

APPLICABILITY OF THE GALVANOSTATIC SINGLE-PULSE METHOD: $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$ ELECTRODE IN $1\text{ M Na}_2\text{SO}_4$, NaClO_4 AND KCl *

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Abstract—The conditions that must be met experimentally in order to obtain reliable i_0 -values for fast reactions with the galvanostatic single pulse method are examined. Distinction must be made between the conditions for systems with low k_{sh} -values, high k_{sh} -values and the intermediate case. This is demonstrated by experiment with the $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$ electrode in $1\text{ M Na}_2\text{SO}_4$, NaClO_4 and KCl , the rate constants being 0.063, 0.5 and $>5\text{ cm/s}$ respectively. The maximum obtainable k_{sh} -value with the galvanostatic single pulse method is about 5 cm/s , provided the value of the double layer capacitance is known. If the latter must be determined with pulse methods in the presence of the electroactive species, the limit is about 1 cm/s .

Résumé—On a examiné de manière rigoureuse les conditions expérimentales qui doivent être remplies afin d'obtenir des valeurs i_0 exactes par la méthode de courant galvanostatique d'impulsion simple. Il apparait qu'il faut différencier les conditions nécessaires pour les systèmes à k_{sh} élevé, à k_{sh} bas et à k_{sh} intermédiaire. Ceci est démontré par l'expérience avec l'électrode $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$ dans les solutions molaires de Na_2SO_4 , NaClO_4 et KCl pour lesquelles les constantes de vitesse sont respectivement: 0,063, 0,5 et $>5\text{ cm/s}$. La valeur maximale du k_{sh} qu'on peut obtenir avec la méthode de courant galvanostatique d'impulsion simple est de 5 cm/s environ, à condition que la valeur de la capacité de la couche double soit connue. Lorsque celle-ci doit être déterminée par méthodes d'impulsions rapides en présence de produits électroactifs, la valeur limite de k_{sh} est de 1 cm/s environ.

Zusammenfassung—Man untersuchte die experimentellen Bedingungen, welche notwendig sind, um zuverlässige Werte für die Austauschstromdichte schneller Reaktionen mittels der galvanostatischen Impulsmethode zu erhalten. Es ist erforderlich, zwischen den Bedingungen für Systeme mit niedrigen K_{sh} -Werten, hohen K_{sh} -Werten und dem dazwischen liegenden Gebiet zu unterscheiden. Dies wird experimentell an der $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$ -Elektrode in $1\text{ M Na}_2\text{SO}_4$, NaClO_4 und KCl gezeigt, wo die entsprechenden Geschwindigkeitskonstanten 0,063, 0,5 und $>5\text{ cm s}^{-1}$ betragen. Die grösste mittels der galvanostatischen Impulsmethode ermittelbare Geschwindigkeitskonstante liegt bei ungefähr 5 cm s^{-1} , falls der Wert der Doppelschichtkapazität bekannt ist. Wenn die Doppelschichtkapazität aus Impulsmessungen in der Gegenwart der elektroaktiven Substanz ermittelt werden muss, liegt die Grenze bei ungefähr 1 cm s^{-1} .

INTRODUCTION

THE THEORY of the galvanostatic single-pulse method for the study of the kinetics of fast electrode reactions was developed and discussed by Berzins and Delahay.¹ One of the simplifying assumptions, necessary to obtain an explicit solution for the overvoltage η as a function of electrolysis time t , is the linearization of the general expression relating current i and overvoltage η , with exchange current i_0 ,

$$i = i_0 \left\{ \frac{C_{\text{R}}(0,t)}{C_{\text{R}}^*} \exp \alpha \varphi \eta - \frac{C_{\text{O}}(0,t)}{C_{\text{O}}^*} \exp -(1 - \alpha) \varphi \eta \right\}, \quad (1)$$

into

$$i = i_0 \left\{ \frac{C_{\text{R}}(0,t)}{C_{\text{R}}^*} - \frac{C_{\text{O}}(0,t)}{C_{\text{O}}^*} + \varphi \eta \right\}, \quad (2)$$

where $C_{\text{R}}(0,t)$, $C_{\text{O}}(0,t)$ are respectively the concentrations of the reduced and oxidized forms at the electrode surface at time t , C_{R}^* , C_{O}^* are respectively the corresponding concentrations in the bulk phases, $\varphi = nF/RT$ and α has its usual meaning.

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This linearization was thought to be valid for overvoltages of the indicator electrode not exceeding 5 mV. In a recent paper² we have shown that this value is an over-estimate; generally the overvoltage may not exceed about 0.5 mV. Consequently, experiments performed with the galvanostatic single-pulse method at overvoltages up to 5 mV do not agree with theory and may yield erroneous values of the exchange current densities, especially if the influence of concentration polarization is large. Measurements at overvoltages below 0.5 mV, however, are not feasible. Therefore we proposed to use a two-indicator electrode cell, one electrode functioning as the cathode and the other identical one as the anode. First order deviations from linearity of the two electrodes cancel, and the maximum value of the overvoltage may be extended to about 5 mV. In this paper this procedure has been applied to the $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$ electrode in various supporting electrolytes.

A theoretical analysis of the conditions that must be met experimentally in order to obtain reliable values of the exchange current density is presented, as these conditions and the scope of the single-pulse galvanostatic method have not previously been clearly stated.

THEORY

According to Berzins and Delahay,¹ the overvoltage/time relation for the response of an electrode process perturbed by a single galvanostatic current pulse is

$$\eta(t) = \frac{i}{C_d(\gamma - \beta)} \left[\gamma/\beta^2 \left(\exp \beta^2 t \operatorname{erfc} \beta\sqrt{t} + 2\beta\sqrt{\left(\frac{t}{\pi}\right)} - 1 \right) - \beta/\gamma^2 \left(\exp \gamma^2 t \operatorname{erfc} \gamma\sqrt{t} + 2\gamma\sqrt{\left(\frac{t}{\pi}\right)} - 1 \right) \right], \quad (3)$$

where

$$\beta + \gamma = \frac{i_0}{nF} \left(\frac{1}{C_O^* \sqrt{D_O}} + \frac{1}{C_R^* \sqrt{D_R}} \right) \text{ and } \beta\gamma = \frac{nFi_0}{RTC_d}.$$

Expansion of the exponential error-function complement for large values of t yields

$$\eta(t) = \frac{i}{C_d\beta\gamma} \left[1 - \frac{(\beta + \gamma)^2}{\beta\gamma} + 2(\beta + \gamma)\sqrt{\left(\frac{t}{\pi}\right)} + \frac{(\beta + \gamma)^3 - 2\beta\gamma(\beta + \gamma)}{\beta^2\gamma^2} \sqrt{\left(\frac{1}{\pi t}\right)} - \frac{1}{2} \frac{(\beta + \gamma)^5 - 4\beta\gamma(\beta + \gamma)^3 + 3\beta^2\gamma^2(\beta + \gamma)}{\beta^4\gamma^4} \sqrt{\left(\frac{1}{\pi t^3}\right)} + \dots \right]. \quad (4)$$

If the last two terms between the brackets are negligibly small with respect to the third,

$$\eta(t) = \frac{RTi}{nF} i \left[\frac{1}{i_0} - \frac{RT}{n^3F^3} C_d \left(\frac{1}{C_O^* \sqrt{D_O}} + \frac{1}{C_R^* \sqrt{D_R}} \right)^2 + \frac{2}{\sqrt{(\pi)}} nF \left(\frac{1}{C_O^* \sqrt{D_O}} + \frac{1}{C_R^* \sqrt{D_R}} \right) t^{1/2} \right]. \quad (5)$$

A plot of $\eta(t)$ against $t^{1/2}$ yields a straight line, the slope of which contains information about the diffusion coefficients. From the intercept of the line with the $\eta(t)$ axis the value of the exchange current density i_0 can be obtained provided that the value of the double layer capacitance, C_d , is known with sufficient accuracy.

In their original paper Berzins and Delahay stated that (5) is valid for a general

time condition $t > 50 \mu\text{s}$. In a more recent paper Inman, Bockris and Blomgren³ used the condition $t > 50/\gamma^2$. For an electrode reaction, measurable with the present method, γ and β are complex quantities and therefore the condition $t > 50/\gamma^2$ is not clearly defined. We prefer the following condition, which must be fulfilled in order that (5) approximate to (4) within 1 per cent,

$$t > 100 \left| \frac{(\beta + \gamma)^2 - 2\beta\gamma}{2\beta^2\gamma^2} \right|. \tag{6}$$

Three cases have to be considered,

(a) $(\beta + \gamma)^2 \ll \beta\gamma$, ie small values of i_0 , then

$$t > \frac{100}{\beta\gamma}, \text{ see Fig. 1a;} \tag{6a}$$

(b) $(\beta + \gamma)^2 \gg \beta\gamma$, ie large values of i_0 , then

$$t > 50 \frac{(\beta + \gamma)^2}{\beta^2\gamma^2}, \text{ see Fig. 1b;} \tag{6b}$$

(c) $(\beta + \gamma)^2 \sim 2\beta\gamma$.

From (4) the following condition can be derived,

$$t > \frac{5}{\beta\gamma}, \text{ see Fig. 1c.} \tag{6c}$$

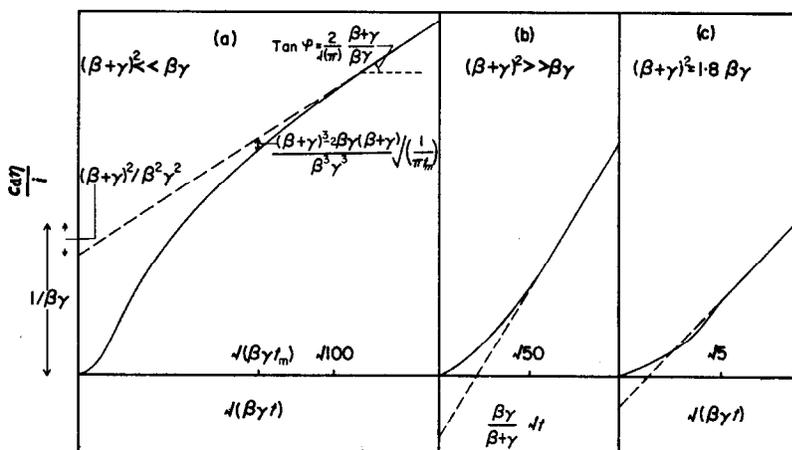


FIG. 1. Examples of η vs $t^{1/2}$ curves for three different cases:
 (a) slow reactions,
 (b) fast reactions,
 (c) the intermediate case.

The validity of (3) and (5) is restricted to small overvoltages of the indicator electrode,² $\eta < 0.02 RT/nF$. For $n = 2$ and $T = 300^\circ\text{K}$ this means $\eta(t) < 0.25 \text{ mV}$, which is too low to be measured accurately. Experiments performed at higher voltages do not agree with theory and yield erroneous values of the exchange current density especially if mass-transfer polarization dominates. Applying overvoltages up to a few mV, Birke and Roe⁴ found that the slope of the $\eta(t)$ vs $t^{1/2}$ curves for the cathodic and anodic reactions of the $\text{Hg}_2^{2+}/\text{Hg}$ electrode never became constant, but continually decreased during the anodic process and increased during the cathodic

process. They ascribed these phenomena to time rather than to voltage effects (their eq. (6)),⁴ and suggested the evaluation of i_0 from measurements at pulse times shorter than those for which the linear relationship between $\eta(t)$ and $t^{1/2}$ should have been attained. A correction due to the neglect of the exponential error-function complement was necessary afterwards. The advantage of this procedure is the fact that the influence of mass-transfer polarization is less at shorter times. However, fast reactions cannot be studied with this method, as the correction for the neglect of the exponential error-function complement cannot be performed with sufficient accuracy for short times, whereas the contribution of mass-transfer polarization to the overvoltage will exceed $0.02 RT/nF$ at longer times.

A better procedure, we believe, is the simultaneous measurement of the cathodic and the anodic overvoltage. It can be shown² that after addition of both responses the first order deviations from linearity cancel, as follows:

$$\begin{array}{l} \text{Anodic reaction:} \quad \eta(t) = iZ_0(t) + i^2Z_1(t) + i^3Z_2(t) \\ \text{Cathodic reaction:} \quad -\eta(t) = -iZ_0(t) + i^2Z_1(t) - i^3Z_3(t) \\ \hline 2\eta(t) = 2iZ_0(t) + 2i^3Z_2(t) \end{array}$$

where $iZ_0(t)$ represents the polarization of the electrode reaction as given by (3), and $i^2Z_1(t)$ and $i^3Z_2(t)$ are the first and second order deviations from linearity that arise at higher amplitudes of current or voltage.

Thus only second order deviations are important and consequently the maximum value of the measured overvoltage may be extended to $0.15 RT/nF$ for each process. It is more convenient to measure the cathodic as well as the anodic reaction simultaneously by the use of a two-indicator electrode cell in which one electrode functions as the cathode, the other identical one as the anode. With such a set-up overvoltages of the over-all cell reaction up to $0.3 RT/nF$ may be measured.

SCOPE OF THE METHOD

In their paper Inman *et al*³ calculated the highest value of the rate constant, which can be determined with the single-pulse method, by taking into account only the sensitivity of present-day oscilloscopes. This implies that the intercept of the $\eta - t^{1/2}$ relation with the $\eta(t)$ axis must be greater than 10^{-4} V. In our opinion there are other sources of error limiting the highest attainable k_{sh} value more seriously. The best method of determining the intercept with the $\eta(t)$ axis is as follows. The value of $\tan \varphi$, Fig. 1a, can be found from experiments at long pulse times, satisfying the conditions of (6). The contribution of diffusion-polarization to $\eta(t_m)$ at a certain time t_m , Fig. 1a, where diffusion polarization is less important, can be subtracted by means of (5). The value thus obtained must be corrected for the influence of the double layer capacitance, (5).

The error in the evaluated exchange current density is mainly determined by:

- (a) the accuracy with which $\tan \varphi$ is known. Non-linearity of the time-base of the oscilloscope and reproducibility of the measurements cause errors of at least 2 per cent. The error in the intercept is

$$\Delta_1 = 0.02 \frac{2}{\sqrt{\pi}} \frac{\beta + \gamma}{\beta\gamma} \sqrt{t_m}$$

(b) A systematic error, due to the assumption that $i_c(t_m) = 0$:

$$\Delta_2 = \frac{(\beta + \gamma)^3 - 2\beta\gamma(\beta + \gamma)}{\beta^3\gamma^3} \frac{1}{\sqrt{(\pi t_m)}}, \text{ see Fig. 1a.}$$

The optimum value for $t_m^{1/2}$, from which an extrapolation to $t^{1/2} = 0$ should be performed, is $(\delta(\Delta_1 + \Delta_2)/\delta t = 0)$:

$$t_m^{1/2} = \sqrt{\left[\frac{25 |(\beta + \gamma)^2 - 2\beta\gamma|}{\beta^2\gamma^2} \right]}. \quad (7)$$

Reliable values of the k_{sh} can be obtained only if the maximum error $\Delta = \Delta_1 + \Delta_2$ does not exceed $0.5/\beta\gamma$, ie if

$$\frac{(\beta + \gamma)^2}{\beta\gamma} = \frac{RT}{n^2 F^3} \left(\frac{1}{C_O^* \sqrt{(D)_O}} + \frac{1}{C_R^* \sqrt{(D)_R}} \right)^2 i_0 C_d \leq 3. \quad (8)$$

We may note that (7) and (8) imply that the intercept from the $\eta(t)$ axis corrected for the influence of the double layer capacitance is always larger than 10 per cent of the total permitted overvoltage at t_m , in our case $0.3 RT/nF$. Therefore the maximum oscilloscope sensitivity, 0.1 mV, is not the limiting factor for the single-pulse method.

On the basis of (8) alone, it appears that the higher the concentrations of the electro-active species, the higher the maximum value of k_{sh} which can be determined. However, the error arising from miscompensation of the ohmic drop limits the highest measurable exchange current density. If the ohmic drop is compensated with a high-frequency set-up, up to a few Mc/s, the compensation can be performed within $2 \times 10^{-3} \Omega \text{ cm}^2$ (ca 0.1 Ω per mercury drop). The activation-polarization resistance must be at least twice as large as this miscompensation,

$$\frac{1}{2} \frac{RT}{nF} \frac{1}{i_0} > \Delta R_\Omega = 2 \times 10^{-3}. \quad (9)$$

Combination of (8) and (9) yields the maximum value of k_{sh} that can be measured with the galvanostatic single-pulse method. Substituting $T = 300^\circ\text{K}$, $D_O = D_R = 10^{-5} \text{ cm}^2/\text{s}$, $C_O^* = C_R^* = C^*$ and $C_d = 3 \times 10^{-5} \text{ F/cm}^2$ into these equations yields

$$k_{sh} \leq 5 \text{ cm/s}, \quad (10a)$$

and an optimum concentration

$$C^* \sim \frac{10^{-5}}{n^2} \text{ M/cm}^3. \quad (10b)$$

The determination of the double layer capacitance in the presence of solute ions under the conditions defined by (10) is not possible with pulse methods. Therefore the derivation of the maximum obtainable k_{sh} value involves the foreknowledge of the value of C_d , eg from measurements at the same dc potentials but at lower concentrations of the solute ions. Further limitations, due to the restriction that C_d must be determined in the presence of the electro-active species, are examined below.

Determination of C_d in the presence of the electro-active species with the single-pulse galvanostatic method

Inman *et al*³ determined the value of C_d in the presence of the solute ions from the initial slope of the $\eta(t)/t$ curve, before the faradaic current has become an important fraction of the total current. Although their electrical set-up was as well as possible adapted to high frequency signals, the information at very short pulse times on the double layer capacitance was small, due to the influence of the ohmic drop. A better procedure, in our opinion, is the measurement of the cell response at larger pulse-times when information on C_d is no longer marginal. The overvoltage will now contain a larger contribution of the faradaic process which must be eliminated by some extrapolation procedure.

(a) *Diffusion-controlled reactions.* The voltage/time relation for a reversible electrode reaction, $(\beta + \gamma)^2 \gg \beta\gamma$, can be derived from (3),

$$\eta(t) = \frac{i}{C_d a^2} \left\{ \exp a^2 t \operatorname{erfc} a\sqrt{t} + 2a \sqrt{\left(\frac{t}{\pi}\right)} - 1 \right\}, \quad (11)$$

where

$$a = \frac{\beta\gamma}{\beta + \gamma} = \frac{n^2 F^2}{RT} \frac{1}{C_d} \frac{C_O^* C_R^* \sqrt{(D_O D_R)}}{C_O^* \sqrt{D_O} + C_R^* \sqrt{D_R}}. \quad (11a)$$

Expansion of (11) for short times yields

$$\eta(t) = \frac{it}{C_d} \left\{ 1 - \frac{4}{3\sqrt{\pi}} a\sqrt{t} + \frac{1}{2} a^2 t - \frac{8}{15\sqrt{\pi}} a^3 t\sqrt{t} + \dots \right\},$$

whence, if $a\sqrt{t} < 1$,

$$\frac{it}{\eta(t)} = C_d \left\{ 1 + \frac{4}{3\sqrt{\pi}} a\sqrt{t} + \left(\frac{16}{9\pi} - \frac{1}{2} \right) a^2 t + \dots \right\}. \quad (12)$$

From a plot of $it/\eta(t)$ vs $t^{1/2}$ the value of C_d can be obtained. As, fortunately, the coefficients of terms of higher order than $t^{1/2}$ in (12) are small, the curve is a straight line up to large values of $at^{1/2}$. From Fig. 2 it can be seen that extrapolation from the region $0.5 < at^{1/2} < 1.0$ to $at^{1/2} = 0$ yields C_d values with only a slight error. The inaccuracy of ohmic drop compensation, ΔR_Ω , limits the application of too short pulse lengths. The error is proportional to t^{-1} ,

$$C_d \cong \frac{it}{\eta} - C_d^2 \frac{\Delta R_\Omega}{t}. \quad (13)$$

Thus, for the evaluation of C_d with an error less than 5 per cent, the minimum pulse length has to be (for $\Delta R_\Omega = 2 \times 10^{-3} \Omega \text{ cm}^2$ and $C_d = 3 \times 10^{-5} \text{ F/cm}^2$)

$$t > 1 \mu\text{s}. \quad (14)$$

The condition $at^{1/2} < 0.5$ together with (14) limits the maximum concentration of the electro-active species to (for $D_O = D_R = 9 \times 10^{-6} \text{ cm}^2/\text{s}$ and $C_O^* = C_R^* = C^*$, $C_d = 3 \times 10^{-5} \text{ F/cm}^2$)

$$C^* < \frac{3}{n^2} 10^{-6} \text{ M/cm}^3. \quad (15)$$

(b) *Activation-controlled reactions.* Expansion of (3) for short times, and rearranging, yields

$$\frac{it}{\eta} = C_d \left(1 + \frac{1}{2} \beta \gamma t + \dots \right). \quad (16)$$

From a plot of $it/\eta(t)$ vs t the value of C_d can be obtained.

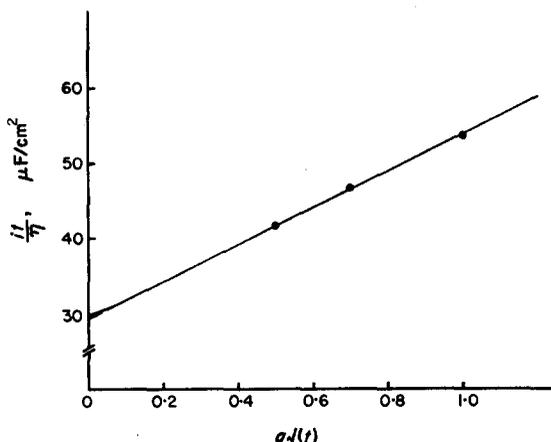


FIG. 2. Shape of the plot of it/η vs $t^{1/2}$ for a reversible electrode reaction in the region $0.5 < a\sqrt{t} < 1.0$. C_d value, $29.5 \mu\text{F}/\text{cm}^2$, obtained from this plot, differs slightly from the theoretical value $30 \mu\text{F}/\text{cm}^2$.

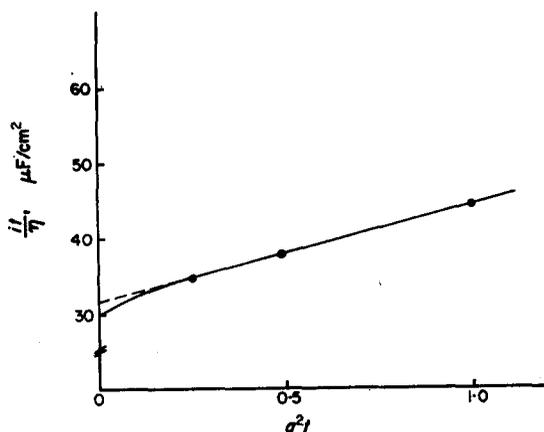


FIG. 3. Shape of the plot of it/η vs t in the region $0.25 < a^2 t < 1.0$ for the case that $(\beta + \gamma)^2 = 2\beta\gamma$. C_d value, $31.5 \mu\text{F}/\text{cm}^2$, obtained from this plot differs by 5 per cent from the theoretical value $30 \mu\text{F}/\text{cm}^2$.

If both activation and diffusion polarization are important, the evaluation of C_d , at least at high concentrations of the solute ions, is more complex. A plot of $it/\eta(t)$ vs $t^{1/2}$ does not give a straight line, nor does a plot of $it/\eta(t)$ vs t . As a consequence, the additional error $\Delta_3 = \frac{m (\beta\gamma)^2}{100 \beta^2 \gamma^2}$, caused by the inaccuracy (m per cent) with which the value C_d can be determined, further lowers the limit given in (8). If, eg, C_d must be determined within 5 per cent, the condition $(\beta + \gamma)^2 < 2\beta\gamma$ holds. Under the latter

conditions it can be shown (see Fig. 3) that the highest permissible concentration of the electro-active species is (for $D_O = D_R = 9 \times 10^{-6}$ cm²/s and $C_O^* = C_R^* = C^*$, $C_d = 3 \times 10^{-5}$ F/cm²)

$$C^* < \frac{3}{n^2} 10^{-6} \text{ M/cm}^3. \quad (17a)$$

From (17a) and the condition $(\beta + \gamma)^2 < 2\beta\gamma$, it is seen that the determination of i_0 by the galvanostatic single-pulse method, utilizing C_d values derived from the method itself, is limited to electrode reactions with k_{sh} values smaller than

$$k_{sh} < 1 \text{ cm/s}. \quad (17b)$$

EXPERIMENTAL ARRANGEMENT

The electrical set-up and apparatus have been described elsewhere.⁵ Compensation of the ohmic drop, which is critical, see (9) and (13), could be performed within 2×10^{-3} Ω cm². Both electrodes of the cell were Cd(Hg) drops hanging at an amalgamated platinum wire sealed in a glass tube. The temperature was 25°C.

RESULTS

The applicability of the galvanostatic single-pulse method was demonstrated with three different types of electrode reactions:

(i) Cd²⁺/Cd(Hg) in 1 M Na₂SO₄. The influence of mass-transfer polarization together with the double layer capacitance is not very large; $(\beta + \gamma)^2/\beta\gamma \ll 1$.

(ii) Cd²⁺/Cd(Hg) in 1 M NaClO₄. This system illustrates the possibilities of the method. At low concentrations the accuracy of the method is limited by the condition of (8) while at high concentrations the compensation of the ohmic drop and the determination of C_d is difficult.

(iii) Cd²⁺/Cd(Hg) in 1 M KCl. In this case the influence of mass transfer polarization together with the double layer capacitance prevents the measurements of the exchange current densities: $(\beta + \gamma)^2/\beta\gamma \gg 3$.

Cd²⁺/Cd(Hg) in 1 M Na₂SO₄ at pH 4

Preliminary experiments showed that the exchange current density of this system was a function of pH. In vicinity of pH 7 readings were not reproducible and were dependent on the age of the amalgam drops. This was probably caused by dissolution of the drops increasing the pH around the electrode. Therefore, final experiments were carried out at pH 4. Here the pH dependency of i_0 was slight.

A typical plot of η vs $t^{1/2}$ is shown in Fig. 4. The data from such plots for different concentrations are listed in Table 1. In Fig. 5 $\log i_0/C_R$ has been plotted against $\log C_O/C_R$. From this plot the following values of α and k_{sh} have been obtained:

$$k_{sh} = 6.3 \pm 0.3 \times 10^{-2} \text{ cm/s}$$

$$\alpha = 0.87 \pm 0.02.$$

These values are in agreement with several data^{1,6-10} obtained from other relaxation methods. Most authors have reported k_{sh} values between 0.01 and 0.1. The large spread of k_{sh} values is probably due to the pH effect mentioned above.

From the slopes of the η vs $t^{1/2}$ curves the following values of the diffusion coefficients could be calculated:

$$D_O = 5.3 \pm 0.5 \times 10^{-6} \text{ cm}^2/\text{s} \text{ and } D_R = 11 \pm 2 \times 10^{-6} \text{ cm}^2/\text{s}.$$

TABLE 1. DATA FOR THE Cd²⁺/Cd(Hg) ELECTRODE IN 1 M Na₂SO₄, pH 4

Cd(Hg) mM	Cd ²⁺ mM	<i>i</i> ₀ mA/cm ²	$\frac{1}{C_0^* \sqrt{(D_0)}} + \frac{1}{C_R^* \sqrt{(D_R)}}$ 10 ⁷ mol ⁻¹ cm s ^{1/2}	<i>C</i> _d μF/cm ⁻²
50	0.5	11.5	83.5	19
50	2.5	45	19.5	19
10	2.5	39	20.0	19
10	10.0	125	8.0	22
2.5	0.5	7.7	98	19
2.5	2.5	31	28.8	20
2.5	10.0	105	16.3	21

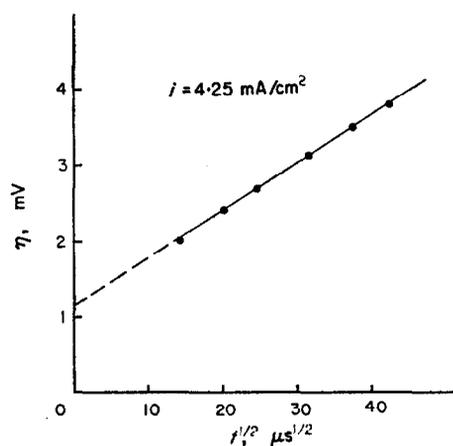


FIG. 4. Plot of η vs $t^{1/2}$ for the 2.5 mM Cd²⁺/50 mM Cd(Hg) electrode in 1 M Na₂SO₄.

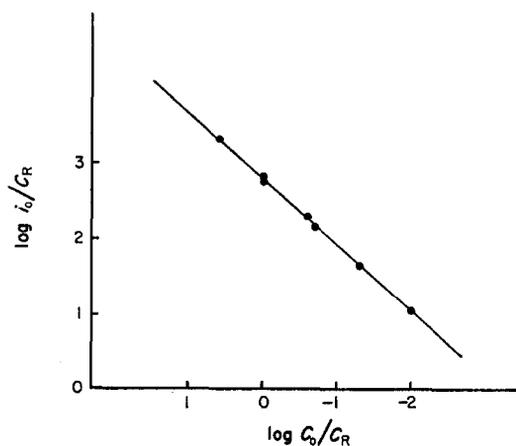


FIG. 5. Plot of $\log i_0/C_R$ vs $\log C_0/C_R$ for the Cd²⁺/Cd(Hg) electrode in 1 M Na₂SO₄.

Cd²⁺/Cd(Hg) in 1 M NaClO₄ at pH 4.

The results of these measurements are listed in Table 2. Some $\eta(t)$ vs $t^{1/2}$ plots are given in Fig. 6. These plots must be analysed with special care. First the value of $(1/C_0^* \sqrt{D_0} + 1/C_R^* \sqrt{D_R})$ must be determined from experiments with long pulse times, where $1/i \, d\eta/dt^{1/2}$ is constant. This value was used to eliminate the contribution of diffusion polarization to the $\eta(t)$ values measured at shorter times. After correction of the influence of the double layer capacitance with (5), the value of i_0 was found. The conditions that must be fulfilled in order that a reliable value of $1/C_R^* \sqrt{D_R} + 1/C_0^* \sqrt{D_0}$ has been obtained, can be checked with (6b). It is noted that an apparent linear relationship was found between $\eta(t)$ and $t^{1/2}$ for all of three plots of Fig. 6, whereas only the conditions in Fig. 6c obey (6a). Moreover the value of $1/i \, d\eta/dt^{1/2}$ obtained from the plots in Figs. 6a and 6b were not consistent with those from longer pulse times. With (7), the optimum value for $t^{1/2}$ could be found, from which the extrapolation to $t^{1/2} = 0$ should be performed.

The curves in Fig. 7 are interesting. The intercept with the $\eta(t)$ axis is negative, which indicates $(\beta + \gamma)^2 > \beta\gamma$. Moreover a real linear relationship is found between $\eta(t)$ and $t^{1/2}$ for shorter values of t than could be expected from (6a). Therefore

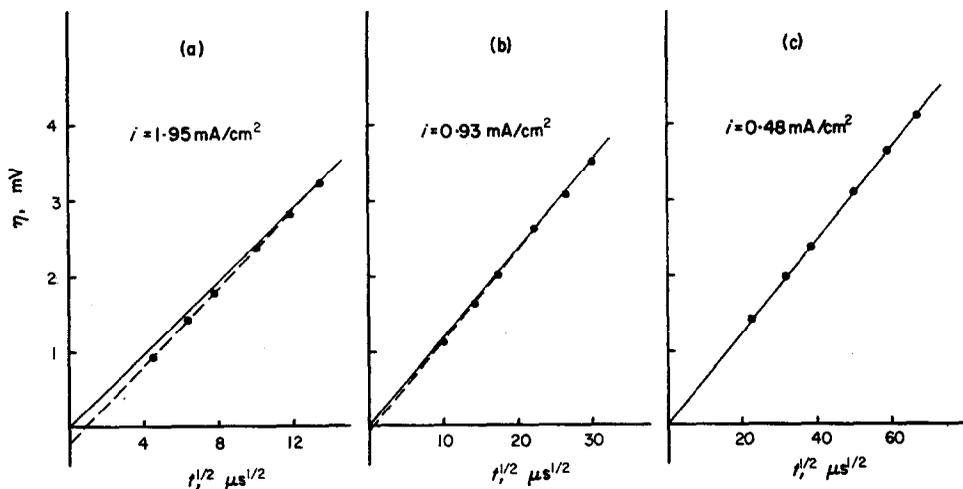


FIG. 6. Plots of η vs $t^{1/2}$ for the 0.23 mM Cd²⁺/2.25 mM Cd(Hg) electrode in 1 M NaClO₄. In a and b the obtained apparent linear relationship (dashed lines) yields erroneous values of the intercept from the η -axis; drawn lines represent the theoretical extrapolation to $t^{1/2} = 0$.

TABLE 2. DATA FOR THE Cd²⁺/Cd(Hg) ELECTRODE IN 1 M NaClO₄, pH 4

Cd(Hg) mM	Cd ²⁺ mM	i_0 mA/cm ²	$\frac{1}{C_0^* \sqrt{D_0}} + \frac{1}{C_R^* \sqrt{D_R}}$	C_d μF/cm ²
			$10^7 \text{ mol}^{-1} \text{ cm s}^{1/2}$	
2.25	0.12	20.5	292	29
	0.23	38	166	29
	0.54	75	82	29
1.19	0.46	70	97	30
	1.19	120	59	30
	2.00	170	43.5	30

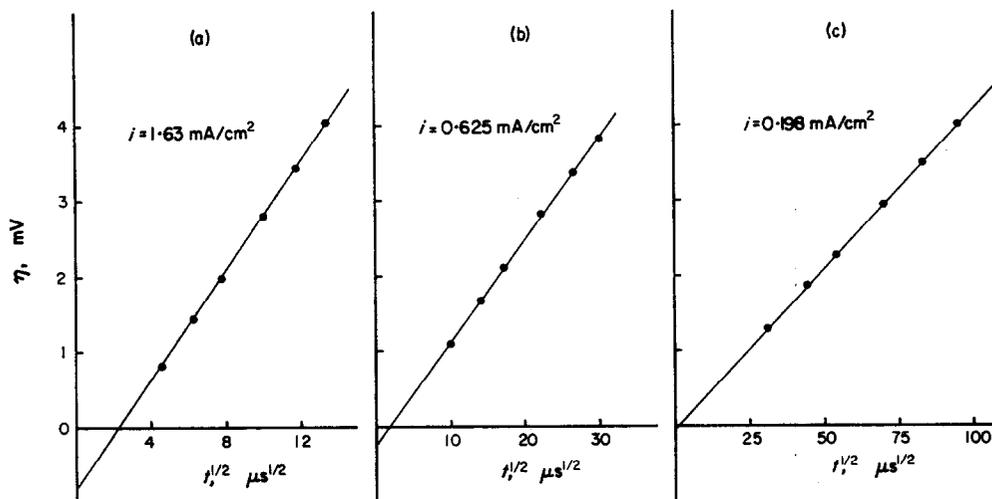


FIG. 7. Plots of η vs $t^{1/2}$ for the 0.12 mM $\text{Cd}^{2+}/2.25$ mM $\text{Cd}(\text{Hg})$ electrode in 1 M NaClO_4 . A real linear relationship is found even at small values of $t^{1/2}$. Compare with Fig. 1c.

without any calculation it can be concluded that in this case $(\beta + \gamma)^2$ is $2\beta\gamma$, see (6c) and Fig. 1c. It is to be noted that in this particular case the methodology of analysing the data of the single-pulse method is more favourable than for the data of the other experiments, although the concentrations of the electro-active species in the latter experiments were higher. This discrepancy suggests that the methodology described first by Berzins and Delahay¹ is not the optimal one. We intend to investigate this matter in more detail.

The values of k_{sh} and α , obtained from a plot of $\log i_0/C_R$ against C_0/C_R , Fig. 8, were $k_{\text{sh}} = 0.55 \pm 0.1$ cm/s and $\alpha = 0.76 \pm 0.03$. From the slopes of the $\eta(t)$ vs $t^{1/2}$ plots the following values of the diffusion coefficients were calculated, $D_O = 8.2 \pm 0.5 \times 10^{-6}$ cm²/s and $D_R = 9.5 \pm 1.0 \times 10^{-6}$ cm²/s.

$\text{Cd}^{2+}/\text{Cd}(\text{Hg})$ in 1 M KCl, pH = 4.

The results are listed in Table 3. The value of the exchange current density could not be determined from the $\eta(t)$ vs $t^{1/2}$ plots, see Fig. 9. The intercept with the $\eta(t)$

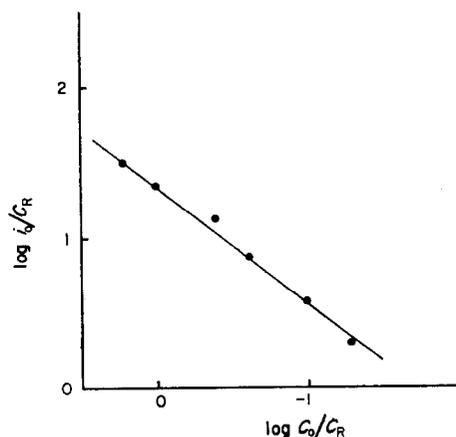


FIG. 8. Plot of $\log i_0/C_R$ vs $\log C_0/C_R$ for the $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$ electrode in 1 M NaClO_4 .

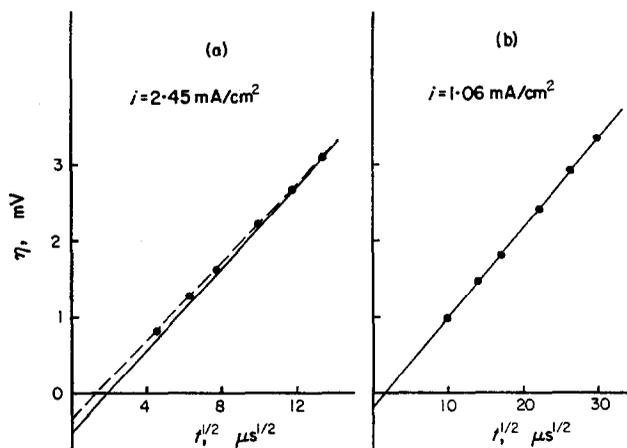


FIG. 9. Plot of $\eta(t)$ vs $t^{1/2}$ for the 0.44 mM Cd^{2+} /0.50 mM Cd(Hg) electrode in 1 M KCl. In (a), the obtained apparent linear relationship (dashed line) would give an intercept from the η -axis, giving rise to a distinct value of the activation overvoltage, whereas the theoretical extrapolation (drawn line) yields an intercept from which no contribution of the activation overvoltage can be detected.

TABLE 3. DATA FOR THE $\text{Cd}^{2+}/\text{Cd(Hg)}$ ELECTRODE IN 1 M KCl, pH 4

Cd(Hg) mM	Cd^{2+} mM	i_0 A/cm ²	$\frac{1}{C_0^* \sqrt{D_0}} + \frac{1}{C_R^* \sqrt{D_R}}$ 10 ⁷ mol ⁻¹ cm s ^{1/2}	C_d^\dagger μF/cm ²
1	9.7	0.60	60.5	(24)
2		1.15	34.0	(25)
3		2.15	19.0	(25)
4	2.0	0.47	88.5	(25)
5		0.95	50.5	(26)
6		1.82	33.5	(26)
7	0.50	0.44	147	25
8		0.91	102	—
9		1.76	90	—

† Values of C_d between parentheses are obtained from measurements at lower concentrations but at the same dc potential.

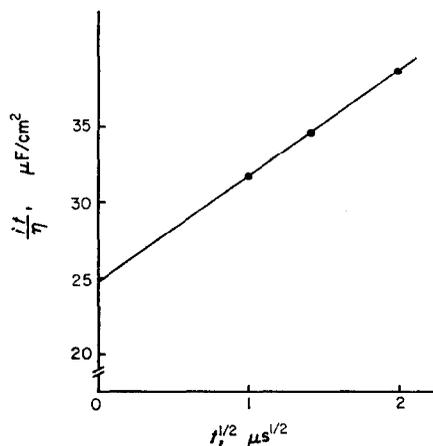


FIG. 10. Plot of i/η vs $t^{1/2}$ for the 0.44 mM Cd^{2+} /0.50 mM Cd(Hg) electrode in 1 M KCl.

axis was negative and the double layer correction was not large enough to deduce reliable i_0 values. From these experiments we could conclude only that k_{sn} must be larger than 5 cm/s. From the slopes of the $\eta(t)/t^{1/2}$ plots, under such condition that (6c) was obeyed, the following values of the diffusion coefficients were calculated:

$$D_O = 8.7 \pm 0.03 \times 10^{-6} \text{ cm}^2/\text{s} \text{ and } D_R = 8.5 \pm 0.5 \times 10^{-6} \text{ cm}^2/\text{s}.$$

The values of C_d were obtained from experiments at the same ratio of C_O/C_R but at lower concentrations than those listed in Table 3, except in the case of experiment 7, see Fig. 10. Experiments with different concentrations with the ratio C_O/C_R kept constant did not indicate that the value of C_d was affected by the presence of the solute ions.

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