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Correction of Experimental Data for the Ohmic Potential Drop Corresponding to a Secondary Current Distribution on a Disk Electrode

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ABSTRACT: A numerical method is presented for adjusting experimental current-potential curves for the ohmic resistance corresponding to a secondary current distribution on a (rotating) disk electrode. The nonuniform current and potential distributions on the disk electrode cause the electrolyte resistance itself to be a function of measured current. The method described here is employed after the experiments are conducted and yields the Tafel slope as well as adjusted values for current density and surface overpotential that apply to the center of the disk. This facilitates the comparison of the experimental data to those obtained using mathematical models of the rotating disk electrode that, in the secondary current regime, apply strictly only to the center of the electrode. The Tafel slopes obtained agree to within 3 mV/decade with standard techniques for ohmic correction such as current interruption because, at the high current densities where the ohmic correction is most significant, the resistance correction approaches the primary resistance obtained by current interruption. The Tafel slope values for the two methods differ most for solutions of low conductivity. The major advantages of the ohmic correction method described here are that the experimental condition is never perturbed and that the method indicates the extent to which the current distribution is nonuniform.

KEY WORDS: ohmic resistance, electrodes, Tafel slopes, electrochemical systems

Nomenclature

- a Constant in Tafel line equation defined in Eq 3
- b Tafel slope, V/decade
- F Faraday's constant, 96 487 °C/equiv
- I Total current, A
- i Current density, A/m²
- i_{corr} Exchange current density of a freely corroding system, A/m²
- i_o Exchange current density, A/m²
- n Number of electrons transferred in reaction
- R Gas constant, 8.314 J/K-mole
- r Radial position, m

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r_o	Radius of a disk-electrode, m
SCE	Saturated calomel electrode
T	Temperature, K
α	Apparent transfer coefficient, dimensionless
β	Apparent anodic or cathodic transfer coefficient (see also Eq 12)
δ	Parameter defined in Eq 8
η_c	Concentration overpotential, V
η_s	Surface overpotential, V
κ_∞	Conductivity, S/m
Φ_o	Ohmic potential drop, V
Φ	Potential, V

Subscripts

a	Anodic
app	Applied
avg	Average
c	Cathodic
corr	Corrosion
∞	Bulk condition far from the electrode surface

Introduction

The reaction mechanisms governing an electrochemical system are commonly identified by comparing experimentally determined Tafel slopes or apparent transfer coefficients with "theoretical values" obtained from simplifications of specific reaction mechanisms. An analysis of experimental data must include a treatment of the contribution to the measured potential of the electric resistance of the electrolyte, a term that can be significant at large currents or in dilute solutions of low conductivity. A number of techniques are available for making this correction. The ohmic contribution, for example, can be reduced but not eliminated by placing the reference electrodes close to the working electrode. A disadvantage of this approach is that exact placement of the reference electrode is critical, and uncertainty in the electrode location can be a significant source of error. Another approach is to place the reference electrode sufficiently far from the working electrode so that the distance can be considered to approach infinity. This allows the ohmic contribution to the measured potential to be calculated mathematically. Current interruption can also be used to obtain the ohmic contribution to the cell potential.

This paper describes a numerical technique used by Lowry [1,2] to correct the polarization data for the ohmic resistance corresponding to a secondary current distribution on a disk electrode. This procedure was suggested by Newman in his analysis of the current and potential distribution on a rotating disk electrode [3,4]. The treatment presented here does not require perturbation of the electrochemical system and takes into account the nonuniform current and potential distribution present on a disk electrode in the Tafel regime. The analysis can therefore be used to determine the extent to which the coupling of ohmic and kinetic effects causes the current distribution on the electrode to be nonuniform. This information could facilitate the interpretation of spatial variations of surface morphology or of electrode profiles after corrosion experiments. The use of this technique is restricted to a disk electrode with a reference electrode located infinitely far away and at currents below values at which mass-transfer effects are seen. Accurate values of solution conduc-

tivity and disk radius are also needed. The Tafel slopes are estimated by an iterative procedure using data within the Tafel region, where the ohmic resistance typically cannot be neglected.

A brief discussion of the use of polarization measurements to measure corrosion rates and Tafel slopes is presented. The method is illustrated by analyzing data taken by Lowry et al. [2] and the results are compared with those obtained from other ohmic compensation methods.

Theoretical Development

The analysis of experimental data is usually based on a simplification of the general Butler-Volmer kinetic expression. The discussion here follows the Butler-Volmer expression, a summary of Newman's analysis of the secondary current distribution on a disk electrode, and the numerical method developed for ohmic compensation.

Identification of Tafel Parameters

The rate at which reversible electrochemical reactions proceed can be described by a Butler-Volmer type equation

$$i = i_o \left\{ \exp \left(\frac{\alpha_a F}{RT} \eta_s \right) - \exp \left(- \frac{\alpha_c F}{RT} \eta_s \right) \right\} \quad (1)$$

The current density i is the sum of the anodic and cathodic contributions where i_o is the exchange current density, α_a and α_c are the apparent anodic and cathodic transfer coefficients, respectively, and η_s is the surface overpotential. The kinetic parameters i_o , α_a , and α_c can be determined from experimental data through use of Eq 1. The exchange current density is a function of the electrolyte composition adjacent to the electrode surface and is large for reactions that are fast or reversible [5]. The surface overpotential provides the driving force for the reaction and is a measure of departure from the equilibrium potential Φ_{eq} . For reversible reaction, Φ_{eq} is given by the Nernst equation.

Electrode kinetic studies are performed by applying an external potential Φ_{app} such that

$$\Phi_{app} = \Phi_{eq} + \eta_s + \Phi_o + \eta_c \quad (2)$$

These potentials are measured relative to a known potential of a reference electrode such as the saturated calomel electrode (SCE). The concentration overpotential η_c is due to changes in concentration and conductivity at the electrode surface relative to the bulk. This term can be neglected for currents sufficiently below the limiting current and will not be treated in this work. The ohmic potential drop Φ_o is attributed to the solution resistance and is a measure of the driving force necessary to pass current through the electrolyte. At low current densities and close to the equilibrium potential, Φ_o is negligible; the contrary is true at high currents. The objective of the ohmic compensation techniques discussed here is to identify the current-potential characteristics of a given system in the absence of this term.

When the surface overpotential becomes large, either the anodic or cathodic current dominates. Equation 1 reduces to an expression in which the surface overpotential becomes linear with respect to the logarithm of the current density. This is called the Tafel

polarization within this regime is essentially activation controlled. In the anodic Tafel region

$$\eta_s = \frac{2.303RT}{\alpha_a F} \log \left(\frac{i}{i_o} \right) = a_a + b_a \log i \quad (3)$$

where

$$a_a = - \frac{2.303RT}{\alpha_a F} \log i_o$$

and the anodic Tafel slope (in units of V/decade) is given by

$$b_a = \frac{2.303RT}{\alpha_a F}$$

Analogous expressions for the cathodic Tafel region can be obtained.

Tafel extrapolations can also be applied to corrosion reactions through the use of the mixed-potential theory [6]. The basis of the polarization techniques found in the literature [7-15] for evaluating kinetic parameters is that the current density for a corroding system consisting of individual reversible reactions can be approximated by

$$i = i_{\text{corr}} \left\{ \exp \left(\frac{2.303\eta_s}{b_a} \right) - \exp \left(- \frac{2.303\eta_s}{b_c} \right) \right\}, \quad (4)$$

where the surface overpotential is defined to be

$$\eta_s = \Phi_{\text{app}} - \Phi_{\text{corr}} - \Phi_o, \quad (5)$$

and i_{corr} and Φ_{corr} are the corrosion current and corrosion potential, respectively. These potentials are likewise measured relative to a reference electrode; the value of Φ_{corr} will shift accordingly with the choice of reference potential. The corrosion potential has a value that falls between the reversible potentials of the individual reaction pairs, and represents the dynamic equilibrium state of the freely corroding system. The principal assumption inherent in Eq 4 is that the major contributors to the overall current are the metal dissolution reaction and the reduction of some electroactive species. For this approximation to be valid, Φ_{corr} must be sufficiently far from the two reversible potentials [8].

The techniques described in Ref 7 to 15 use current-potential data in the pre-Tafel region. The measurements are performed at low currents and close to Φ_{corr} , where the ohmic contribution to the potential in Eq 5 is negligible. The experimental data are fitted into Eq 4 to yield values for i_{corr} , b_a , b_c , and Φ_{corr} . The methods Mansfeld and coworkers [8-12] used to analyze polarization data, and Barnartt's three-point method [13,14] and its variation [15], do not require the assumption of a linear polarization curve near the corrosion potential.

The Secondary Current Distribution on a Disk Electrode

At large current densities, the contribution of the ohmic potential drop to the applied potential must be considered. The ohmic resistance is a function of the distance between

the reference and working electrodes, the conductivity of the solution, and the geometry of the working electrode. Experimental errors in the measurement of ohmic drop could be reduced by setting the reference electrode at "infinity" with respect to the working electrode. The ohmic resistance is insensitive to changes in the position of the reference electrode when the latter is placed relatively far from the working electrode [3]. This simplifies the experimental apparatus (that is, no Luggin capillary is necessary) and allows some leeway on electrode placement.

A procedure for Ohmic potential drop correction was derived from Newman's analysis of the current and potential distribution on a disk electrode [3,4]. The current distribution can be described as primary or secondary depending on the applied potential. The term Φ_{eq} can be neglected in Eq 2 when the applied potential is measured against a reference electrode of the same kind as the working electrode. The concentration overpotential η_c can also be neglected at high convection rates. Each of the remaining terms vary with radial position to keep the Φ_{app} constant over the entire disk.

A uniform potential in the solution adjacent to the electrode surface is obtained when both η_c and η_s are negligible. In this regime, the reaction rate constants are high and the current distribution is determined by the ohmic drop throughout the solution. The primary current distribution on an equipotential surface is

$$i = \frac{0.5i_{avg}}{\sqrt{1 - (r/r_o)^2}} \quad (6)$$

and the primary resistance is given by

$$\Phi_o = \frac{I}{4\kappa_{\infty}r_o} \quad (7)$$

where I represents the total current, κ_{∞} is the solution conductivity, and r_o is the radius of the disk electrode [3].

The secondary current distribution applies when the surface overpotential cannot be neglected and the current at a point on the electrode becomes a function of the potential of the adjacent solution. The secondary current distribution under Tafel kinetics [4] is presented in Fig. 1 as a function of radial position with $\beta\delta$ as the parameter where δ is given by

$$\delta = |i_{avg}| \frac{zFr_o}{RT\kappa_{\infty}} \quad (8)$$

and represents the dimensionless average current density. For solutions with supporting electrolyte, z is defined to be equal to $-n$, the number of electrons transferred in the reaction. The term βz is the apparent cathodic or anodic transfer coefficient α_c or α_a . The current distribution is now determined by the requirement that the current at any location satisfy both Ohm's law, relating current to a gradient in potential at that location, and the kinetic expression relating current to the local value of the surface potential. This is in contrast to the primary case, in which the local value of current density need only satisfy Ohm's law. The potential in the solution for both primary and secondary distributions is governed by Laplace's equation. As $-\beta\delta$ tends toward ∞ , the current distribution approaches the primary distribution where the current density approaches infinity at the disk edge and is equal to one-half the average current value at the center of the disk. As

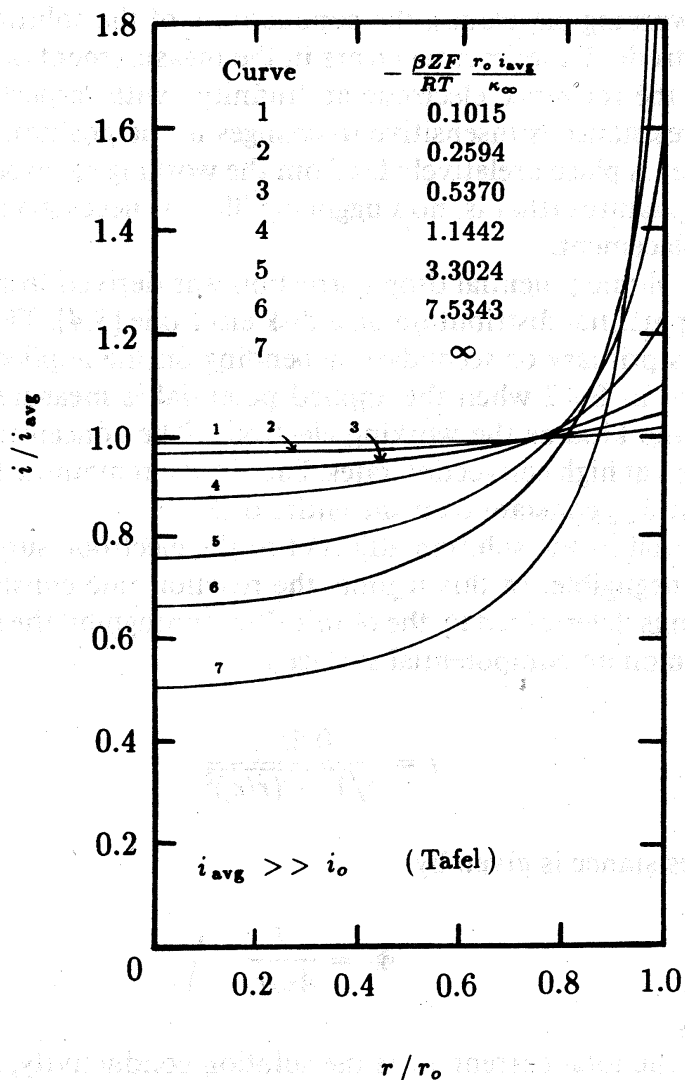


FIG. 1—Secondary current distribution on a disk electrode for Tafel kinetics (Ref 4, reprinted by permission of the publisher, The Electrochemical Society, Inc.).

— $\beta\delta$ approaches zero, the current distribution becomes uniform. This means that kinetic limitations to the electrode reaction cause the current distribution to become more uniform and cause the potential adjacent to the electrode surface to deviate from a uniform value to overcome the tendency of current to favor the edge of the electrode [4,5].

One consequence of the nonuniform secondary distribution for the potential of the solution adjacent to the electrode is that subtraction of the ohmic correction for a primary distribution applies strictly only for a single radial position on the disk, and the location of this position is a function of the average current density. One can, however, reference the ohmic potential drop and the current density to values appropriate for the center of the disk. This approach requires that the ohmic resistance be a function of the average current density. The primary ohmic potential drop is therefore corrected by a factor given in Fig. 2 as a function of the ratio of the current density at $r = 0$ to the average current density. This factor is equal to unity for the primary current distribution (where the potential of the solution adjacent to the disk is uniform) and approaches 1.273 when the current distribution becomes uniform.

If one could obtain the ratio $i/i_{avg}|_{r=0}$ from Fig. 1, the applied potential could be corrected for the ohmic drop to obtain the surface overpotential at the center of the disk elec-

trode, that is

$$\eta_s|_{r=0} + \Phi_{\text{corr}} = \Phi_{\text{app}} - \Phi_o|_{r=0} \quad (9)$$

or

$$\eta_s|_{r=0} + \Phi_{\text{corr}} = \Phi_{\text{app}} - \frac{I}{4\kappa_{\infty}r_o} \left[\frac{\Phi_o 4\kappa_{\infty}r_o}{I} \Big|_{r=0} \right] \quad (10)$$

where I is the total current to the disk at an applied potential Φ_{app} measured relative to a reference electrode. The term in the bracket is the correction factor for the primary resistance to the center of the disk electrode determined from Fig. 2.

The Numerical Method for Ohmic Compensation

Data obtained from potentiostatic or potentiodynamic experiments may be corrected for ohmic potential drop at the center of the disk to acquire the surface overpotential and current density at $r = 0$ using the procedure derived from Newman's treatment of the disk electrode. Reliable estimates for the ohmic contribution can be obtained since the calculations are referenced to a radial position where the ohmic potential drop and current density are known.

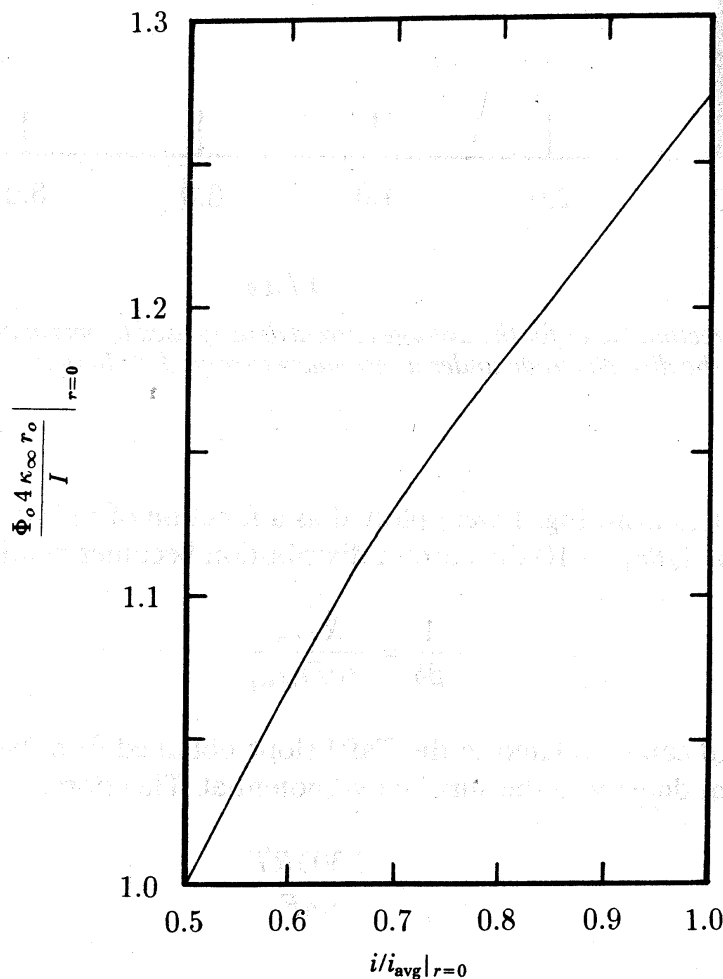


FIG. 2—Correction factor for the primary resistance used to correct for the ohmic potential drop to the center of the disk electrode under a secondary current distribution (Ref 4, reprinted by permission of the publisher, The Electrochemical Society, Inc.).

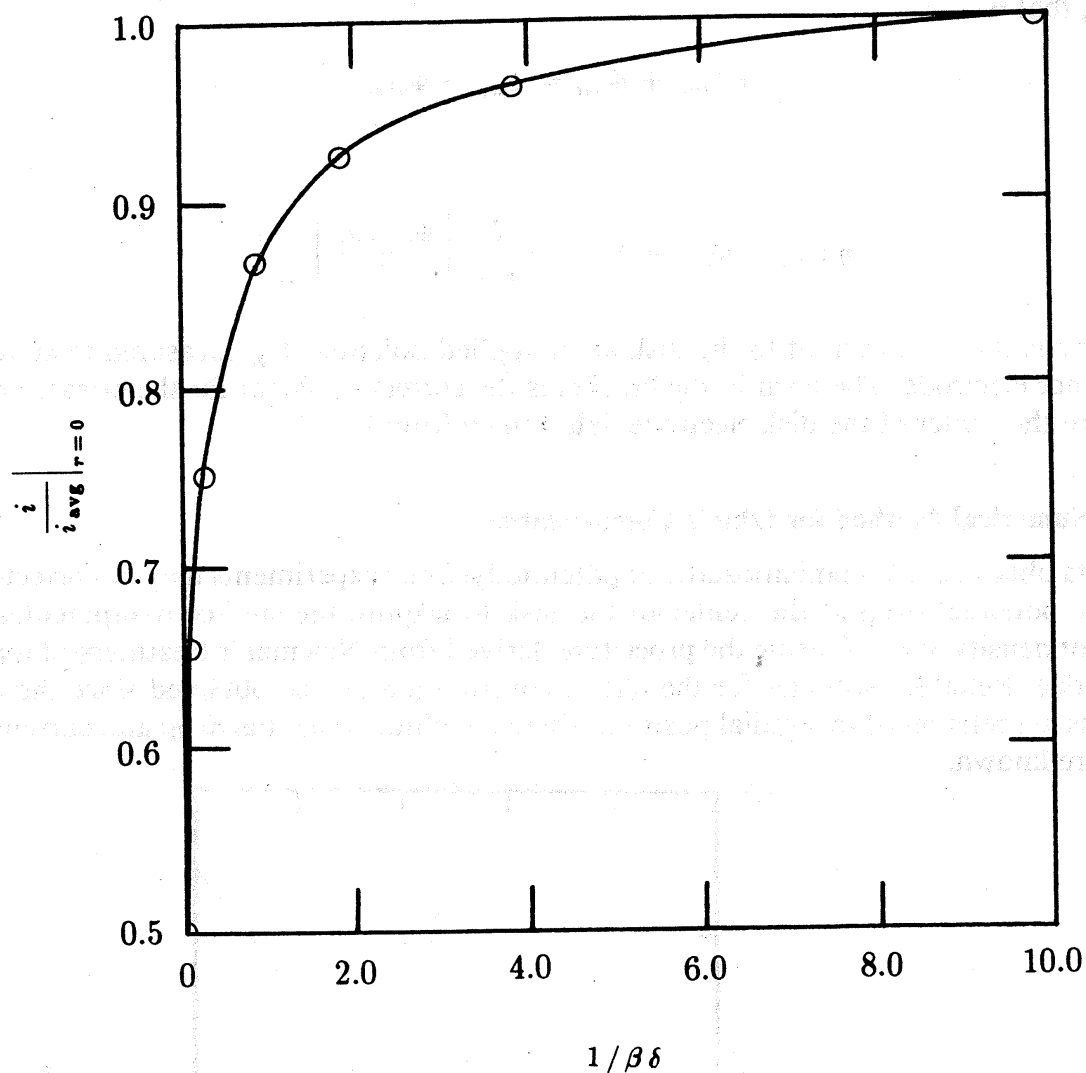


FIG. 3—Correction factor for the average current density used to obtain the current density at the center of the disk electrode under a secondary current distribution.

Values for $i/i_{avg}|_{r=0}$ from Fig. 1 were plotted as a function of $|1/\beta\delta|$ to yield Fig. 3. This plot shows that as $|1/\beta\delta| \rightarrow 10$ the current distribution becomes nearly uniform. Since

$$\frac{1}{\beta\delta} = \frac{RT_{K_{\infty}}}{\beta n F r_0 i_{avg}} \quad (11)$$

an expression for β can be related to the Tafel slope obtained from Newman's expression relating the current density to the surface overpotential. Therefore,

$$b = \frac{2.303RT}{\beta n F} \quad (12)$$

or

$$\beta = \frac{2.303RT}{bnF} \quad (13)$$

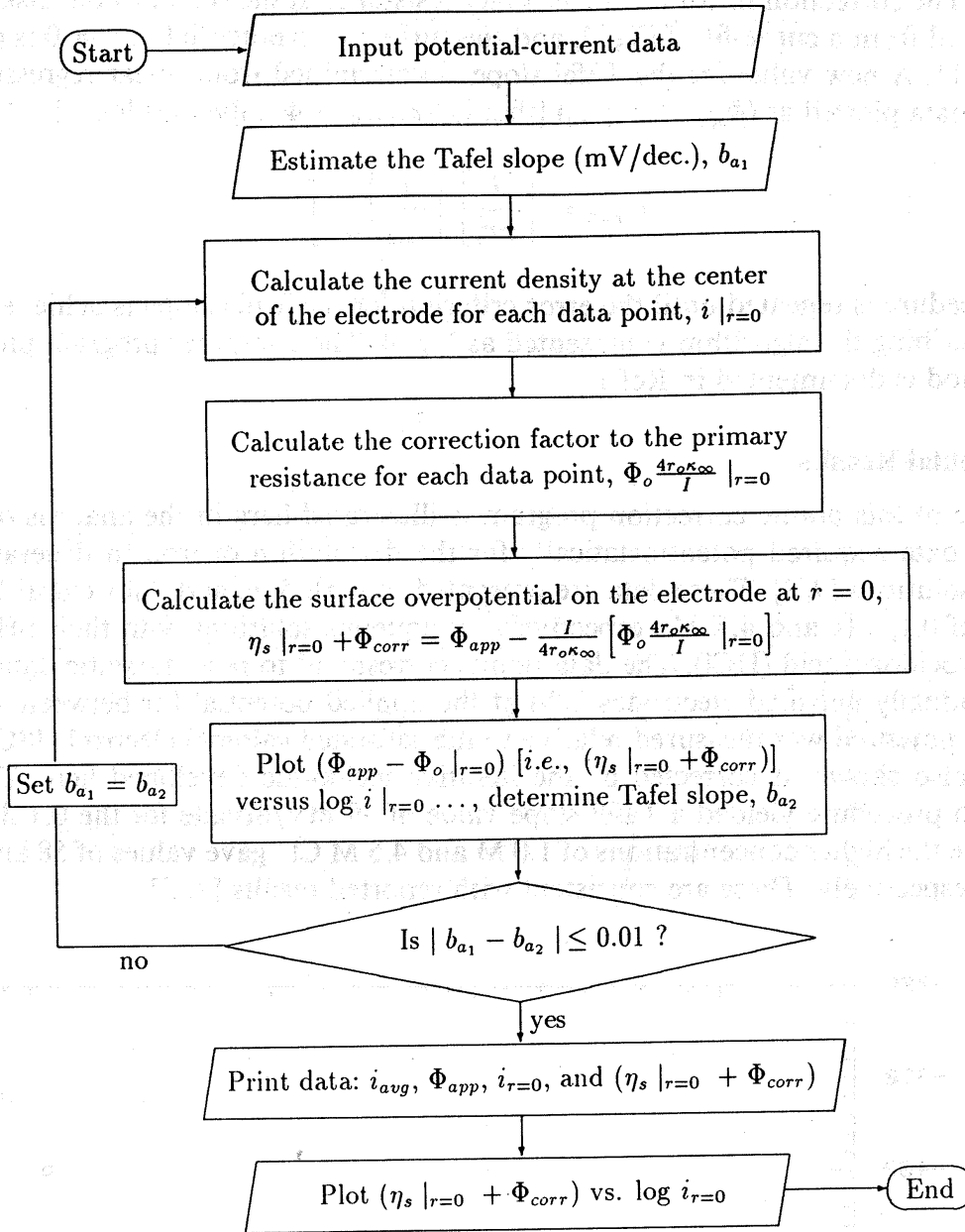


FIG. 4—The flowchart describing the ohmic drop correction algorithm.

With

$$i_{avg} = \frac{I}{\pi r_o^2} \tag{14}$$

Equation 13 becomes

$$\frac{1}{\beta \delta} = \frac{b \kappa_{\infty} \pi r_o}{2.303 I} \tag{15}$$

The iterative procedure used to obtain $\eta_s |_{r=0}$ requires an initial guess for the Tafel slope and calculation of the parameter $1/\beta \delta$ from Eq 15 for each pair of current-potential data. The corresponding value of $i/i_{avg} |_{r=0}$ is subsequently obtained from a discretized version

of Fig. 3. The correction factor for the primary resistance at the center of the disk electrode is estimated from a curve-fit of Fig. 2, and the surface overpotential at $r = 0$ is calculated from Eq 11. A new value for the Tafel slope is determined from linear regression of the adjusted data plotted as $(\Phi_{\text{app}} - \Phi_o|_{r=0})$ [that is, $(\eta_s|_{r=0} + \Phi_{\text{corr}})$] versus $\log(i|_{r=0})$ where

$$i|_{r=0} = \left[\frac{I}{\pi r_o^2} \right] \left[\frac{i}{i_{\text{avg}}} \right]_{r=0} \quad (16)$$

This procedure is repeated until the error criterion for the Tafel slope is achieved. A flow-chart describing the algorithm is presented as Fig. 4. The computer program prepared for this method is documented in Ref 1.

Experimental Results

The use of this ohmic correction program is illustrated here in the analysis of current-potential data acquired potentiostatically for the dissolution of iron in deaerated acidic chloride solutions [1,2]. These data are presented in Figs. 5, 6, and 7 for chloride concentrations of 0.1, 1.0, and 4.5 M, respectively, in aqueous solutions with their pH adjusted with hydrochloric acid (HCl). The data points correspond to potentiostatic data obtained for individually polished electrodes held at the applied potential for between 15 and 45 min. The potential was measured relative to the saturated calomel electrode (SCE). These data are also shown as corrected by the iterative technique developed here. The ohmic correction procedure yielded a Tafel slope value of 39 mV/decade for the 0.1 M Cl^- system, while the higher concentrations of 1.0 M and 4.5 M Cl^- gave values of 58 and 60 mV/decade, respectively. These are consistent with reported results [1, 2].

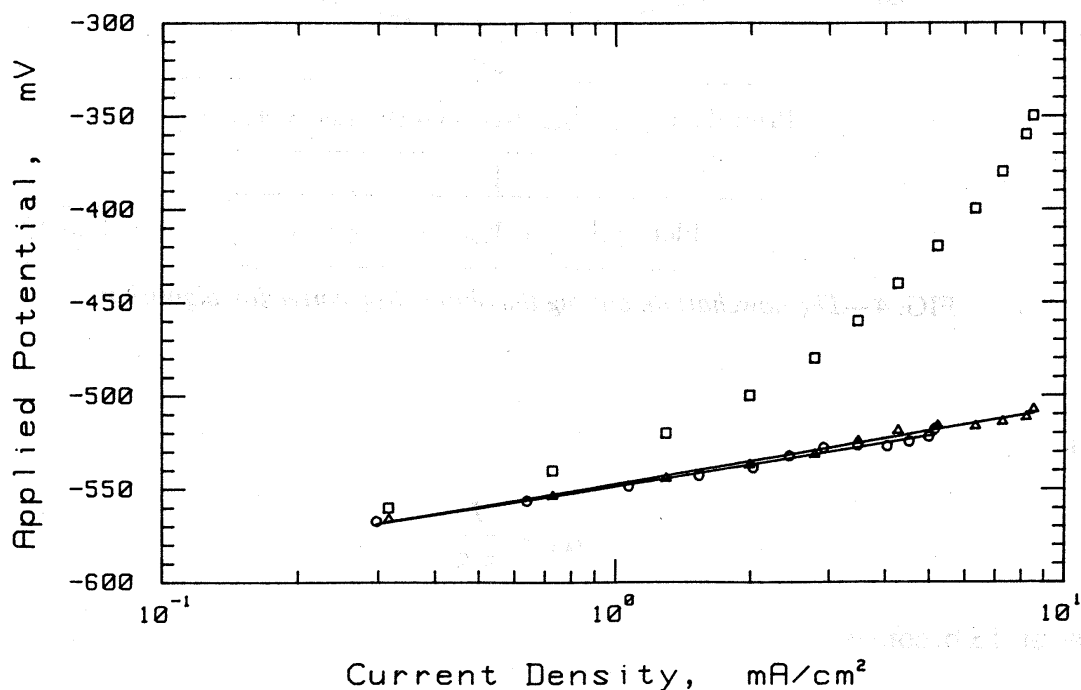


FIG. 5—Tafel plot for measured current density as a function of applied potential for the corrosion of an iron disk in a 0.1 M Cl^- solution with a pH of 2. \square , raw data, that is, averaged current density as a function of measured potential; \circ , data corrected by the iterative program, that is, current density as a function of overpotential appropriate for the center of the disk electrode; and \triangle , averaged current density as a function of overpotential obtained by a primary resistance correction, that is, the current-interrupt method.

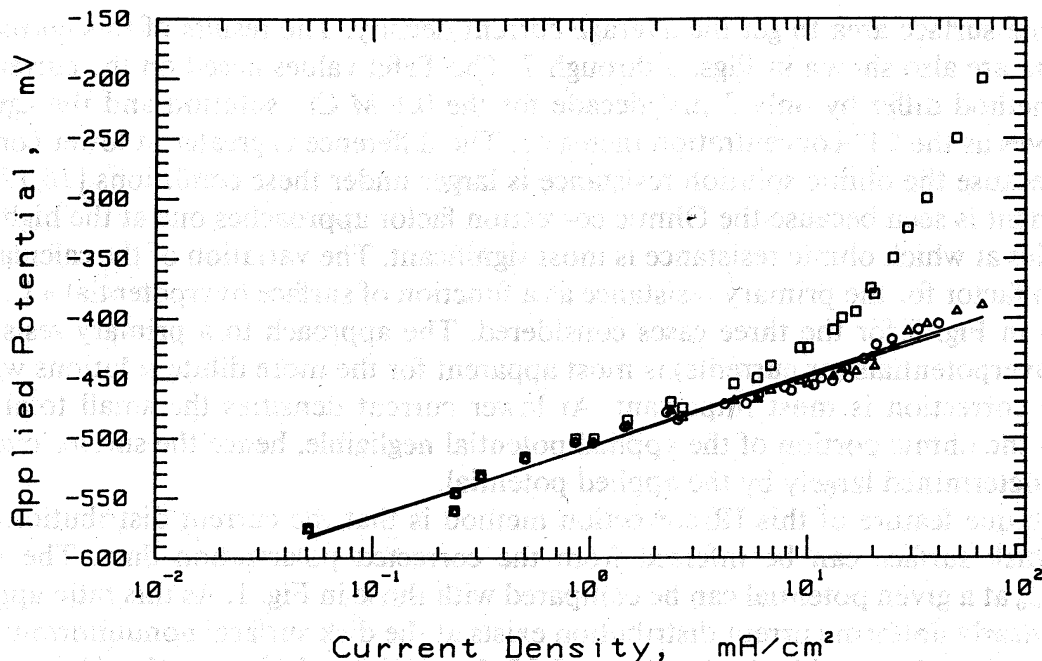


FIG. 6—Tafel plot for measured current density as a function of applied potential for the corrosion of an iron disk in a 1.0 M Cl^- solution with a pH of 2. Symbols as in Fig. 5.

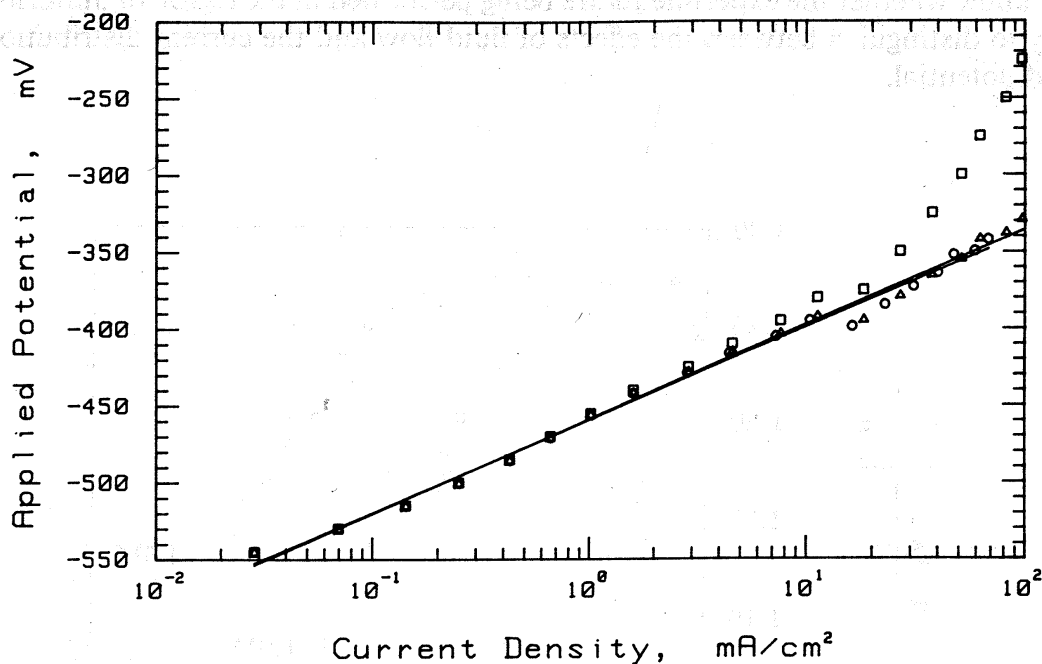


FIG. 7—Tafel plot for measured current density as a function of applied potential for the corrosion of an iron disk in a 4.5 M Cl^- solution with a pH of 2. Symbols as in Fig. 5.

The correction of data for the ohmic resistance by Newman's method was compared to that which would have been obtained by the current-interrupt technique. The ohmic drop measured by the current-interrupt technique corresponds to the primary resistance of the system being studied [16]. This is a consequence of the small time constant for the interruption, which does not allow time for the discharge of the nonuniformly charged double layer associated with a nonprimary current distribution. Therefore, to estimate the correction for the interrupter technique, the primary resistance was subtracted from the applied potential to give the surface overpotential, and the measured current was divided by the

electrode surface area to get the average current density. The results of this correction to the data are also shown in Figs. 5 through 7. The Tafel values based on the current-interrupt method differ by only 3 mV/decade for the 0.1 M Cl⁻ solution and the agreement improves as the Cl⁻ concentration increases. The difference is greater at lower conductivities because the ohmic solution resistance is larger under these conditions [16,17]. Close agreement is seen because the Ohmic correction factor approaches one at the high current densities at which ohmic resistance is most significant. The variation of the calculated correction factor for the primary resistance as a function of surface overpotential $\eta_s|_{r=0}$ is presented in Fig. 8 for the three cases considered. The approach to a primary resistance at large overpotentials (or currents) is most apparent for the more dilute solutions where the ohmic correction is most important. At lower current densities the small total current makes the ohmic portion of the applied potential negligible, hence the surface overpotential is determined largely by the applied potential.

A unique feature of this IR-correction method is that the current distribution existing on a disk surface can be inferred from the corrected polarization data. The value of $i/i_{avg}|_{r=0}$ at a given potential can be compared with those in Fig. 1. As this ratio approaches 1.0, a nearly uniform current distribution exists at the disk surface; nonuniformities at the edge become discernable for $i/i_{avg}|_{r=0} < 0.95$. Increasing solution conductivity makes the current distribution more uniform over a wider range of surface overpotentials, as illustrated in Fig. 9. When employing disk electrodes for erosion-corrosion studies, it is important to know whether the experiments are being performed in the region of uniform current density to distinguish between the effects of fluid flow and the current distribution at the applied potential.

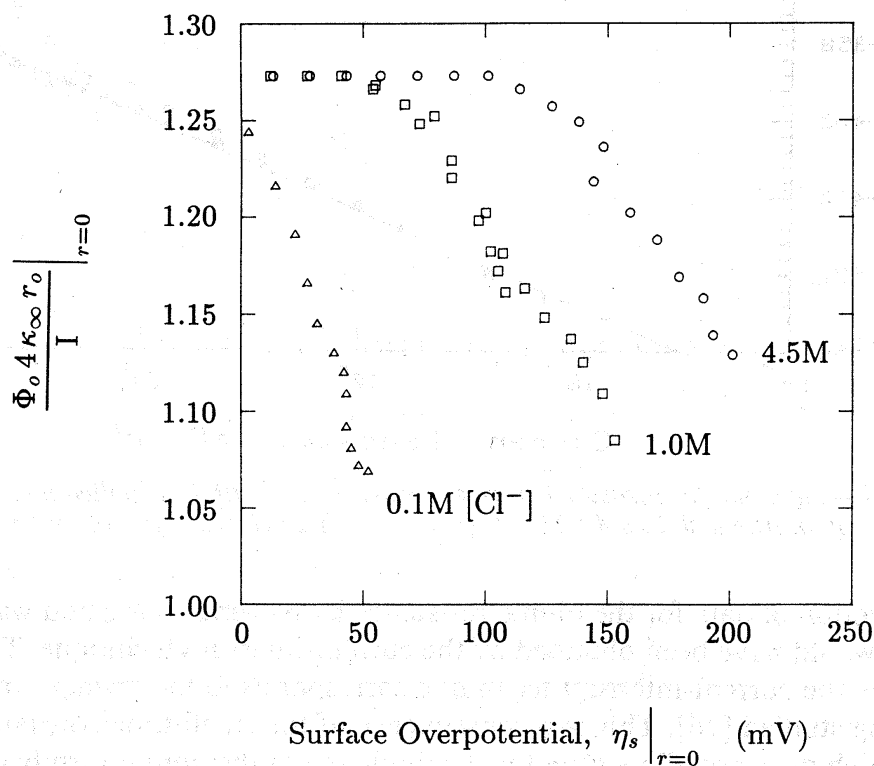


FIG. 8—Correction factor for the primary resistance used to correct for the Ohmic potential drop to the center of the disk electrode under a secondary current distribution for Δ , 0.1 M Cl⁻ solution [$\Phi_{corr} = -570$ mV (SCE)] \square , 1.0 M Cl⁻ solution [$\Phi_{corr} = -558$ mV (SCE)]; and \circ , 4.5 M Cl⁻ solution [$\Phi_{corr} = -543$ mV (SCE)](Fig. 5, 6, and 7, respectively).

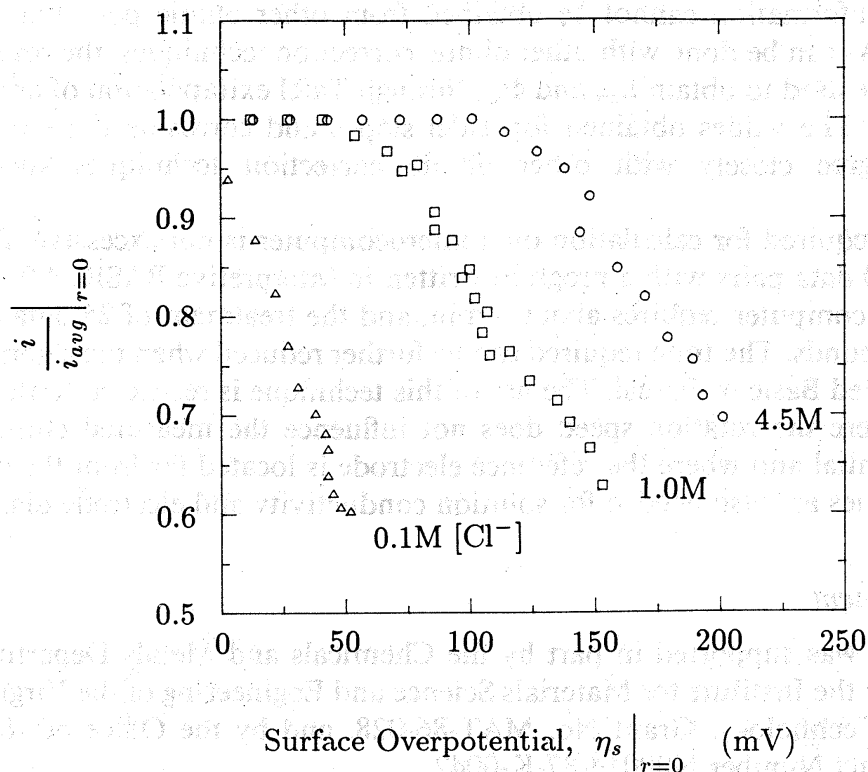


FIG. 9—Ratio of the current density at the center of the disk to the average current density $i/i_{avg}|_{r=0}$ as a function of surface overpotential at the center of the disk electrode under a secondary current distribution. Symbols as in Fig. 8.

This correction procedure requires accurate values for the solution conductivity and electrode diameter. At the lower conductivities, such as those observed for the 0.1 M Cl^- solution, the magnitude of the Tafel slope was strongly dependent on the value of the conductivity. A variation of $0.0005 \Omega^{-1}cm^{-1}$ (4%) in κ_∞ caused a variation in the calculated Tafel slope of as much as 20 mV/decade. At higher concentrations, small changes in the conductivity had little influence on the Tafel slope. The conductivities used in the calculations presented here were obtained in independent experiments.

The "tangent method" described by Asakura and Nobe [18] was also employed for the polarization data. The polarization data were fitted to a Tafel equation in which the surface overpotential was modified by an ohmic term corresponding to a constant solution resistance. The anodic Tafel slopes obtained (40, 56, and 59 mV/decade for the 0.1, 1.0, and 4.5 M Cl^- systems, respectively) were comparable to those obtained through the iterative calculations.

Conclusions

The numerical technique for correcting polarization data for the ohmic resistance corresponding to a secondary current distribution on a disk electrode provides a useful tool for the analysis of experimental data. The analysis is conducted after data are taken and does not require the interruption of an experimental condition. This technique is most useful when it is desirable to account for the nonuniform nature of the current and potential distribution at a disk electrode surface. The referencing of corrected current-potential data to the center of the disk is convenient in comparing it with the results of one-dimensional models of rotating disks, and the results of the correction procedure provide information on the current distribution and the extent of nonuniformity across the disk elec-

trode. This information cannot be obtained from other ohmic potential compensation procedures. As can be done with other ohmic correction techniques, the results of the correction can be used to obtain i_{corr} and Φ_{corr} through Tafel extrapolation of anodic and cathodic regions. The values obtained for Tafel slopes and corrosion current densities and potentials agree closely with other ohmic correction techniques such as current interruption.

The time required for calculation on a microcomputer is not excessive. Iterative treatment of 3000 data pairs with a program written in interpretive BASIC 4.0 on an Hewlett Packard-310 computer requires about 3 min, and the treatment of 25 data pairs requires only a few seconds. The time required can be further reduced when the algorithm is rewritten in compiled Basic or Pascal. The use of this technique is restricted to the Tafel regime for cases where the rotation speed does not influence the measured current at a given applied potential and where the reference electrode is located far from the disk electrode. Accurate values are also needed for solution conductivity and electrode diameter.

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