Field-Induced Dissociation at the Ion-Selective Membrane-Solution Interface

Sir:

The rate of dissociation of a weak electrolyte was shown by Onsager to be increased in strong electric fields, while the rate of recombination was unaffected.[1] The field effect is quite small; a field of 10^4 v./cm. increases the dissociation constant by but 1%. These considerations apply only to processes occurring in homogeneous systems and fields.

We have shown that at certain kinds of interfaces a modest field can affect the rate of *recombination* profoundly.

When a direct current is passed across a porous membrane interposed between neutral electrolytic solutions, significant changes in their pH can occur.[2] With ion-exchange membranes this effect may be enormously magnified. For example, across cation-exchange membranes the hydrogen ion transport number (t_{H^+}) increases with current until a critical current density I^* is reached and t_{H^+} attains 0.3-0.8. Gregor and Peterson[3] measured the boundary layer thickness δ and t_{H^+} independently with a cation-permeable membrane in solutions of potassium chloride at different, high rates of stirring and identified I^* (in equiv. cm.$^{-2}$ sec.$^{-1}$) as equal to $2Dc/\delta$, where D is the mean diffusion coefficient and c the bulk salt concentration.

A detailed analysis of the flux equations for the potassium (1), chloride (2), hydrogen (3), and hydroxide (4) ions employing the Nernst-Planck equation gives

$$-\frac{J_i}{D_i} = \frac{dc_i}{dx} + \frac{z_i \mathfrak{F} c_i}{RT}\frac{d\psi}{dx}$$

with D_i the diffusion coefficient, c_i the local concentration, z_i the valence, ψ the electrical potential, and J_i the mass flux density in equiv. cm.$^{-2}$ sec.$^{-1}$. With flat membranes, only the x-direction needs to be considered. At steady state, in the adjacent boundary layers $I = J_1 + J_3 - J_4$, $dJ_1/dx = 0$, and $J_2 = 0$; within the membrane J_4 is zero. Electroneutrality requires $c_1 + c_3 = \bar{c}$ (the capacity) in the membrane where the field is small; in the boundary layers where the field is large, considerations of the space charge give

$$d^2\psi/dx^2 = (4\Pi/\epsilon)(c_2 + c_4 - c_1 - c_3)$$

The equal rates of generation of hydrogen and hydroxide ions by dissociation or association or a consideration of constant current both lead to $dJ_3/dx = dJ_4/dx$. In solution phases the ordinary field-induced dissociation (Wien effect) must be included: $c_3c_4 = K_w F(d\psi/dx)$.[1] The equilibrium distribution of exchange ions is $c_3/c_1 = k_{13}\bar{c}_3/\bar{c}_1$, where the superscript bar refers to the membrane phase. For high currents, k_{13} approaches unity.

At the (left-hand) boundary where potassium ions enter the membrane from solution, the ionic atmosphere is inhomogeneous. Hydroxide ions can be present
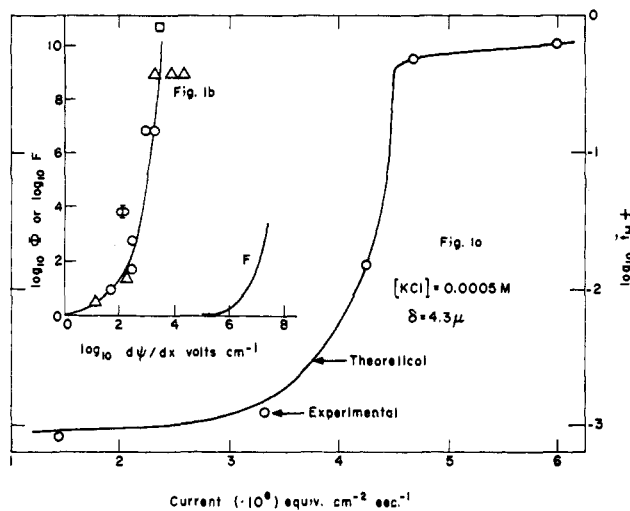

Figure 1.

only to the left of hydrogen ions in solution at this boundary; the membrane phase is a forbidden domain to mobile negative ions. Here, the field can act only to draw these hydrogen ions into the membrane and the hydroxide ions away from the membrane surface. Their rate of recombination is thereby decreased, with a resultant increase in the dissociation constant for water. This change in c_3c_4 is treated mathematically by introducing a step function $c_3c_4 = K_w\Phi(d\psi/dx) \cdot F(d\psi/dx) = K_{34}^*$ into the last step of the numerical integration process at the boundary. Then, knowing the boundary layer thickness and the bulk concentrations, one can compute $\bar{l}_3$ and K_{34}^* by fitting computed to experimental curves (Fig. 1a). At $I/I^* = 1.05$, at the interface this computation leads to $[H^+] = 2.0 \times 10^{-4}$ M, $[OH^-] = 5.1 \times 10^{-4}$ M, with $K_{34}^* = 1 \times 10^{-7}$. The computed field here is a modest 1076 v. cm.$^{-2}$, far below the ordinary Wien region. At this point $\Phi(d\psi/dx) = 1 \times 10^7$. Figure 1b shows the $\Phi(d\psi/dx)$ and $F(d\psi/dx)$ functions. The points were computed from experiments[3] performed in 0.0005 M (○), 0.005 M (△), and 0.05 M (□) potassium chloride solutions.

A semiquantitative, direct experimental verification of this effect was obtained by observation of the hydroxide ion concentration at the boundary (using indicators), the concentration of hydrogen ions in the membrane phase there (by direct analysis), and a consideration of the requisite fluxes. Further experimental and theoretical work on water and other weak electrolytes is in progress.

The implications of this effect are widespread. It offers a simple, experimental procedure for measuring the rates of rapid ionic reactions in solution and at interfaces, and for studying the role of water structure as envisioned by Frank[4] and by Eigen.[5] Many biological phenomena may embody this effect including the production of hydrochloric acid in the stomach,[6] changes in membrane permeability and structure, and the like.

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(4) H. S. Frank and W. Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957).

(5) M. Eigen, *Z. Physik Chem.* (Frankfurt), **1**, 176 (1954).

(6) W. S. Rehm, *Am. J. Physiol.*, **144**, 115 (1945).

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Polarography of Hemin. Evidence for a Two-Electron Transfer

Sir:

The nature of oxidation–reduction in hemoglobin-type systems has been reinvestigated by imaginative "model experiments" in recent years.[1] In this context, elucidation of the electron-transfer behavior of metalloporphyrin complexes is of considerable interest. The question whether the reduction of hemin to heme involves one or two electrons has been the subject of an important controversy. In a classical potentiometric study,[2] Conant, *et al.*, postulated that a dimeric
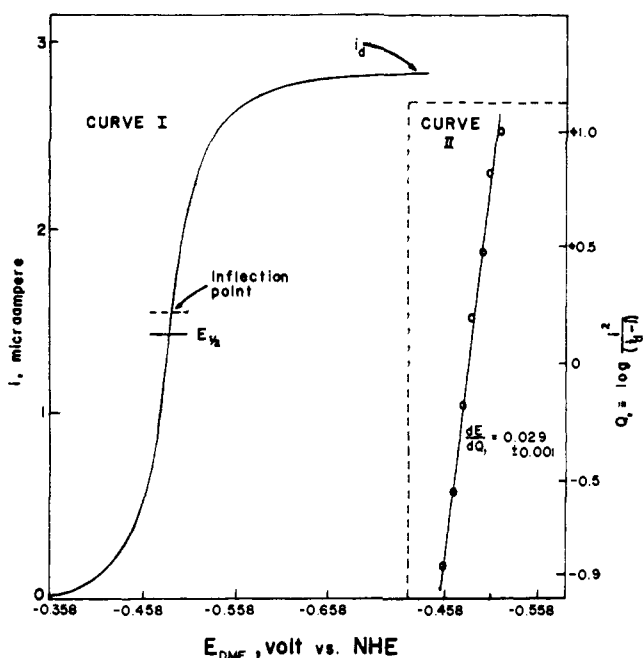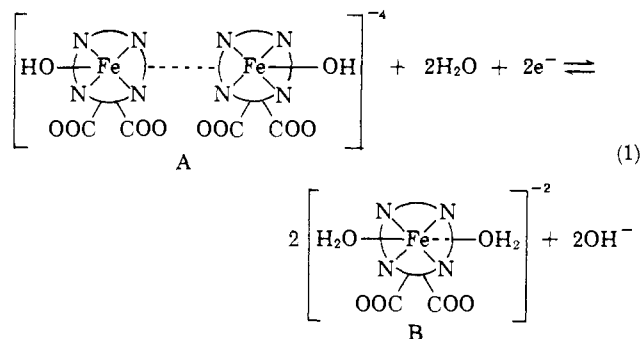

Fig. 1.—Polarography of 2.775 × 10⁻³ *M* hemin in 0.1 *M* aqueous KOH at 25°: curve I, current–voltage curve corrected for residual current and *iR* drop; curve II, wave analysis plot according to eq. 2.

hemin reactant yielded a monomeric heme product *via* a two-electron reduction. Later potentiometric investigations[3] by Barron appeared compatible with a one-electron transfer process in which the reactant as well as the product were monomeric. In contradistinction, spectrophotometric data reported by Shack and Clark[4] indicated that both were dimeric species. We have obtained conclusive evidence that the reduction of hemin chloride in 0.1 *M* aqueous potassium hydroxide proceeded at the dropping mercury electrode (d.m.e.) with "Nernstian reversibility" in accordance with the equation

(1) J. H. Wang, *J. Am. Chem. Soc.*, **80**, 3168 (1958).
(2) J. B. Conant, C. A. Alles, and C. O. Tongberg, *J. Biol. Chem.*, **79**, 89 (1928).
(3) E. S. Barron, *ibid.*, **121**, 285 (1937).
(4) J. Shack and W. M. Clark, *ibid.*, **171**, 143 (1947).

The electroreducible species A is a soluble ferric protoporphyrin chelate dimer. It functions as a two-electron acceptor yielding the monomeric *trans*-diaquoprotoporphyrin ferrate(II) B, which is also soluble under the prevailing experimental conditions. The formulation of A and B in eq. 1 is consistent with current knowledge of the chemistry of the prosthetic group of hemoglobin.[5]

A typical polarogram is illustrated in Fig. 1, curve I. The well-defined limiting current, i_d, varied linearly with the concentration of hemin in the bulk of the solution and was diffusion controlled (*i.e.*, proportional to the square root of the mercury pressure effective above the d.m.e.). A reversible polarogram corresponding to eq. 1, with currents controlled solely by rates of diffusion between the electrode surface and the bulk of the solution, is described by the "wave equation"[6]

$$E_{dme} = E° + \frac{\mu RT}{2\mathfrak{F}} \log \frac{f_A D_B}{f_B{}^2 D_A{}^{1/2} K_w{}^2} - \frac{\mu RT}{\mathfrak{F}} pH +$$
$$\frac{\mu RT}{2\mathfrak{F}} \log \frac{(i_d - i)}{i^2} \quad (2)$$

where μ (= 2.303) denotes the modulus which converts natural logarithms to their decadic counterparts, $E°$ is the standard potential of the heme–hemin couple, the subscripts refer to the chemical entities identified in eq. 1, the other symbols conform to the notation used by Kolthoff and Lingane,[7] and potentials are assigned in concordance with the Stockholm IUPAC convention. The analytic geometry of a current–voltage curve governed by eq. 2 has several distinctive features. While the plot is sigmoid, it is, however, unsymmetrical about the inflection point which does not coincide with the half-wave potential. These characteristics are indeed evident in the experimental polarogram shown in Fig. 1.

The last term in eq. 2 would have the form $(\mu RT/\mathfrak{F}) \cdot \log [(i_d - i)/i]$ or $(\mu RT/2\mathfrak{F}) \cdot \log [(i_d - i)/i]$, respectively, if the hemin and heme species involved in the electrode reaction were either both monomeric or both dimeric and Nernst control prevailed. Thus the linearity and slope of plots of the quantities $Q_1 \equiv \log [(i_d - i)/i^2]$ and $Q_2 \equiv \log [(i_d - i)/i]$ *vs.* E_{dme} may provide diagnostic criteria for differentiating between the Conant, Barron, and Shack reactions. The relevant wave analysis plot of Q_1 *vs.* E_{dme} is shown in Fig. 1, curve II. This has a reciprocal slope of 0.029 ±

(5) W. M. Clark, J. F. Taylor, T. H. Davies, and C. S. Vestling, *ibid.*, **135**, 543 (1940).
(6) Derived from the applicable Nernst equation; see G. Charlot, J. Badoz-Lambling, and B. Tremillon, "Electrochemical Reactions," Elsevier Publishing Co., New York, N. Y., 1962, p. 36.
(7) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1952, pp. 190 ff.