

Voltammetric reduction of hydrogen ion in solutions of polyprotic strong acids with and without supporting electrolyte ¹

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Abstract

Voltammetric reduction of strong polyprotic acids in solutions with excess and without supporting electrolyte was studied both theoretically and experimentally. A theoretical model based on the transport (diffusion and migration) equations and the electroneutrality principle was used to compute voltammograms by finite difference simulation under both steady state and transient conditions. Simulated voltammograms are compared with experimental reduction curves obtained at platinum microelectrodes without and with excess electrolyte for two strong polyprotic acids, sulfuric (H_2SO_4) and tungstosilicic ($\text{H}_4\text{W}_{12}\text{SiO}_{40}$) acids. Perchloric acid (HClO_4) was used as the reference for comparison. The experimental results agree well with the calculated voltammetric curves both without and with excess supporting electrolyte. The dependence of voltammetric response on the concentration of acids is also discussed. © 1997 Elsevier Science S.A.

Keywords: Transport model; Hydrogen ion; Polyprotic acid; Voltammetric reduction; Voltammogram simulation

1. Introduction

Reduction of hydrogen ion from solutions of strong and weak acids at platinum microelectrodes under steady state conditions results in a well defined transport-controlled wave [1–4]. The height of the wave is proportional to the concentration of hydrogen ion over a wide range of acid concentration, which makes this type of experiment useful for analytical monitoring of hydrogen ion concentration in a variety of systems. The concentration of hydrogen ion has been monitored near a large electrode during the oxidation of polyaniline films [5]. The steady state reduction of hydrogen ion has also been used for determination of acid concentration in buffered solutions [1], and for determination of acidity of fluid lubricants based on phosphate esters [6]. The plateau current of hydrogen ion reduction also depends on the rate of transport of hydrogen ion to the electrode. This feature has been used to study the transport of hydrogen ion in such complicated systems as colloids [7] and polyelectrolyte solutions [8–10], includ-

ing solutions of very low ionic strength, without added supporting electrolyte.

The transport of hydrogen ion in solutions without supporting electrolyte involves a significant contribution from electrical migration as predicted by theory [11–15]. For acids of the type H_nA , the ratio of the steady state currents obtained without and with excess supporting electrolyte depends on the charge of the anion and is predicted to be $(1 + 1/n)$, where n is the number of dissociated hydrogen ions [14]. This prediction has been confirmed by experimental results for steady state reduction of such acids as HClO_4 , H_2SO_4 and $\text{H}_4\text{W}_{12}\text{SiO}_{40}$ [1,6,16]. Also, the dependence of the limiting steady state current on the concentration of supporting electrolyte has been studied. The theoretical solution given by Oldham for the case of all monovalent ions present in the solution [14] has been extended for the other charges of anion associated with hydrogen ion and ions of supporting electrolyte [16]. The theoretical predictions have been confirmed by experiments performed for reduction of hydrogen ion in sulfuric acid and for reduction of metal cations in solutions of various metals salts [16].

The dependence of currents on the applied potential without supporting electrolyte has been analyzed theoretically by Oldham [14] and by Palys et al. [17]. Steady state voltammograms have been constructed, and wave parame-

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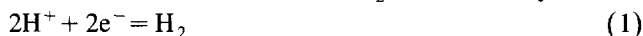
ters have been determined for the cases of the reduction of monovalent cation associated with anions of various charge [14]. This is the appropriate model for the reduction of hydrogen ion from the solutions of strong polyprotic acids. The analytical solution obtained by Oldham allows calculations only under pure steady state conditions. Additionally, the model assumes that the reaction is a reversible one-electron reduction to a neutral product, and that the diffusion coefficients of reactant and product are equal. In contrast, it has been reported, for the case of the charge-neutralization electrode reaction (uncharged product) under steady state conditions, that the difference in the diffusion coefficient values of species present in the solution does not influence significantly the ratio of limiting current without supporting electrolyte to diffusional current [17].

The first aim of this paper is to present a theoretical model and to simulate voltammograms for reduction of hydrogen cation from solutions of strong polyprotic acids under two limiting conditions, without and with excess supporting electrolyte. The model does not have the limitation of the steady state condition, and, additionally, it allows for different diffusion coefficient values for all species. The second objective is to compare voltammograms computed from the model with experimental voltammograms for reduction of hydrogen ion from polyprotic acid solutions. The behavior of di- and tetraprotic acids is compared with that of a monoprotic acid.

2. Theoretical development

2.1. Assumptions

The reduction of hydrogen ion at the electrode surface is assumed to have a 2:1 ($2\text{H}^+:\text{H}_2$) stoichiometry:



Additionally, under our conditions we assume that the electrode reaction is a reversible process. The electron transfer is fast, and the rate of the reaction is controlled only by the transport of the reactant. The possible adsorption of hydrogen ion at the electrode surface is neglected. The scope of these assumptions has already been discussed [18]. Under the present conditions the electrode potential is described by the Nernst equation:

$$E_{\text{H}^+/\text{H}_2} = E_{\text{H}^+/\text{H}_2}^{0,c} + \frac{RT}{2F} \ln \frac{(c_{\text{H}^+}^0)^2}{c_{\text{H}_2}^0} + \frac{RT}{2F} \ln \frac{(f_{\text{H}^+}^0)^2}{f_{\text{H}_2}^0} \quad (2)$$

The quantities $c_{\text{H}^+}^0$ and $c_{\text{H}_2}^0$ are the concentrations of H^+ and H_2 at the electrode surface respectively. The quantities $f_{\text{H}^+}^0$ and $f_{\text{H}_2}^0$ are the activity coefficients at the electrode surface for the H^+ and H_2 respectively. In the case of the solution without supporting electrolyte, the last term on the right hand side of Eq. (2) is approximately -2mV (for $2\text{mM H}_2\text{SO}_4$) at the wave foot and approaches zero for the currents close to the steady state current I_s . For the solution with excess supporting electrolyte (0.1M LiClO_4) the value of the last term is practi-

cally constant (the contribution of the acid ions is negligible) and equals -7.1mV . The reference potential used in our calculations is a hydrogen concentration normal potential (HCNP), $E_{\text{H}^+/\text{H}_2}^{0,c}$ [18]. This is the potential of the H^+/H_2 system that corresponds to unit concentration of both forms in solution. The HCNP reference potential differs from the standard hydrogen electrode (SHE) potential $E_{\text{H}^+/\text{H}_2}^0$ which is a mixed concentration–pressure potential. The difference between SHE and HCNP potentials is given by

$$E_{\text{H}^+/\text{H}_2}^{0,c} = E_{\text{H}^+/\text{H}_2}^0 + \frac{RT}{2F} \ln [c_{\text{H}_2}^0 (p_{\text{H}_2} = 101.325\text{kPa})] \quad (3)$$

where $c_{\text{H}_2}^0 = (p_{\text{H}_2} = 101.325\text{kPa})$ is the hydrogen concentration at the electrode surface and in the solution that results from a partial hydrogen pressure of 101.325kPa .

The reaction in Eq. (1) predicts a dependence of the half-wave potential on the concentration of hydrogen ion in the solution. This result will be discussed later.

The transport equations for all species and the local potential gradient are given in spherical coordinates by [19,20]

$$\frac{\partial c_k}{\partial t} = D_k \left[\frac{\partial^2 c_k}{\partial r^2} + \frac{2}{r} \frac{\partial c_k}{\partial r} + \frac{z_k F}{RT} \left(\frac{2c_k}{r} \frac{\partial \phi}{\partial r} + \frac{\partial c_k}{\partial r} \frac{\partial \phi}{\partial r} + c_k \frac{\partial^2 \phi}{\partial r^2} \right) \right] \quad (4)$$

$$\frac{\partial \phi}{\partial r} = \frac{-1}{\sum z_k^2 c_k D_k} \frac{RT}{F^2} \left(F \sum z_k D_k \frac{\partial c_k}{\partial r} + \frac{I}{2\pi r^2} \right) \quad (5)$$

where c_k , D_k and z_k are the local concentration, diffusion coefficient, and charge of the k th species respectively, and I is the current flowing in the cell.

2.2. Initial conditions

The initial conditions are given by the same expressions for the case of excess supporting electrolyte and for no supporting electrolyte for all spatial boxes:

$$c_{\text{H}_2}^i = 0 \quad c_{\text{H}^+}^i = nc \quad c_{\text{A}^{n-}}^i = c \quad \text{for } i \geq 1 \quad (6)$$

where c is the analytical concentration of the strong acid H_nA and the index i is a spatial box number.

The initial conditions for the last concentration box are identical with boundary conditions for this box.

2.3. Boundary conditions at the electrode surface with excess supporting electrolyte

The fluxes at the surface of the electrode of r^0 radius with excess supporting electrolyte are given by

$$J_{\text{H}^+}^0 = -D_{\text{H}^+} \left(\frac{\partial c_{\text{H}^+}}{\partial r} \right)^0 = \frac{-I}{2\pi (r^0)^2 F} \quad (7)$$

$$J_{\text{H}_2}^0 = -2D_{\text{H}_2} \left(\frac{\partial c_{\text{H}_2}}{\partial r} \right)^0 = \frac{I}{2\pi (r^0)^2 F} \quad (8)$$

$$J_{A^{n-}}^0 = -D_{A^{n-}} \left(\frac{\partial c_{A^{n-}}}{\partial r} \right)^0 = 0 \quad (9)$$

We sum Eqs. (7) and (8) and integrate by dr to obtain:

$$2D_{H_2}c_{H_2} + D_{H^+}c_{H^+} = D_{H^+}c_{H^+}^b \quad (10)$$

where $c_{H^+}^b$ is the bulk concentration (superscript b) of H^+ ion.

The sum of the products of diffusion coefficient, inverse stoichiometric number and concentration for H_2 and H^+ is constant as a function of the distance from the electrode. Therefore, Eq. (10) is valid for all spatial points. The specific form of Eq. (10) at the electrode surface (superscript 0) can be written as

$$2D_{H_2}c_{H_2}^0 + D_{H^+}c_{H^+}^0 = D_{H^+}c_{H^+}^b \quad (11)$$

From Eqs. (2) and (11) we can calculate the boundary conditions at the electrode surface. Then, using Eq. (4) we can calculate the transport of molecular hydrogen from the electrode. Consequently, from the calculated concentrations of H_2 and Eq. (10), we can calculate the concentration of H^+ in all concentration boxes.

2.4. Boundary conditions at the electrode surface without supporting electrolyte

Without supporting electrolyte, the fluxes at the electrode surface are given by

$$J_{H^+}^0 = -D_{H^+} \left[\left(\frac{\partial c_{H^+}}{\partial r} \right)^0 + \frac{c_{H^+}^0 F}{RT} \left(\frac{\partial \phi}{\partial r} \right)^0 \right] = \frac{-I}{2\pi(r^0)^2 F} \quad (12)$$

$$\left(\frac{\Delta \phi}{\Delta r} \right)^i = \frac{- \left\{ F \left[-nD_{A^{n-}} \left(\frac{c_{A^{n-}}^{i+1} - c_{A^{n-}}^{i-1}}{\Delta r^{i+1} + \Delta r^i} \right) + D_{H^+} \left(\frac{c_{H^+}^{i+1} - c_{H^+}^{i-1}}{\Delta r^{i+1} + \Delta r^i} \right) \right] + \frac{I}{2\pi(r^i)^2} \right\} RT}{(n^2 c_{A^{n-}}^i D_{A^{n-}} + c_{H^+}^i D_{H^+}) F^2} \quad (19)$$

where Δr^i and Δr^{i+1} are i th and $(i+1)$ th space increments respectively and r^i is the distance between the i th spatial box and the geometrical center of the spherical electrode.

We calculate a sum of results of multiplication of Eq. (19) by the corresponding spatial increment for the entire depletion layer. The assumption here is that the thickness of the depletion layer at the end of the experiment is given by $\delta = 2(\pi D_{H^+} t_t)^{1/2}$, where t_t is the total time of the experiment. Formally, the resistance between the electrodes should be calculated by summing up to infinity.

$$J_{A^{n-}}^0 = -D_{A^{n-}} \left[\left(\frac{\partial c_{A^{n-}}}{\partial r} \right)^0 - \frac{nc_{A^{n-}} F}{RT} \left(\frac{\partial \phi}{\partial r} \right)^0 \right] = 0 \quad (13)$$

The third equation, describing the flux of molecular (uncharged) hydrogen, is identical with Eq. (8).

With only two kinds of ion present in the solution, H^+ and A^{n-} , the condition of electroneutrality is satisfied by

$$c_{H^+} = nc_{A^{n-}} \quad (14)$$

Under the conditions employed, we can assume that electroneutrality is maintained at the electrode surface, since the size of the depletion layer is much larger than the size of the double layer [21]. Thus

$$c_{H^+}^0 = nc_{A^{n-}}^0 \quad (15)$$

Eq. (13) multiplied by the ratio $D_{H^+}/D_{A^{n-}}$ gives

$$-D_{H^+} \left[\left(\frac{\partial c_{A^{n-}}}{\partial r} \right)^0 - \frac{nc_{A^{n-}}^0 F}{RT} \left(\frac{\partial \phi}{\partial r} \right)^0 \right] = 0 \quad (16)$$

We sum Eqs. (8), (12) and (16), apply Eq. (14), and integrate the result by dr to obtain

$$D_{H^+}c_{A^{n-}} + D_{H^+}c_{H^+} + 2D_{H_2}c_{H_2} = D_{H^+}(n+1)c \quad (17)$$

At the electrode surface, Eq. (17) becomes

$$D_{H^+}c_{A^{n-}}^0 + D_{H^+}c_{H^+}^0 + 2D_{H_2}c_{H_2}^0 = D_{H^+}(n+1)c \quad (18)$$

Now, using Eqs. (2), (15) and (18), we calculate the boundary conditions at the electrode surface. The electrode potential is calculated using the method given by Jaworski et al. [22], with the equation for the potential gradient in differential form for the i th spatial box:

However, when the electrode process is advanced, the total resistance is more controlled by the layers next to the electrode surface and the summation can be limited. The total resistance \mathfrak{R}_i at the electrode surface is a sum of two resistances:

$$\mathfrak{R}_i = \mathfrak{R}_\delta + \mathfrak{R}_s \quad (20)$$

where \mathfrak{R}_δ is the resistance of the depletion layer and \mathfrak{R}_s the resistance of the bulk layer.

Using expressions from Ref. [22] and adapting them to our case of polyprotic strong acids, we can derive the

following expression for total resistance in partially discretized and partially integrated form:

$$\mathfrak{R}_t = \frac{-\sum_{i=0}^m \left(\frac{\Delta\phi}{\Delta r} \right)^i \Delta r^{i+1}}{I} + \frac{RT}{2\pi F^2} \left(\frac{-1}{r^\infty} + \frac{1}{r^0 + \delta} \right) \left(\frac{1}{n^2 D_{A^{n-}} c_{A^{n-}}^b + D_{H^+} c_{H^+}^b} \right) \quad (21)$$

where m is the number of spatial boxes. The value of m is determined by diffusion layer thickness as described in Section 3. Eq. (21) is equivalent to summation from the electrode surface to infinity.

The diffusion of the product H_2 from the electrode is calculated from the boundary conditions using Eq. (4), and then the concentrations of H^+ and A^{n-} in the diffusion layer are calculated from Eqs. (14) and (17).

This model can be applied to both steady state and transient conditions. The limitation here is that to assume electroneutrality the depletion layer must be thicker than the double layer [21], which is not a very stringent condition. The thickness of the double layer is approximately $1.5\kappa^{-1}$, where κ^{-1} is the Debye–Hückel length given by

$$\kappa^{-1} = \left(\varepsilon \varepsilon_0 k_B T / \sum n_k z_k^2 e_0^2 \right)^{1/2} \quad (22)$$

where n_k is the number of k th ions per volume unit and z_k is the charge of the k th ion, k_B is the Boltzmann constant, e_0 is the electron charge, ε_0 is the permittivity of the vacuum, ε is the dielectric constant. In aqueous solution of strong, univalent electrolyte, approximate κ^{-1} -values are 10 nm, 100 nm and 1 μ m for concentrations of 10^{-3} M, 10^{-5} M and 10^{-7} M respectively. This thickness diminishes significantly when the electrode potential departs from the potential of zero charge. Thus, under our conditions the double layer is not thicker than 10 nm, much thinner than the depletion layer, even for relatively short times of experiment (for 1 ms, the depletion layer is approximately 10 μ m thick).

3. Simulation

Simulations were performed by the finite difference method using unequal space intervals with $\Delta r^i = 1.02 \Delta r^{i-1}$. The number of time steps was 180 000 ($\Delta t = t_i / 180\,000$). The thickness of the first space interval equals $\Delta r^1 = (D_{H^+} \Delta t / 0.45)^{1/2}$. The number of spatial boxes m was obtained from the expression $\sum_{i=1}^m \Delta r^i \approx \delta$. The values of diffusion coefficients ($\times 10^5 \text{ cm}^2 \text{ s}^{-1}$) used in the calculations were $D(H_2) = 5.85$ [23], $D(H^+) = 9.34$ [24], and $D(SO_4^{2-}) = 1.08$ [24], $D(W_{12}SiO_{40}^{4-}) = 0.61$ [25], and $D(ClO_4^-) = 1.45$ [24] (infinite dilution, 25°C). Linear sweep voltammograms were calculated for sweep rate $v =$

20 mV s^{-1} and a hemispherical electrode of radius $r^0 = 2/\pi \times 5.5 \mu\text{m}$. Since the steady state current at a hemispherical microelectrode is $\pi/2$ times higher than at disc microelectrode of the same radius, the chosen radius of the electrode yields the value of the steady state limiting current corresponding to the experimental data, obtained with a disc microelectrode of radius of 5.5 μ m. The program was written in Turbo Pascal 6.0 and run on a 486 PC.

4. Experimental

Staircase voltammetry (SCV) with the potential step height ΔE of 1 mV and frequency f of 20 Hz was applied with a Model 273 potentiostat (EG&G PARC) connected with a Keithley Model 427 current amplifier and controlled by software via a 486 PC. The platinum working disc microelectrode of 5.5 μ m in radius (Project Ltd., Warsaw, Poland) was polished to mirror finish with 1 μ m diamond water-based paste (Buehler Ltd.). Subsequent renewals before voltammetric scanning were accomplished by polishing with 0.1 μ m diamond paste. The electrode was rinsed with a direct stream of water and dried with Kimwipes. The surface of the platinum disc was inspected with an inverted microscope (Leitz Wetzler, Germany) before using. Also, a platinum disc electrode of radius of 0.8 mm (Bioanalytical Systems Inc.) was used as a working electrode. The reference saturated calomel electrode (SCE) was separated from the cell by an electrolyte bridge filled with the same solution as that in the cell. A platinum wire served as a counter electrode. The experiments were performed in a jacketed cell (25°C) enclosed in an aluminum Faraday cage. Solutions were deoxygenated before voltammetric scans and blanketed during experiments with a stream of water-saturated argon.

All reagents were of analytical reagent purity and were used as-received. The following acids were used: perchloric (MCB Reagents), sulfuric (Fisher) and tungstosilicic (Fluka). Lithium perchlorate (Aldrich) served as supporting electrolyte. Ultrapure water (Milli-Q, Millipore Corp.) was employed in all rinsing and preparation of solutions. The concentration of acids was determined by conductimetric titration using a YSI Model 31 conductivity bridge (Yellow Springs Instrument Co.) against a sodium hydroxide solution which was standardized vs. potassium hydrogen phthalate in the same manner.

The reproducibility of all limiting currents was very good, both without and with excess supporting electrolyte, with relative standard deviation lower than 2.5%. However, the shape of voltammograms was not as reproducible. The shape of voltammetric waves depends strongly on the state of the electrode surface and is very sensitive to the quality of the polishing process. The variability in shape is more pronounced in solutions with excess electrolyte than without electrolyte. However, as demonstrated

below, proper attention to cleanliness and electrode preparation is rewarded with reversible voltammograms.

5. Results and discussion

Our first experiments were designed to test the assumption of Eq. (1) that the stoichiometry of reaction of reduction of hydrogen ion is 2:1. The electrode reaction



results in the dependence of the half-wave potential on the bulk concentration of the electroactive substrate Ox, c_{Ox}^b . The half-wave potential of the system for a general electrode reaction stoichiometry is given by Shuman [26] with correction [18] as

$$E_{1/2} = E^{0,c} - \left(\frac{RT}{nF} \right) \left[q \ln c_{\text{Ox}}^b (\gamma q/p) + (q-p) \ln \left(\frac{p-q}{p+q} \right) \right] \quad (24)$$

where

$$\gamma = \left(\frac{D_{\text{Ox}}}{D_{\text{Red}}} \right)^{1/2}$$

Under our conditions, $p = 2$, $n = 2$, $q = 1$, and $\gamma = 1.261$. Thus the half-wave potential for the reduction of hydrogen ion should depend on the concentration of H^+ according to

$$E_{1/2} = E^{0,c} - 0.116RT/F + (1.15RT/F) \log c_{\text{Ox}}^b \quad (25)$$

and the dependence of $E_{1/2}$ on the logarithm of the concentration of hydrogen ion in the solution should result in the linear equation

$$E_{1/2} = 29.5 \log c_{\text{Ox}}^b + (E^{0,c} - 2.98) / \text{mV} \quad (26)$$

We performed voltammetric measurements using a large platinum disc electrode in solutions of H_2SO_4 with LiClO_4 as supporting electrolyte. The concentration of acid was varied over the range 0.1–2 mM. Exemplary voltammograms are presented in Fig. 1. As one can see, the half-wave potential moves to more positive potential with increase in

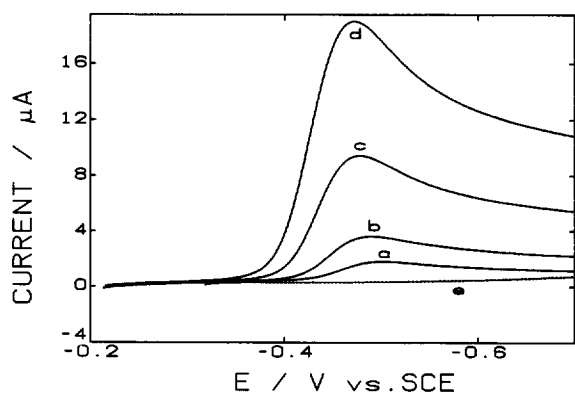


Fig. 1. Staircase voltammograms of reduction of H^+ from solutions of H_2SO_4 : (a) 0.13, (b) 0.26, (c) 0.65, (d) 1.3 mM; (e) background, 0.1 M LiClO_4 , Pt disc $r^0 = 0.8$ mm, $\Delta E = 1$ mV, $f = 20$ Hz.

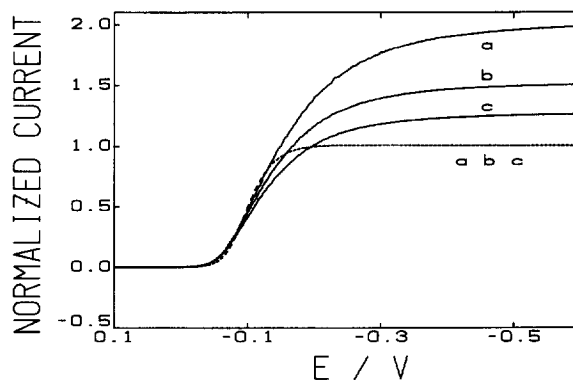


Fig. 2. Simulated voltammograms for reduction of (a) 1 mM HClO_4 , (b) 0.5 mM H_2SO_4 , (c) 0.25 mM $\text{H}_4\text{W}_{12}\text{SiO}_{40}$, without (—) and with (---) 100-fold excess supporting electrolyte. Disc electrode $r^0 = 5.5$ μm , $v = 20$ mV s^{-1} . Potentials referred vs. HCNP.

hydrogen ion concentration. Values of $E_{1/2}$ were calculated from the peak potential ($E_p - E_{1/2} = 1.109RT/nF$), assuming a two-electron, reversible process [27]. The dependence of $E_{1/2}$ on $\log c_{\text{H}^+}$ was found to be

$$E_{1/2} = 31.6 \log c_{\text{Ox}}^b + 37.1 / \text{mV} \quad (27)$$

with correlation coefficient 0.9997. As one can see, the slope of the experimental dependence, 31.6 mV, is only 7% higher than the predicted value. This agreement indicates that the diffusion-controlled reduction of H^+ at a platinum electrode can be treated with reasonable approximation as a two-electron process with the stoichiometry of Eq. (1).

5.1. Voltammetry

Simulations and experiments were performed under two limiting conditions, without and with excess supporting electrolyte. The concentration of supporting electrolyte was adjusted to 100-fold excess with respect to the concentration of hydrogen ion. Fig. 2 presents simulated voltammetric curves for reduction of the three acids, HClO_4 , H_2SO_4 and $\text{H}_4\text{W}_{12}\text{SiO}_{40}$, at a hemispherical electrode. This geometry was chosen because of the ease conferred by the one-dimensional description of the transport. As has been shown by Bruckenstein [28] and Oldham [29], the ohmic drop at microelectrodes under steady state conditions does not depend on the geometry of the electrode. Therefore, under our conditions, we can expect similar values of ohmic drop for both hemispherical and disc microelectrodes. The currents were normalized to the steady state current I_s controlled by pure diffusion of hydrogen ion, $I_s = 4Fc_{\text{H}^+}^b D_{\text{H}^+} r^0$ [30]. The concentration of hydrogen ion in solution was the same for all acids.

With excess supporting electrolyte the same concentration of H^+ results, of course, in the same voltammogram for all acids. In the absence of electrolyte, the voltammograms lose their symmetry, and the limiting current is reached at much more negative potential than with excess

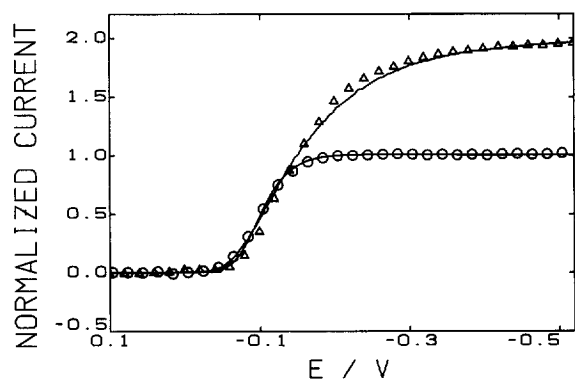


Fig. 3. Simulated (—) and experimental (○, △) voltammograms for reduction of H^+ in solution of 1 mM $HClO_4$ with 100-fold excess (○) supporting electrolyte ($LiClO_4$) and without electrolyte (△). Potentials referred vs. HCNP.

supporting electrolyte. The limiting normalized currents depend on the type of acid, and they equal 2.0, 1.5, and 1.25 for $HClO_4$, H_2SO_4 , and $H_4W_{12}SiO_{40}$ respectively. These ratios of limiting to diffusional current agree exactly with the theory given by Oldham [14], and with the previous experimental findings [1,3,6,16].

We compared the calculated voltammograms with experimental results obtained at the Pt microelectrode. From the experimental point of view, under our experimental conditions, 'no supporting electrolyte' corresponds to a concentration of adventitious univalent electrolyte of about $1 \mu M$ [9,16]. Voltammetric curves obtained for the reduction of hydrogen ion in all acids were very well defined under both limiting conditions, without and with excess supporting electrolyte. Without electrolyte, the waves were not symmetrical, and the constant limiting current was reached at more negative potentials than in solutions with excess electrolyte.

The experiments were performed using an SCE as reference electrode, whereas the calculated potentials are

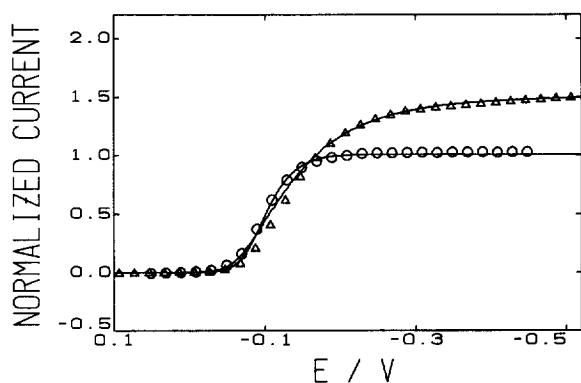


Fig. 4. Simulated (—) and experimental (○, △) voltammograms for reduction of H^+ in solution of 0.5 mM H_2SO_4 with 100-fold excess (○) supporting electrolyte ($LiClO_4$) and without electrolyte (△). Potentials referred vs. HCNP.

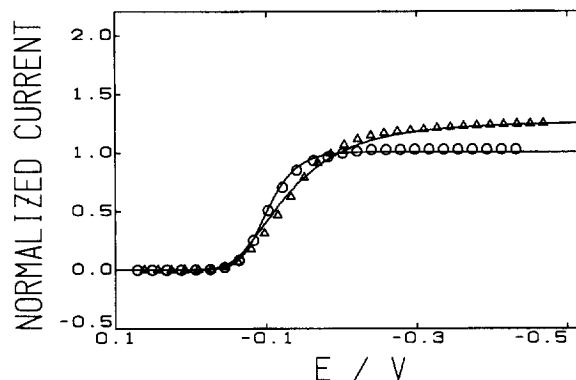


Fig. 5. Simulated (—) and experimental (○, △) voltammograms for reduction of H^+ in solution of 0.25 mM $H_4W_{12}SiO_{40}$ with 100-fold excess (○) supporting electrolyte ($LiClO_4$) and without electrolyte (△). Potentials referred vs. HCNP.

referred to the HCNP. Therefore, the potentials of experimental voltammograms were normalized by moving $E_{1/2}$ of the experimental voltammograms in excess electrolyte to the position of $E_{1/2}$ of the appropriate calculated voltammogram. The experimental voltammograms were moved by 353 mV towards positive potentials. Calculated and experimental voltammograms are compared in Figs. 3–5 for $HClO_4$, H_2SO_4 and $H_4W_{12}SiO_{40}$ respectively. Without supporting electrolyte, the experimental current for all acids rises slightly faster with increasing potential than does the current in the calculated waves. The reason for this could be the level of adventitious electrolyte. However, the shapes and limiting current values of experimental curves agree very well with the simulated curves.

An interesting situation appears when the concentration of acid is changed when no electrolyte is present. Increasing concentration decreases resistance but increases current. Voltammograms simulated for five concentrations of H_2SO_4 without supporting electrolyte are presented in Fig. 6. Fig. 6 also shows, for comparison, the changes of voltammetric waves with change in acid concentration in

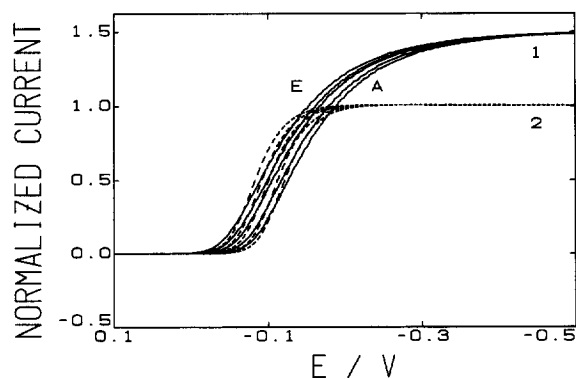


Fig. 6. Simulated voltammograms for reduction of (A–E) 0.1, 0.2, 0.5, 1 and 2 mM H_2SO_4 without (1, —) and with excess (2, ---) supporting electrolyte. Potentials referred vs. HCNP.

