Coupled Electron-Proton Transfer Kinetics of Galvinol Attached to Self-Assembled Monolayers on an Electrode.

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Redox couples with coupled proton transfer are found frequently in biology. Important examples include quinones/hydroquinones, catechols/*o*-quinones, and the isoalloxazine ring system of flavins. Their relevance to biological electron transfer has resulted in extensive investigation on the kinetics of these systems at electrodes. A review of quinone/hydroquinones by Chambers illustrates the effort expended on just this particular class of redox couples.[1] Our interest is stimulated by the recent efforts to apply Marcus theory to coupled proton-electron transfer,[2] the importance of coupled proton-electron transfer in enzymes containing redox centers like the Fe-S clusters,[3] and the slow kinetics exhibited by dopamine and related catechol compounds during in-vivo analytical measurements.[4,5]

An extensive theoretical treatment of heterogeneous electron transfer of coupled electron-proton redox couples has been given by Laviron.[6-9] In that treatment, single electron and proton transfer steps are separate (which leads to a square scheme), proton transfer is assumed to be at equilibrium, and the transfer coefficient is assumed to be 0.5 independent of potential. We have rederived the expressions describing the kinetic behavior in order to include the potential dependence of the transfer coefficient predicted by Marcus Density-of-States theory.[10] The potential dependence of the rate constant is a function of the Marcus reorganization energy lambda. Two significant differences are noted with respect to the behavior predicted by Laviron. The path of electron transfer (the sequence of electron and proton transfer steps) is dependent on the overpotential η (= $E - E^{0'}$) as well as the pH, and the increase in rate constants with overpotential are not the same for the oxidation and reduction steps (in electrochemical terms, the apparent transfer coefficient differs from 0.5).

Galvinol exhibits a 1-electron, 1-proton oxidation to form the organic radical galvinoxyl.[11] Mixed self-assembled monolayers on gold are prepared using a galvinol with a 10-methylene alkanethiol tail and alkanethiols of equal length.[12] The thermodynamic and kinetic behavior of the galvinol/galvinoxyl system is examined by cyclic voltammetry over a wide range of scan rates in high ionic strength Brittain-Robinson buffers (pH 2 to pH 13). While some anomalies are observed, the overall behavior is consistent with the theory. The pH dependence of the formal potential yields a pK_a of galvinol of 12.8 (Fig. 1). Above pH 7, the dependence of the apparent standard rate constant on pH fits the theory; a limiting standard rate constant of 5600/s is obtained at high pH (Fig. 2). The cause for the deviation from theory at lower pH's is unknown. Asymmetry in cyclic voltammograms and Tafel plots is consistent with a potential-dependent transfer coefficient. However, the data are insufficient to extract the Marcus reorganization energy for galvinol.

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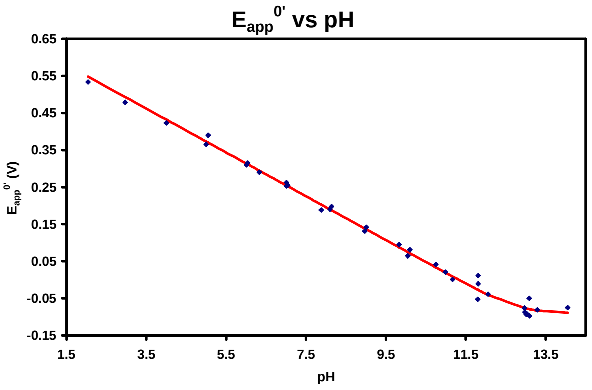

Fig. 1. Formal potential vs pH for galvinol redox centers.

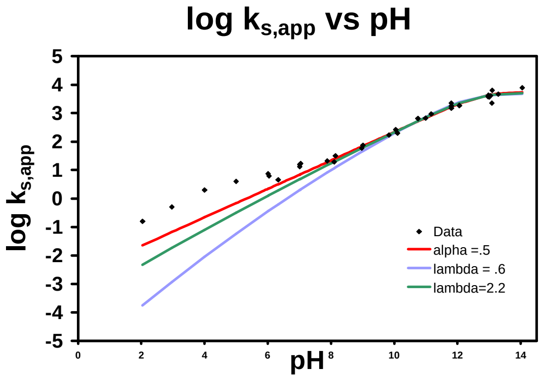

Fig. 2. Apparent standard rate constant vs pH for galvinol redox centers.