Theory of the diffuse layer when a strong acid is reduced without supporting electrolyte

Koichi Aoki *

Department of Applied Physics, Faculty of Engineering, Fukui University, 3-9-1, Bunkyo, Fukui-shi 910-8507, Japan

Received 8 March 2000; received in revised form 25 April 2000; accepted 27 April 2000

Abstract

The value of the limiting current for reduction of a strong acid, HA, without supporting electrolyte is known to be twice the current value in a solution containing a supporting electrolyte. This enhancement is ascribed to acceleration of the flux of H⁺ toward the electrode by the electric field. Since the electrical neutrality equates [A⁻] with [H⁺], the depletion of H⁺ by the electrode reduction decreases also [A⁻] to zero. Consequently, no ion may be present near the electrode, indicative of infinite solution resistance. This is inconsistent with the experimental observation that the voltammogram is sigmoid. The inconsistency is discussed in this report by considering the Nernst–Planck equations and Poisson’s equation for H⁺ and A⁻ at the hemi-spherical electrode under the steady-state condition. Because of strong non-linearity in the differential equations, numerical solutions are obtained by combining the Newton method and the iterative method for simultaneous equations. They demonstrate the presence of two domains of collapse of the electrical neutrality. One domain close to the electrode has the relation [A⁻] > [H⁺] owing to the electroreduction of [H⁺], whereas the other domain further from the electrode has the opposite relation owing to the electrostatic effect. The non-zero value of [A⁻] is responsible for a finite value of the solution resistance and hence enables the voltammetric measurement to be made without a supporting electrolyte. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Electrical neutrality; Diffuse double layer; Microelectrodes; Strong acids; Solution resistance; Migration

1. Introduction

An interesting feature of the microelectrode technique is voltammetric measurements without deliberate addition of supporting electrolyte [1]. This is useful not only for highly sensitive detection of redox species without the influence of impurity of supporting electrolyte but also for studies on ionic interaction. Some examples of the latter are an enhancement of the limiting current for the reduction of hydrogen ion of acids [2,3], effects on the dissociation rate constants in weak acids [4,5], a relationship between ionic interaction parameters and the diffusion coefficient in polyelectrolytes [6–13], the decrease in the limiting current of counterions of microspheres with an decrease in concentration of supporting electrolyte [14–19], and lability of coordination in metal complexes [20–23]. These studies are based on analysis of the classical migration current. They are different from classical polarography [24], in that they aim at ionic interaction on a molecular level rather than the phenomenological migration current itself.

Measurements of the migration current involve two difficulties: one being to determine accurately the diffusion–migration controlled current from voltammograms with non-well-defined plateaus, the other being to reduce the potential shift caused by the solution resistance (IR-drop). The former can be circumvented by differentiation of the curve, especially for the case of reduction of hydrogen ion in acids. In contrast, it is not possible to eliminate the IR-drop sufficiently from current–potential curves even if one can control a positive feedback circuit well. Reasons for the impossibility are that the migration current depends on the applied voltage, and that the solution resistance varies with the electrode potential, as well as the charge consumed by the electrode reaction. Therefore, interpretation of the potential shift requires complicated theoretical analysis [25,26].
The theoretical analysis involves equations for mass balance of all ions and Poisson’s equation. The flux, \( f_j \), for ion \( j \) caused by diffusion and migration can be expressed as the Nernst–Planck equation [27]

\[
-f_j = D_j \nabla c_j + \frac{z_j F}{RT} D_j c_j \nabla \phi
\]  

(1)

where \( D_j \) is the diffusion coefficient, \( c_j \) is the concentration, \( z_j \) is the charge number, and \( \phi \) is the inner potential in the solution. If a solution contains a soluble redox couple and a 1:1 supporting electrolyte, four Nernst–Planck equations hold. Eq. (1) is usually combined with the equation of continuum (\( \nabla c_j/\partial t = - \text{div} f_j \)) to give the time-dependent mass balance relationship. In contrast, the Poisson equation is given by

\[
\Delta \phi = - \frac{\rho}{\varepsilon} = - \sum_j F z_j c_j / \varepsilon
\]  

(2)

where \( \rho \) is the charge density, and \( \varepsilon \) is the permittivity of the solution. Even under the steady state condition, which is a typical simplification, the product of \( c_j \) by \( \phi \) in Eq. (1) gives rise to a non-linear complication through Eq. (2). Higher simplification has been made by use of the electrical neutrality at every local point [28], i.e. the left hand side in Eq. (2) being regarded as zero to be reduced to the Laplace equation. Then, \( \phi \) is determined only by boundary conditions independently of \( c_j \) to make Eq. (1) linear with respect to \( c_j \). This simplification seems to bring about large errors in estimating the migration current, as reported in Ref. [29], for ultra-small electrodes.

The simplification of the electrical neutrality leads to the unrealistic prediction that no limiting current of reduction of hydrogen ion could be observed in acids without supporting electrolyte [30] for the following reason: the reduction depletes the concentration of the hydrogen ion near the electrode, causing also the depletion of the counterion owing to the electrical neutrality; then, no ion may exist near the electrode, suggesting high solution resistance. This prediction is inconsistent with the experimental results [3–5], which show well-defined limiting currents. The resistance of HCl solution has been evaluated with the ac technique during the reduction of the hydrogen ion [30], and was of the order of 20 MΩ. The lower than suggested value of the resistance can be ascribed to the presence of the counter-ion near the electrode owing to the deviation from electrical neutrality [30]. A theoretical approach may support this lower resistance value. The present work describes the theoretical analysis of Eqs. (1) and (2) for a strong 1:1 acid in the context of collapse of the electrical neutrality.

2. Theoretical

The electrochemical system concerned here is a strong monovalent acid, HA, in an aqueous solution without a supporting electrolyte at a hemi-spherical electrode. The ionic species relevant to the electrode reaction, \( H^+ + e^- \rightarrow H \), are \( H^+ \), \( OH^- \) and \( A^- \). When \( c_{H^+} \) decreases to zero near the electrode, hydroxyl ion is generated from water. Then it may disturb the potential distribution. Since solutions often contain more than 1 μM foreign ions, we assume that 1 μM \( OH^- \) disturbs the potential profile. This concentration corresponds to \( c_{H^+} = 10^{-8} \) M. According to the curve (a) in Fig. 1, the distribution of hydrogen ion is given approximately by \( c_{H^+}/c^* = r/a - 1 \). Inserting the \( c_{H^+} \) value into this equation yields \( r = 0.1 \) nm for \( a = 10 \) μm (electrode radius).

The generation of \( OH^- \) occurs only within the domains of molecular size. Therefore the effect of \( OH^- \) is not necessarily taken into account. Concentrations of \( H^+ \) and \( A^- \) in the bulk should obey the electrical neutrality condition, \( c_{H^+} = c_{A^+} \). In all solution domains, we use Poisson’s equation in polar coordinates.

---

Fig. 1. Concentration profiles of (b) \( c_{H^+} \) and (c) \( c_A \), for \( \phi_L - \phi_R = (A) -0.1 \) and (B) \(-0.5 \) V at 25°C. Profile (a) is for \( c_{H^+} \) without any migration effect, expressed by \( c^*(1 - a/r) \). Curves (b) and (c) were computed at \( n = 500 \), \( \varepsilon = 78 \varepsilon_\infty \), \( \varepsilon^* = 1 \) mM, and \( a = 10 \) μm. These parameters gives \( h = 5.3 \times 10^5 \). Circles and solid line in insets are, respectively, for (a) and (c) in a wide domain of \( r/a \). Domains (I) and (II) are, respectively for \( c_A > c_{H^+} \) and \( c_A < c_{H^+} \).
\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\phi}{dr} \right) = -\frac{F}{\epsilon} (c_H - c_A) \quad (3)
\]

The negative electric field in the solution attracts H\(^+\) to the electrode and repulses A\(^-\) toward the bulk. The accumulation of H\(^+\) and the depletion of A\(^-\) is smoothed by diffusion through the Nernst–Planck equation. Under the steady-state condition, Eq. (1) with \(\text{div} f_j = 0\) for H\(^+\) and A\(^-\) is rewritten as

\[
\frac{d}{dr} \left( r^2 \frac{d\phi_H}{dr} \right) + \frac{F}{RT} \frac{d}{dr} \left( \phi_H \frac{d\phi_H}{dr} \right) = 0 \quad (4)
\]

\[
\frac{d}{dr} \left( r^2 \frac{d\phi_A}{dr} \right) - \frac{F}{RT} \frac{d}{dr} \left( \phi_A \frac{d\phi_A}{dr} \right) = 0 \quad (5)
\]

The electrode potential is sufficiently negative that the concentration of the hydrogen ion at the electrode surface is actually zero, i.e. in the limiting current domain. Then, the boundary conditions are

\[
r = a: \quad c_H = 0, \quad dc_H/dr = 0, \quad \phi = \phi_E \quad (6)
\]

\[
r \to \infty: \quad c_H \to c^*, \quad c_A \to c^*, \quad \phi = \phi_B \quad (7)
\]

where \(a\) is the radius of the hemispherical electrode.

From Eq. (1), the limiting current density is given by

\[
\text{div} f_j = 0
\]

because of \((c_H)_{-a} = 0\).

It is convenient to change variables:

\[
x = a/r \quad (9)
\]

\[
y = F\phi/RT \quad (10)
\]

Then, Eqs. (3)–(7) are simplified to

\[
\frac{d^2y}{dx^2} = \frac{F^2a^2}{RT\epsilon x^4} (c_A - c_H) \quad (11)
\]

\[
\frac{dc_H}{dx} + c_H \frac{dy}{dx} = B_1 \quad (12)
\]

\[
\frac{dc_A}{dx} - c_A \frac{dy}{dx} = B_2 \quad (13)
\]

\[
x = 1: \quad c_H = 0, \quad dc_H/dx = 0, \quad y = F\phi_E/RT \quad (14)
\]

\[
x = 0: \quad c_H = c^*, \quad c_A = c^*, \quad y = F\phi_B/RT \quad (15)
\]

where \(B_1\) and \(B_2\) are constants to be determined. The boundary value problem (Eqs. (11)–(15)), cannot be solved by use of usual software, partly because Eq. (11) includes singularity at \(x = 0\) and partly because Eqs. (12) and (13) include strong non-linearity. Solutions of Eqs. (12) and (13) for any function of \(y(x)\) are given by

\[
c_H = B_1 e^{-y(x)} \int_{-y(1)}^{y(x)} e^{F\phi(u)} du + B_3 e^{-y(x)} \quad (16)
\]

\[
c_A = B_2 e^{y(x)} \int_{-y(1)}^{y(x)} e^{F\phi(u)} du + B_4 e^{y(x)} \quad (17)
\]

where \(B_3\) and \(B_4\) are constants. When boundary conditions (Eqs. (14) and (15)) are applied to the above two equations, we can determine \(B_1 - B_4\) and rewrite Eqs. (16) and (17) as

\[
c_H = e^{\phi} e^{-y(x)} q(x) \quad (18)
\]

\[
c_A = e^{\phi} e^{y(x)} p(x) \quad (19)
\]

where

\[
q(x) = \int_{-y(1)}^{y(x)} e^{F\phi(u)} du \quad (20)
\]

\[
p(x) = e^{-y(x)} \int_{-y(1)}^{y(x)} e^{F\phi(u)} du \quad (21)
\]

Here \(c_H\) and \(c_A\) vary exponentially with \(y\), whereas \(q(x)\) and \(p(x)\) have slower variations than \(c_H\) and \(c_A\). Inserting Eqs. (18) and (19) into Eq. (11), we can rewrite Eq. (11) as

\[
\frac{d^2y}{dx^2} = \frac{2h\sqrt{pq}}{x^4} \sinh[y + \ln(p(x)/q(x))] \quad (22)
\]

where

\[
h = \frac{F^2a^2e^\phi}{RT\epsilon} \quad (23)
\]

Eq. (22) is non-linear with respect to \(y\), and furthermore \(p(x)\) and \(q(x)\) are complicated functions of \(y\). Therefore it cannot be solved analytically. We made a numerical computation for Eq. (22) by use of the finite difference method. Details of the computation are described in the Appendix.

### 3. Results and discussion

Fig. 1 shows examples of the concentration profiles at two values of \(\phi_E - \phi_B\). The entire profiles of \(c_A\) (circles in insets of Fig. 1(A) and (B)) are almost the same as the profile of \(c_H\) without the migration effect, which is expressed by \(c_H = e^\phi(1 - a/r)\) (solid curves in insets of Fig. 1). Thus, the electrical neutrality holds on the scale shown by the inset. It is, however, not valid near the electrode. The boundary conditions, \(c_H = 0\) and \(dc_H/dr = 0\) at \(r = a\) indicate that \(c_H\) decreases linearly to zero at the electrode and that \(c_A\) remains constant near the electrode. Consequently, \(c_A > c_H\) in domain (I) of Fig. 1. It is the difference in these boundary conditions that brings about the collapse of the electrical neutrality. In other words, \(c_A > c_H\) results from whether the species is electroactive or inactive. A degree of the collapse \((c_H - c_A)\) increases with an increase in \(\phi_E - \phi_B\). In contrast, the opposite relation, \(c_A < c_H\), is found in domain (II) slightly far from the
electrode. This is ascribed to the electric field; \( \text{H}^+ \) being attracted to and \( \text{A}^- \) being repelled from the electrode. The relation \( c_A > c_{\text{H}} \) is not compensated with domain (I), but gives rise to unbalance of the charge, as will be discussed below (Fig. 5).

As \( \phi_E - \phi_B \) decreases (Fig. 1((A) → (B)), domain (II) extends toward the bulk to relax the electric field. Then, the concentration profiles also extend toward the bulk and hence values of \( c_A \) in domain (II) are smaller than those of \( \phi_E - \phi_B \). An intuitive prediction is that concentration profiles also extend toward the bulk to relax the electric field. Then, the resistance between the electrode and the bulk. The big difference between (b) and (d) may be ascribed to the depletion of the concentrations. We attempted to replace \( c^* \) in [24] by the concentration profile without migration, \( c^*(1 - a/r) \). Curve (e) is the concentration-corrected profile, suggesting still, a large discrepancy from (b). That is, the non-linear term of \( c_{\text{H}} \) and \( \phi \) in Eqs. (4) and (5) contributes largely to the potential profile.

The concentration profiles, especially \( c_A \) near the electrode, are mainly responsible for the conductance between the electrode and the bulk. The ionic conductance caused by \( \text{H}^+ \) and \( \text{A}^- \) in a cylinder of height \( l \) and base area \( A \) is expressed by \( (c_{\text{H}}A_{\text{H}} + c_AA_A)A/l \), where \( A_{\text{H}} \) and \( A_A \) are molar conductance of \( \text{H}^+ \) and \( \text{A}^- \), respectively. Then, the resistance between the working hemi-spherical electrode and the concentric hemi-spherical counter electrode is given by

\[
R = \int_{a}^{\infty} \frac{1}{c_{\text{H}}A_{\text{H}} + c_AA_A} \frac{dr}{2\pi r^2}
\]

where \( A \) and \( l \) have been replaced by \( 2\pi r^2 \) and \( dr \), respectively. Applying the change of variable in Eq. (9) gives the expression for the dimensionless resistance:

\[
(ac^*A_A)R = \frac{1}{2\pi} \int_{0}^{1} \frac{c^*A_A dx}{c_{\text{H}}A_{\text{H}} + c_AA_A}
\]

This integral was evaluated numerically by combining Eqs. (18)–(22) for several values of \( \phi_E - \phi_B \) and \( h \) when \( \text{Cl}^- \) is \( \text{Cl}^- \) (\( A_{\text{H}} = 35 \) and \( A_A = 7.6 \text{ mS m}^{-1} \) [32]). Variations of \( (ac^*A_A)R \) with \( \phi_E - \phi_B \) are shown in Fig. 3. For typical experimental values (see Fig. 1) of \( a \) and \( c^* \) corresponding to curve (C) in Fig. 3, values of \( (ac^*A_A)R \) range from 0.18 to 0.21. Thus, the resistance is almost independent of the applied potential, although the concentration profiles vary largely with \( \phi_E - \phi_B \), as shown in Fig. 1.

The quantity, \( (ac^*A_A)R \), is a function of \( h \) and \( A_{\text{H}}/A_A \). \( \text{Br}^- \), \( \text{Cl}^- \), \( \text{I}^- \), \( \text{ClO}_2^- \) and \( \text{NO}_3^- \) have values of \( A_{\text{H}}/A_A \) close to 4.5. The variation of \( (ac^*A_A)R \) with \( h \) for the value of \( A_{\text{H}}/A_A \) is shown in Fig. 4. This curve predicts values of \( (ac^*A_A)R \) for a given electrochemical system, showing little dependence on \( h \). For example, \( (ac^*A_A)R \) is approximately equal to 0.2 for halogen ions (C):


\[ 1/R = 5ae^*A_A \]  

Therefore, the conductance is proportional to \( c^* \), as is demonstrated experimentally [30]. The intuitive derivation (Eq. (8) of Ref. [30]) says that the conductance is expressed by \( 1/R = 4ac^*A_A \), which is close to Eq. (27). The measurement of \( R \) at various values of \( c^* \) for HCl results in \( 1/R = 1.7ac^*A_A \) at the microdisk electrode. Since the area of the hemi-spherical electrode is twice that of the microdisk surface, the coefficient (5) should be taken to be a half (2.5). More detailed discussion may be dangerous because of geometrical differences between theory and the experiment.

The collapse of the electrical neutrality localizes \( H^+ \) and \( A^- \) to cause an excess of the charge near the electrode, like a diffuse double layer. The excess of the charge density at \( r \) is given by \( F(c_{H} - c_A) \), which is equal to \( -(\varepsilon/r^2)[d(r^2(d\phi/dr))/dr] \) by Eq. (3). Thus, the total excess of the charge is expressed by

\[ q = \int_{a}^{\infty} 4\pi r^2 F(c_{H} - c_A)dr = -4\pi\varepsilon \int_{a}^{\infty} d[r^2(d\phi/dr)] \]

(28)

Carrying out the change of variable through Eqs. (9) and (10), we obtain

\[ q = -4\pi\varepsilon a(RT/F)(dy/dx)_{x=1} \]

(29)

where we have assumed that \( (dy/dx)_{x=0} \) or \( (d\phi/dr)_{r=a} \) is much smaller than \( (dy/dx)_{x=1} \) or \( (d\phi/dr)_{r=a} \). Values of the charge density \( q/a \) per electrode length were computed from Eq. (29) and the equations described in the Appendix. They are plotted against \( \phi_E - \phi_B \) for some values of \( h \) in Fig. 5. They increase with a decrease in \( \phi_E - \phi_B \) because the electric field attracts \( H^+ \) to and repels \( A^- \) from the electrode. It is reasonable that the excess charge is positive for negative values of \( \phi_E - \phi_B \). However, the positive values seem to conflict with \( c_A > c_H \) in domain (I) in Fig. 1. Domain (I) is caused by both the limiting current condition for \( H^+ \) and zero flux of \( A^- \), whereas domain (II) is ascribed to the electrostatic effect. As a result of the competition, \(|q|\) in domain (II) is predominant over \(|q|\) in domain (I). When \( \phi_E - \phi_B \) is larger than \(-0.1\), the predominance is opposite, and \( q \) becomes negative.

An experimentally accessible quantity relevant to the excess charge is the differential capacitance defined by \( C_d = [dq/d\phi_E] \). Values of \( C_d \) were calculated numerically, and are plotted against \( \phi_E - \phi_B \) in Fig. 6. Since the diffuse double layer is extended widely toward the bulk, as seen in Fig. 2, the expression for the differential capacitance can be simplified mathematically to the form, \( C_d/a \) rather than \( C_d/2\pi a^2 \). The maximum value of \( C_d/a \) for \( h = 5.3 \times 10^5 \), corresponding to the conditions \( c^* = 1 \) mM and \( a = 10 \mu m \), is equivalent to \( C_d/2\pi a^2 = 0.24 \mu F \ cm^{-2} \). This value is much smaller than the value (8 \( \mu F \ cm^{-2} \)) calculated from the Gouy–Chapman theory. The small value comes from the low electric field owing to the wide dispersion of the diffuse double layer.
4. Conclusions

A solution resistance of the order of 20 MΩ when a strong acid is reduced at the microelectrode was demonstrated theoretically to be ascribed to the presence of A− which results from the collapse of electrical neutrality. Owing to the support of the conductance by A−, microelectrodes can provide voltammograms without deliberately adding supporting electrolyte. The collapse of electrical neutrality results mathematically in a domain (I). This relation is, however, inconsistent with the electrostatic attraction of H+ to and the repulsion of A− from the electrode. The electrostatic effect (∥cA) < (∥cH) is realized in domain (II). Since two domains coexist, values of the excess charge and the differential capacitance are much smaller than those predicted from Gouy–Chapman theory. The common sense view that application of negative potentials increases concentrations of cations is not true when the solution contains no supporting electrolyte.

Acknowledgements

This work was financially supported by Grants-in-Aid for Scientific Research (grant nos. 11640060 and 11118230) from the Ministry of Education in Japan.

Appendix A

This appendix describes the technique of solving Eq. (22) numerically. The variable xi, ranging from 0 to 1, was discretized into n equi-distances, Δx, i.e. n(Δx) = 1. After taking the finite difference, we define a dummy function, g(yi), which should be zero:

\[ g(y_i) = \left[ 2h \sqrt{p(q(Δx)^2/x_i^2)} \sinh[y_i + \ln\sqrt{p(x_i)/q(x_i)}] + 2y_i - y_{i+1} - y_{i-1} \right] \]

for \(1 \leq i \leq n - 1\), where \(x_i = iΔx\). Even if values of \(y_{i+1}\) and \(y_{i-1}\) are known, it is difficult to extract \(y_i\) from \(g(y_i) = 0\) analytically. A strategy for estimating \(y_i\) is the Newton method. Although \(p(x)\) and \(q(x)\) vary with \(y\), they are not explicit functions of \(y_i\). Thus, they can be regarded as a function of only \(x\) in evaluating \(∂g(y_i)/∂y_i\). Then we obtain

\[ ∂g(y_i)/∂y_i = \left[ 2h \sqrt{p(q(Δx)^2/x_i^2)} \cosh[y_i + \ln\sqrt{p/q}] + 2 \right] \]

The boundary conditions are \(y_0 = F_0φ_t/RT\) and \(y_n = F_0φ_t/RT\). The evaluation of \(p(x_i)\) requires (dy/dx)_x=i, which can be rewritten as

\[ (dy/dx)_x = (y_{n+1} - y_{n-1})/2Δx \]

Unfortunately, \(y_{n+1}\) is not defined. Function \(g(y_n)\) includes \(y_{n+1}\), i.e.

\[ h(Δx)^2 \exp(y_n) \]

\[ \left[ (y_{n+1} - y_{n-1})/2Δx \exp(y_n) \right]^{1/2} e^{-y_0 dt} \]

\[ + 2y_n - y_{n+1} - y_{n-1} = 0 \]

which was derived from Eq. (22) by taking a limit, \(q \to 0\) (\(x \to 0\)). Eq. (33) is a quadratic equation with respect to \(y_{n+1}\) for known values of \(y_{n-1}\) and \(y_n\). Combining the solution of the quadratic equation and Eq. (32), we evaluated (dy/dx)_x=i.

Initial values of \(y_i\) were set using a linear interpolation between \(y_0\) and \(y_n\). Integrals in \(p\) and \(q\) were evaluated by the trapezoidal rule. A new value of \(y_i\) was determined from the Newton method: \(y_i = y_i - g(y_i)/[∂g/∂y_i]\) for \(i = 1\) to \(n - 1\). This process was iterated until \(y_i\) values became independent of the iteration with errors less than \(10^{-7}\). The iteration numbers at \(h = 5.3 \times 10^5\) and \(N = 500\) were 70 and 700 for \(φ_t - φ_B = -0.1\) and \(-0.5\), respectively. When values of \(n\) ranged from 50 to 500, the deviation in \(y_i\) was less than 0.2%. As a measure of the validity of the computation, we evaluated the flux at each \(x\). Values of the flux were independent of \(x\), supporting the steady-state flux.

The program was coded in Turbo C language for a 32-bit IBM PC. It is available on request.

References

[27] A.J. Bard, L. Faulkner, Electrochemical Methods, Wiley, New York, 1980, p. 120.