of 1,1 valent electrolyte (like salt) adjacent to an ideal cation exchange membrane. The governing equations were taken to be the one dimensional stationary Nernst–Planck–Poisson (NPP) equations

$$\frac{\partial}{\partial x}\left(\frac{\partial c_p}{\partial x}+(-1)^{p+1}c_p\frac{\partial \phi}{\partial x}\right)=0, \qquad p=1,2; \tag{1 a, b}$$

$$\varepsilon\frac{\partial^2\phi}{\partial x^2}=c_2-c_1, \tag{2}$$

with the plausible boundary conditions

$$c_p|_{x=0}=1, \quad p=1,2; \quad \phi|_{x=0}=0. \tag{3a, b}$$

$$c_1|_{x=1}=P; \quad \left(\frac{\partial c_2}{\partial x}-c_2\frac{\partial \phi}{\partial x}\right)\Big|_{x=1}=0; \quad \phi|_{x=1}=-v. \tag{4a-c}$$

Here c_1 and c_2 are dimensionless concentrations of cations and anions respectively, ϕ is the dimensionless electric potential, and x is the dimensionless coordinate normal to the membrane planes. $x=0$ corresponds to the outer boundary of the unstirred layer where the ion concentrations and the electric potential are given, while $x=1$ corresponds to the membrane–solution interface. The problem contains three dimensionless parameters: ε is the squared ratio of equilibrium Debye radius to the thickness of the unstirred layer, P is the ratio of the fixed charge concentration within the membrane to the bulk salt concentration, and v is the ratio of the voltage applied across the unstirred layer to kT/e, where k is the Boltzmann constant, T is the absolute temperature and e is the charge of the proton.

The mathematical problem, eqn (1)-(4), has been shown [3] to have the following asymptotic solution (ϕ^0, c_1^0, c_2^0) for large v:

$$\phi^{0\prime}=-v+\mathcal{O}(1), \quad c_1^{0\prime}=v\frac{1-P}{1-e^v}(e^{vx}-1)+\mathcal{O}(1), \quad c_2^{0\prime}=-ve^{-vx}+\mathcal{O}(1), \tag{5a-c}$$

$$c_1^0=\frac{1-P}{1-e^v}(e^{vx}-1)+1, \quad c_2^0=e^{-vx}, \quad \phi^{0\prime\prime}=\frac{1}{\varepsilon}\left[e^{-vx}-\frac{1-P}{1-e^v}(e^{vx}-1)-1\right]. \tag{6a-c}$$

[Here $' = \mathrm{d}/\mathrm{d}x$. Note that because of the asymptotic nature of eqn (5) and (6) it is not true, for example, that $c_1^{0\prime}=(\mathrm{d}/\mathrm{d}x)c_1^0$].

Fig. 1 depicts a close correspondence between the asymptotic results and numerical solutions to eqn (1)-(4). Both numerical and analytical results show that development of a broadened region of bulk charge near the membrane leads to an inflection of the (V, C) curve that has the qualitative features of the observed "overlimiting" climb in current at high voltage.

In the present paper we report the conclusions of an investigation of the stability of eqn (5)-(6) regarded as a solution of the three-dimensional time-varying Nernst–Planck–Poisson equations

$$\text{div}\,[\text{grad}\,c_p+(-1)^{p+1}c_p\,\text{grad}\,\phi] = \frac{\partial c_p}{\partial t}, \quad p = 1, 2; \tag{7a, b}$$

$$\varepsilon\Delta\phi = c_2 - c_1 \tag{8}$$

with boundary conditions (3) and (4). Our investigation employed the standard normal modes approach wherein one looks for a solution of the form

$$c_p = c_p^0+\tilde{c}_p,\ p = 1,2;\ \phi = \phi^0+\tilde{\phi}; \tag{9a, b}$$

$$\tilde{c}_p = u_p(x)\exp[\mathrm{i}(\kappa_y y+\kappa_z z)+\sigma t],\ p = 1,2; \tag{10a, b}$$

$$\tilde{\phi} = \phi(x)\exp[\mathrm{i}(\kappa_y y+\kappa_z z)+\sigma t]. \tag{10c}$$

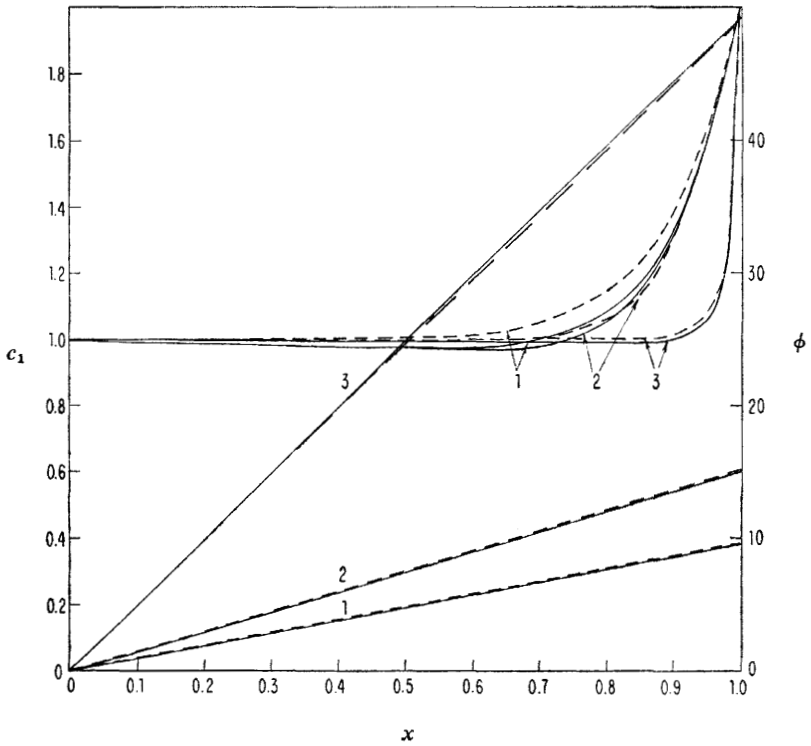

FIG. 1.—Dimensionless electrical potentials ϕ (straight lines starting at the origin) and cation concentration profiles c_1 as functions of fractional distances x in the unstirred layer. Dashed lines: asymptotic solutions, eqn (5) and (6). Solid lines: numerical solutions of eqn (1)-(4). Curves marked 1, 2, 3 correspond respectively to $v = 9.7, 15, 49$ ($\varepsilon = 1$, $P = 2$).

Substituting eqn (9) into eqn (7) and (8) and linearizing eqn (7) and (8) with respect to $\tilde{c}_p$, $\tilde{\phi}$, one obtains, using eqn (10),

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}x^2}-\kappa^2\right)u_p+(-1)^{p+1}\left[c_p^{0\prime}\frac{\mathrm{d}\phi}{\mathrm{d}x}+\phi^{0\prime}\frac{\mathrm{d}u_p}{\mathrm{d}x}+\frac{c_p^0}{\varepsilon}(u_2-u_1)+\phi^{0\prime\prime}u_p\right] = \sigma u_p, \tag{11}$$

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}x^2}-\kappa^2\right)\phi = \frac{1}{\varepsilon}(u_2-u_1), \quad \kappa^2 \equiv \kappa_y^2+\kappa_z^2, \tag{12a, b}$$

with homogeneous boundary conditions

$$u_1(0) = u_2(0) = \phi(0) = 0, \tag{13a-c}$$

$$u_1(1) = \phi_1(1) = 0, \tag{14a, b}$$

$$\left(\frac{du_2}{dx} - c_2^0 \frac{d\phi}{dx} - u_2\phi^{0\prime}\right)\Big|_{x=1} = 0. \tag{15}$$

The problem eqn (11)-(15) was solved by one of the classical methods of linear stability theory. A fundamental set of solutions to eqn (11) and (12) was constructed numerically. Substitution of these solutions into the boundary conditions (13)-(15) leads to a set of homogeneous linear equations that will possess a nontrivial solution only if the determinant of coefficients vanishes. A search procedure was used to find those values of $\sigma \equiv \mathrm{Re}\sigma + i\mathrm{Im}\sigma$ that renders the determinant zero for a given set of parameter values v, ϕ, and P and a given " overall wavenumber " κ. Note that the set of eqn (11)-(15) is not selfadjoint, so that the u_p, ϕ, and σ are generally complex.

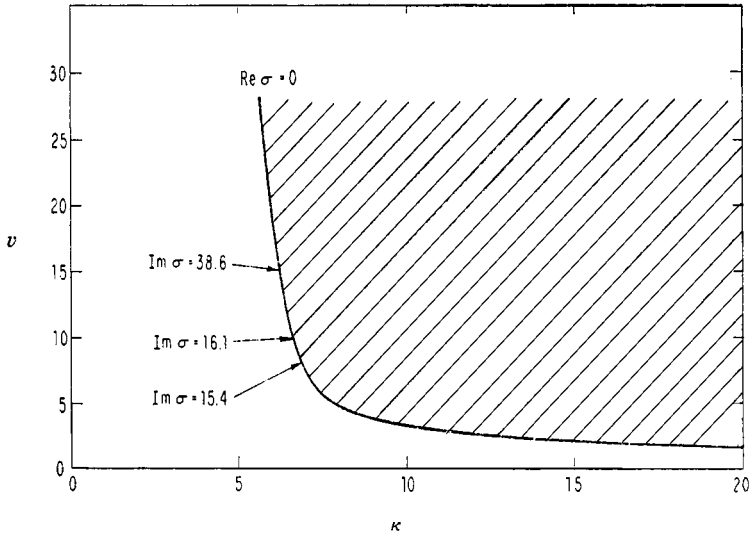

FIG. 2.—Neutral stability curve Re $\sigma = 0$ bounding the shaded region of instability in the (voltage, wavenumber) parameter plane. Values of Im σ are given for three points on the neutral curve.

All computations were carried out for the values $\varepsilon = 1$, $P = 2$. The results are summarized in fig. 2. Here we depict the neutral stability curve Re $\sigma = 0$ that bounds the shaded region of the (voltage, wavenumber) plane whose points correspond to a growth rate σ having a positive real part. Every point (v, κ) in the hatched instability region corresponds to a temporally growing disturbance to the basic solution of eqn (5)-(6) at the voltage v, with x- and y-wavenumbers κ_x and κ_y such that $\kappa_x^2 + \kappa_y^2 = \kappa^2$.

We find that $\sigma_i \equiv \mathrm{Im}\,\sigma \neq 0$ when $\sigma_r \equiv \mathrm{Re}\,\sigma = 0$ (see fig. 2). This means that just above the neutral curve, solutions are proportional to $\exp(\sigma_r r)\cos\sigma_i t$ or $\exp(\sigma_r t)\sin\sigma_i t$, σ_r small and positive, so that perturbations will begin to grow in an oscillatory manner (overstability).

The fact that the unstable region broadens as voltage is increased makes it likely that the instability we have found is not limited to the asymptotic solution of eqn (5)

and (6), but also will turn out to be a property of the appropriate exact solution to eqn (1)-(4) for typical experimental values of the parameters. Investigation of this matter would require considerable extension of the already lengthy calculations. Thus, we shall content ourselves at present with this demonstration that oscillatory instabilities can be a property of certain solutions to the NPP equations.

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